Dynamically vulcanized PP/EPDM thermoplastic elastomers

Exploring novel routes for crosslinking with peroxides

Kinsuk Naskar

The research described in this thesis was financially
supported by the Dutch Polymer Institute (DPI).

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Ph.D. Thesis, University of Twente, Enschede, The Netherlands 2004

ISBN 90 365 2045 2

Cover design: by Ramapati De and Kinsuk Naskar, Color Magic, Calcutta, India

Printed by Print Partners Ipskamp, Post Box 33, 7500 AH Enschede, The Netherlands

DYNAMICALLY VULCANIZED PP/EPDM THERMOPLASTIC ELASTOMERS

EXPLORING NOVEL ROUTES FOR CROSSLINKING WITH PEROXIDES

DISSERTATION

to obtain
the doctor's degree at the University of Twente,
on the authority of the rector magnificus,
prof. dr. F.A. van Vught,
on account of the decision of the graduation committee,
to be publicly defended
on Friday, 11th June 2004 at 16:45

by

Kinsuk Naskar

born on 23rd October 1973
in Calcutta, India

This dissertation has been approved by:

Promoter	Prof. Dr. J.W.M. Noordermeer
Assistant promoter	Dr. R.N. Datta

to my parents…

Contents

Chapter 1

General introduction

1.1 Introduction

Polymers play a vital role in the field of material science nowadays. In performance characteristics, applications and diversity, they offer a degree of versatility, not found with any other kind of materials. From a performance point of view, polymers are generally classified into three main categories: rubbers or elastomers, thermoplastics and thermoset resins.

The technology of rubber started with the natural latex product, known as natural rubber (NR). Historically, NR has been used as a material for many centuries already.[1-7] During his second voyage to the "Indies" (1493 – 1496), Christopher Columbus found the natives of Haiti playing with balls made out of an extract from a tree called 'cau-uchu' or weeping wood. The early reported uses of NR were only limited to such items as playing balls and waterproof fabrics or garments. The English scientist Joseph Priestley coined the word 'rubber', because the material could rub out pencil or ink marks. In 1839, Charles Goodyear in USA filed a patent that, when rubber was heated with sulfur, it became stronger and more elastic, but more importantly its properties were no longer strongly dependent on changes in temperature. This process was also developed at about the same time in London by Thomas Hancock, who applied for another patent on vulcanization or curing of rubber in 1843. The discovery of vulcanization (from 'Vulcan', the God of Fire) literally caused a revolution in the rubber industry and a whole range of consumer and industrial rubber products soon became available in the market. The era of NR continued until about the time of the Second World War (1939 – 1940) without substantial introduction of synthetic rubbers in the market.[1] The empirical formula of NR was recognized to be C_5H_8 by Michael Faraday in 1826. In 1860, the Englishman C. Greville Williams broke down rubber by distillation into three parts – oil, tar, and 'spirit' – this last part being the more volatile fraction and the main constituent, which Williams named isoprene. The establishment of the structure of NR led to sustained efforts for the development of synthetic rubbers using diene monomers, such as butadiene, isoprene and chloroprene. The early synthetic rubbers of commercial importance were polybutadiene (1910 – 1914) (butadiene polymerized by sodium, commonly named as BuNa in Germany) and polychloroprene (1932 – 1933).

The emergence of thermoplastic rubbers or elastomers (TPEs) in the late 1950s[8] provided a new horizon to the field of polymer science and technology. A TPE is a rubbery material with properties and functional performance similar to those of conventional vulcanized rubber at ambient temperature, yet it can be processed in a molten state as a thermoplastic polymer at elevated temperature.[9,10] Most of the TPEs meet the standard ASTM D 1566[11] definition of a rubber because; (1) they recover quickly and forcibly from large deformations, (2) they can be elongated by more than

100 percent and (3) their tension set is less than 50 percent. In most cases, TPEs are block copolymers consisting of soft and mobile ‘rubbery’ blocks with a low glass transition temperature (T_g), and rigid or hard ‘glassy’ blocks with a high melting temperature (T_m) or high T_g. The unique characteristics of TPEs make them very useful and attractive alternatives to conventional elastomers in a variety of applications and markets, such as the automotive industry.

TPEs have both advantages and disadvantages in their practical use over conventional vulcanized rubbers.[12,13] They are as follows:

Advantages:

(1) No vulcanization and very little compounding are required.
(2) Amenable to methods of thermoplastic processing, like injection molding, blow molding, thermoforming, heat welding etc., which are unsuitable for conventional rubbers; short mixing and processing cycles and low energy consumption. Figure 1.1 shows a common processing scheme for vulcanized rubbers and for TPEs.
(3) Scrap can be recycled and reused without significant deterioration in performance.
(4) Properties can easily be manipulated by changing the ratio of the components.
(5) Better quality control.
(6) Good colorability.

Disadvantages:

(1) TPEs soften or melt at elevated temperature above which they lose their rubbery behavior.
(2) TPEs show creep behavior on extended use.

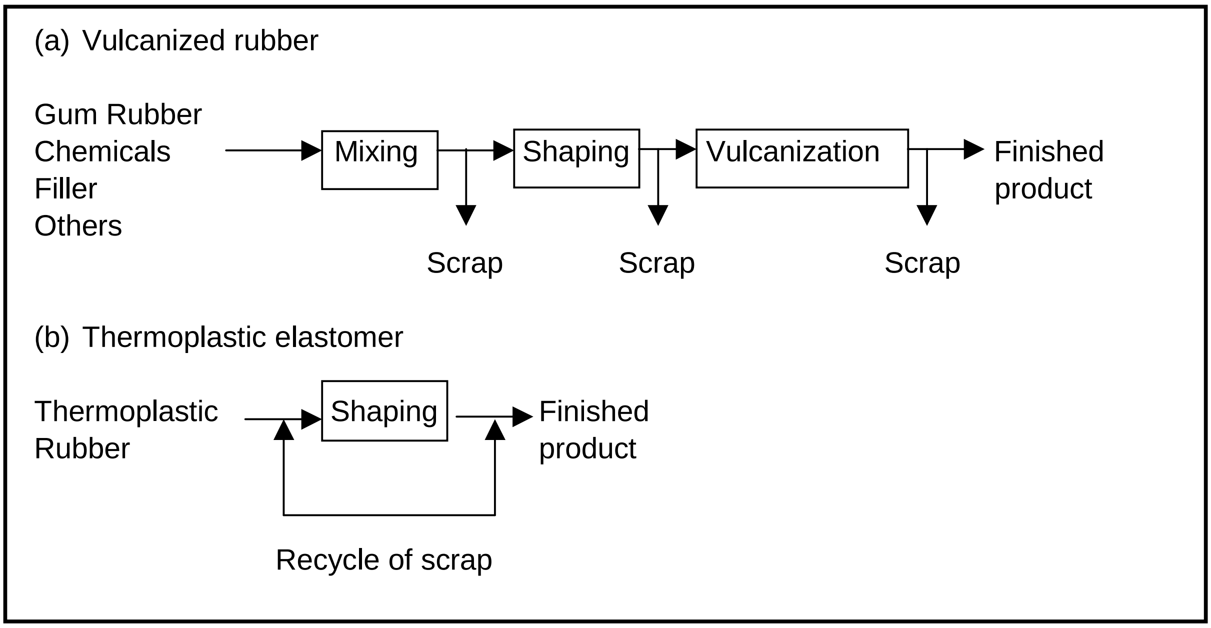

Figure 1.1: Processing scheme of vulcanized rubbers and thermoplastic elastomers.

The field of TPEs based on polyolefin rubber/thermoplastic compositions, has grown along two distinctly different product-lines or classes: one class consists of simple blends and is commonly designated as thermoplastic elastomeric olefins (TEO) according to ASTM D 5593.[14] In the other class, the rubber phase is dynamically vulcanized, giving rise to a thermoplastic vulcanizate (TPV) or dynamic vulcanizate according to ASTM D 5046.[15] TPVs have shown a consistently strong market growth (~ 12 % per year) over the last two decades. They are characterized by finely dispersed crosslinked rubber particles distributed in a continuous thermoplastic matrix. Generally, the rubber particles size varies in the range of 0.5 – 2.0 μm. If the rubber particles of such a blend are small enough and if they are well enough vulcanized, then the properties of the blend are generally improved.[10] Examples of such improvements are:

(1) Reduced permanent set and better elastic recovery;
(2) Higher ultimate mechanical properties;
(3) Improved fatigue resistance;
(4) Greater resistance to attack by fluids e.g. hot oils;
(5) Improved high temperature utility;
(6) Greater stability of phase morphology in the melt and
(7) Higher melt strength.

TPVs based on polypropylene/ethylene propylene diene rubber (PP/EPDM) blends are most important from a commercial point of view. Several crosslinking agents are in use to crosslink the EPDM phase in PP/EPDM blends. Each and every crosslinking system has its own merits and demerits. The crosslinking systems most commonly used for the production of PP/EPDM TPVs are activated phenol-formaldehyde resins, commonly known as resol-resins. There are two major problems associated with this crosslinking system[16] : (a) hygroscopicity of the TPV produced with this system; the tendency to absorb moisture, even at ambient temperature, that must be removed through lengthy, high-temperature drying procedures before processing, to eliminate product defects and (b) appearance of a dark brown color, which is difficult to mask and sometimes necessitates the use of two different pigment systems in order to achieve a desired color. The above-mentioned disadvantages of the resol-resins create a demand for other alternatives. Crosslinking of TPVs with peroxides is a potential alternative.

Crosslinking elastomers with peroxides has been employed for more than fifty years already. The general advantages of peroxide crosslinking systems can be summarized as follows[17]:

(1) Simple formulation;
(2) Ability to store the peroxide containing compound over a long time without scorching;
(3) Rapid vulcanization without reversion;
(4) Ability to crosslink saturated as well as unsaturated rubbers;
(5) High temperature resistance of the vulcanizates;
(6) Good compression set properties of the vulcanizates (elastic recovery) at elevated temperature;
(7) No moisture uptake of the TPVs and
(8) No staining or discoloration of the finished products; etc.[18]

However, when peroxide is added to a PP/EPDM blend, two competing processes may take place simultaneously: EPDM-crosslinking and PP-degradation. It is generally accepted that degradation proceeds through β-chain scission by abstraction of tertiary hydrogen atoms from the main chain of the olefinic polymer.[19-21] A simplified reaction scheme is shown in Figure 1.2.

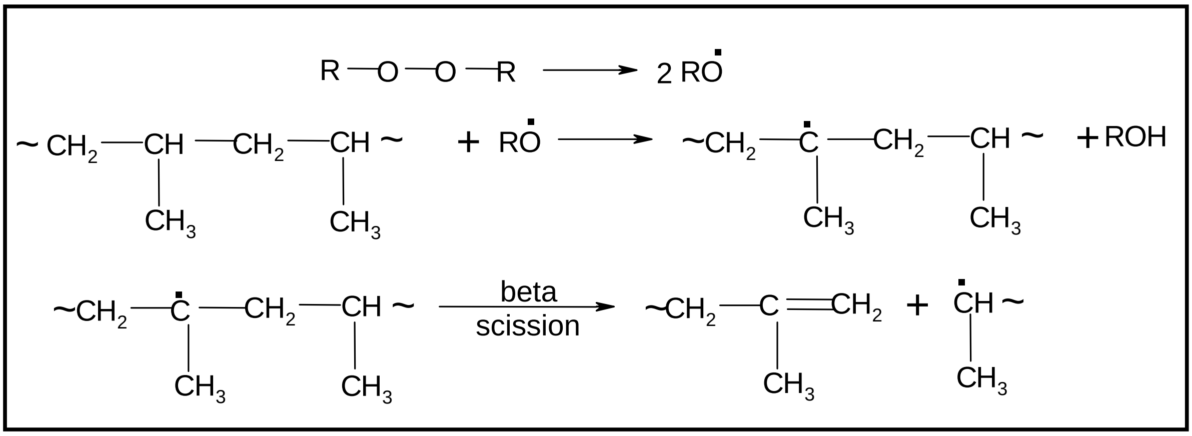

Figure 1.2: Simplified reaction scheme for peroxide degradation of PP by β-scission.

The detrimental effects of β-scission can be partially avoided, respectively the crosslink yield of a peroxide can be increased by the employment of a suitable co-agent in the presence of the peroxide. Co-agents are multifunctional reactive compounds, which are used to enhance the peroxide crosslinking efficiency, thereby acting as a booster.[22] The role of co-agents[19, 22-24] can be described as follows:

1. To remove the steric hindrance for coupling;
2. To minimize the chain scission by stabilizing the macroradicals via resonance;
3. To modify the tight C-C crosslink formed by the peroxy-radical and
4. To suppress unwanted side reactions of polymer radicals, like termination via disproportionation.

1.2 Aim of the project

In case of the selection of peroxides as crosslinking agents for the preparation of TPVs, a proper balance between EPDM-crosslinking and PP-degradation is still a problem of major concern. This is the main reason, which limits the applicability of peroxides-cured TPVs, in spite of all their potential benefits.

Some research[25-32] in this field has been done in the industrial area, but little is openly published because of its commercial sensitivity. Despite the various random attempts, an indepth study to optimize these systems has not been made. Therefore, the basic aim of the investigations described in this thesis is to widen and explore the possible use of peroxides for the production of PP/EPDM TPVs. The work is primarily focused on the extensive study of the effects of various structurally different peroxides in PP/EPDM TPVs. A better insight in understanding the structure-property relationships is aimed at. The work specified in this thesis is therefore directed to find a proper peroxide/co-agent combination for PP/EPDM TPVs, in order to keep the extent of PP-degradation to a minimum and to maximize the degree of EPDM-crosslinking at fixed as well as at varied PP/EPDM blend ratios. In addition, the potential of recently developed multifunctional peroxides, having peroxide and co-agent functionality in a single molecule, is also explored for such systems.

1.3 Structure of this thesis

The use of TPEs has significantly increased since they were first produced almost fifty years ago. Nowadays the development of TPEs is the real state of the art. In Chapter 2 of this thesis, a literature survey is presented on the thermoplastic elastomers obtained by dynamic vulcanization. Classification of TPEs, development of TPVs, employment of various types of crosslinking systems and especially aspects of peroxides and co-agents as crosslinking agents are addressed in this chapter.

The studies reported in Chapter 3 deal with the effects of various structurally different peroxides on the properties of TPVs. This chapter concerns the study at a fixed as well as at varied PP/EPDM blend ratios. Understanding of structure-property relationships is basically aimed at.

Commonly used peroxides produce more or less volatile decomposition products, which sometimes possess a typical smell or show a blooming effect or voids formation. Recently, multifunctional peroxides were developed to reduce those problems. They combine peroxide and co-agent-functionality (reactive unsaturated groups) in a single molecule. Chapter 4 describes the results of multifunctional peroxides as good alternatives for conventional peroxide-classical co-agent combinations. In order to obtain more insight into the chemistry and reactivity involved between the multifunctional peroxides and EPDM rubber, several characterization techniques were employed, as specified in Chapter 5.

There is a possibility of the formation of in-situ graft-links of PP with EPDM during the process of dynamic vulcanization in co-agent assisted peroxide-cured PP/EPDM blends. The above-mentioned in-situ graft-links can act as a compatibilizer in such a system. Since it is very difficult to detect the in-situ formed graft-links, PP/EPDM graft copolymer as compatibilizer has been synthesized as reference. Chapter 6 deals with effects of pre-made compatibilizers influencing the morphology and final properties of TPVs.

Stabilizers play a significant role in determining the durability of the final products. However, since peroxide consumes a part of the stabilizers during the vulcanization process, it is an important issue to select the suitable stabilizer for the peroxide being used. Chapter 7 describes the effects of various kinds of thermal and processing stabilizers in peroxide-cured PP/EPDM TPVs.

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Chapter 2

Thermoplastic elastomers by dynamic vulcanization: The state of the art

The present chapter introduces various topics and aspects which are relevant for the work described in this thesis. Classification of polymer blends in general and that of thermoplastic elastomers, the development of thermoplastic vulcanizates, the use of various types of crosslinking systems with special emphasis on peroxides and co-agents as crosslinking agents for PP/EPDM blends, are reviewed in this chapter. The morphology and rheology of thermoplastic vulcanizates and their typical end-use applications are also touched upon.

2.1 Introduction

Polymer blends have played a significant role in the last few decades in revolutionizing polymer technology, leading to important and useful applications. The term ‘polymer blend’ may be defined as a combination of two or more structurally different polymers or copolymers giving rise to materials with a range of properties, not delivered by any of the constituents. Thus, reasons for using blends include attainment of specific article performance, by improving the technical properties of the original polymers, by adjusting the processing characteristics and reducing the cost.[1-5]

Part of this chapter has been submitted to Progress in Rubber, Plastics and Recycling Technology.

2.2 Thermodynamics of polymer blends

Blending of two different kinds of polymers usually results in an immiscible two-phase blend, because of thermodynamic reasons. The phase behavior of polymer mixtures is generally determined by the thermodynamic parameter ΔG_m, the Gibbs free energy change of mixing, which is given by the following equation:

$$\Delta G_m = \Delta H_m - T\,\Delta S_m \tag{2.1}$$

where, ΔH_m = enthalpy change of mixing (J), ΔS_m = entropy change of mixing (J/K) and T = absolute temperature (K).

The value of the entropy change of mixing, ΔS_m, is generally very small in polymer blends due to the high molecular weights of the polymers. This fact, combined with an enthalpy change of mixing, ΔH_m, which in general is positive for most non-polar polymer, makes it unlikely to realize the necessary negative Gibbs free energy change for mixing to occur. Because of these thermodynamic aspects, the number of miscible blends is very limited. The miscibility on a molecular scale will be improved, when certain specific interactions are involved, resulting in a negative heat of mixing. Consequently, ΔG_m will be negative despite the small entropy change. These interactions may range from strong ionic to weak non-bonding interactions, such as hydrogen bonding, ion-dipole, dipole-dipole and donor-acceptor interactions.[5,6]

2.3 Classification of polymer blends

Polymer blends may be categorized in general into two broad classes: immiscible and miscible blends. Immiscible blends are those which exist in two distinct phases, but are practically still very useful materials, e.g., toughened plastics. Miscible blends are those, which exist in a single homogeneous phase and may exhibit synergistic properties, different from the pure components. Apart from these two, there exists a third category of blends, often known as technologically compatible blends or alloys. Alloys are those, which exist in two or more different phases on micro-scale, but exhibit macroscopic properties akin to that of a single-phase material.[5,6]

Rubber-thermoplastic blends can be classified broadly into three types:

1. Impact resistant rubber toughened thermoplastics;
2. Blends of vulcanizable rubbers, which contain various amounts of resins that can act as reinforcing or stiffening agents and
3. Blends showing thermoplastic elastomeric behavior, commonly known as thermoplastic elastomers (TPEs).[6-10]

2.4 Classification of TPEs

TPEs may be rationally divided into the following classes according to their chemistry and morphology:

1. (Soft) triblock copolymers; e.g., styrene-butadiene-styrene (S-B-S) or styrene-ethylenebutylene-styrene (S-EB-S) etc.
2. (Hard) multiblock copolymers; e.g., thermoplastic polyurethane (TPU), thermoplastic polyamide (TPA) etc.
3. Blends of rubbers with thermoplastics and application of dynamic vulcanization; e.g., polypropylene/ethylene propylene diene rubber (PP/EPDM) uncrosslinked and partially or fully crosslinked.[6-10]

The field of TPEs based on polyolefin rubber/thermoplastic compositions, has grown along two distinctly different product-lines or classes: one class consists of simple blends and is commonly designated as thermoplastic elastomeric olefins (TEO) according to ASTM D 5593.[11] In the other class, the rubber phase is dynamically vulcanized, giving rise to a thermoplastic vulcanizate (TPV) or dynamic vulcanizate (DV) according to ASTM D 5046.[12]

2.5 Dynamic vulcanization

The dynamic vulcanization process was first claimed by Gessler[13] in 1962. The first TPE introduced to the market based on a crosslinked rubber-thermoplastic composition (1972), was derived from W.K.Fisher's[14] discovery of partially crosslinking the EPDM phase of PP/EPDM with peroxide. Fisher controlled the degree of vulcanization by limiting the amount of peroxide, to maintain the thermoplastic processability of the blend. Significant improvements of the properties of these blends were achieved in 1978 by Coran, Das and Patel[15] by fully vulcanizing the rubber phase under dynamic shear, while maintaining the thermoplasticity of the blends. These blends were further improved by Sabet Abdou – Sabet and Fath[16] in 1982 by the use of phenolic resins as curatives, to improve the rubber-like properties and the flow (processing) characteristics. A series of extensive studies on dynamically vulcanized TPEs were carried out by Coran and Patel in the early 1980s.[17-23] Compositions containing all possible combinations of selected types of rubber with selected types of thermoplastics were prepared. The rubbers included butyl rubber (IIR), EPDM, natural rubber (NR), butadiene rubber (BR), styrene-butadiene-rubber (SBR), ethylene vinyl acetate (EVA), acrylate rubber (ACM), chlorinated polyethylene (CM), polychloroprene (CR) and nitrile rubber (NBR). The thermoplastics included polypropylene (PP), polyethylene (PE), polystyrene (PS), acrylonitrile butadiene styrene (ABS), styrene acrylonitrile (SAN), polymethyl methacrylate (PMMA), polybutylene terephthalate (PBT), polyamide (PA) and polycarbonate (PC).[24] Only a few of them were commercialized, because of the fact that most of these blends were not technologically compatible and hence required one or more steps to make them compatible.

The TPVs represent the second largest group of soft thermoplastic elastomers, after styrenic-based block copolymers. Commercialized dynamic vulcanizates are commonly based on blends of unsaturated EPDM rubber and polypropylene, and to a lesser extent on a combination of butyl rubber[25], natural rubber[26-28] or nitrile rubber[6,23] with polypropylene. These systems show the closest match in properties with regularly vulcanized rubbers within a hardness range of Shore A 40 – 90.

2.6 The production of TPVs

Polymer blends are generally prepared by melt mixing, solution blending or latex blending. TPVs are normally produced by melt mixing techniques. In general, mixing extruders and co-rotating close intermeshing twin screw extruders with a high L/D ratio are suitable for the preparation of TPVs in a continuous process. For batch processes, generally internal mixers are employed.

Dynamic vulcanization processes are not entirely satisfactory for making soft compositions, because as the rubber level rises, the resulting compositions become more difficult to produce. For example, the compositions give poor extrudates and sometimes cannot be extruded at all. Accordingly, there is a need for a process for preparing soft, extrusion-fabricable thermoplastic elastomeric compositions. S. Abdou-Sabet[29] found, that in a process for preparing TPVs based on PP/EPDM blends by dynamic vulcanization, improved properties can be achieved when the mixing shear rate is at least 2000 s^{-1} in a co-rotating twin screw extruder, with the thermoplastic component in the molten condition typically at about 170 – 230°C. Preferably, the blend is subjected during vulcanization to a shear rate of about 2500 – 7500 s^{-1}. In that case, vulcanization is complete within 20 – 60 seconds. The TPVs so produced exhibit superior tensile properties including higher tensile strength and greater elongation and also exhibit better processability.

2.7 PP/EPDM TPVs

Commercially available PP/EPDM TPVs are produced by Advanced Elastomer Systems (AES): Santoprene®; DSM Thermoplastic Elastomers: Sarlink®; Softer Sp A: Forprene®; Himont: Dutralene®; and Mitsui: Milastomer® and several others.[30] A whole range of grades of varying hardnesses is made available by changing the PP/EPDM ratio and adding an extender oil.

2.7.1 Crosslinking agents for PP/EPDM TPVs

Several crosslinking agents have been employed to crosslink the EPDM phase in PP/EPDM blends: co-agent assisted peroxides; activated phenol-formaldehyde resins, commonly known as resol-resins; platinum catalyzed hydrosiloxane; vinyltrialkoxysilane/moisture; catalyzed quinonedioxime and bisthiols; etc.[31] Very recently, the use of a special crosslinking agent like benzene-1,3-bis(sulfonyl)azide for the preparation of TPVs was investigated by Lopez Manchado et al.[32] They concluded that the sulfonyl-azide group can act as an effective crosslinking agent for the elastomeric phase and also as a coupling agent between the elastomeric and thermoplastic phases. The cure rate, the final crosslink density, the thermal stability of the crosslinks formed, the safety, health and environmental characteristics of the chemicals used and the cost price are relevant parameters for the final choice of the crosslinking system.[31]

Static sulfur vulcanization of EPDM rubber and other elastomers is normally performed in the presence of activators (ZnO and stearic acid) and accelerators e.g., dibenzothiazole disulfide (MBTS), tetramethyl thiuram disulfide (TMTD) etc. It is proven, that the mechanism of sulfur vulcanization of EPDM is more or less similar to the mechanism, which is normally accepted for polydiene elastomers.[33,34] Sulfur/accelerator combinations have in principle been demonstrated to be applicable to dynamic vulcanization of PP/EPDM blends by Coran and Patel.[17] A typical recipe of TPV composition is shown in Table 2.1.

Table 2.1 Typical recipe of TPV composition (sulfur cured).

Component	Amount (phr)*
EPDM	100
Polyolefin resin	X
ZnO	5
Stearic acid	1
Sulfur	Y
TMTD	Y/2
MBTS	Y/4

* phr is parts per hundred rubber

where, X, phr of polyolefin resin, and Y, phr of sulfur, were varied. An increase in the amount of sulfur from 0 to 2.0 phr in the above recipe resulted in a dramatic improvement of the elasticity of a PP/EPDM 40/60 blend. The tensile strength increased from 4.9 to 24.3 MPa, the elongation at break from 190 to 530 % and the tension set decreased from 66 % to 16 %. Particle size in the dynamically vulcanized blends had a pronounced effect on mechanical properties, also demonstrated by Coran and Patel.[17] As the particle size was reduced, the elongation at break and tensile strength increased rapidly. However, sulfur crosslinking systems are not applied in commercial PP/EPDM TPVs, since PP has a relatively high melting point and the crosslinks lack in thermal and UV-stability. Moreover, the production and processing of these TPVs suffer from severe stench problems.[30]

The most important crosslinking agents for PP/EPDM TPVs are peroxides, phenolic resins and grafted silane. They are discussed in the next paragraphs.

2.7.1.1 Peroxides

Crosslinking elastomers with peroxides has been known for many years already. In 1915, Ostromyslenski published that natural rubber could be transferred into a crosslinked state after treatment with dibenzoyl peroxide.[35,36] However, serious interest in vulcanization with peroxides commenced only with the commercial introduction of dicumyl peroxide in the late 1950s.[37] Based on this interest, a number of peroxide types and formulations were developed, which overcame the drawbacks in thermal stability, crosslinking efficiency and handling and safety aspects of the few existing peroxide types.

The mechanism of peroxide crosslinking of EPDM is less complicated as compared to sulfur vulcanization. In principle, the crosslinking process of high polymers by organic peroxides can be divided into three successive steps.[38-40] A general scheme for the mechanism of action of a peroxide is shown in Figure 2.1. The first step is the homolytic decomposition of peroxide and generation of free radicals. This step is the rate determining step of the overall reaction. The second step is the abstraction of hydrogen atom from the polymer chain, resulting in stable peroxide decomposition products and polymer radicals. The final step consists of the combination of two polymer radicals to form a C–C crosslink. Sometimes, undesired side reactions like disproportionation or β-chain scission can also take place during the crosslinking process, also shown in Figure 2.1.

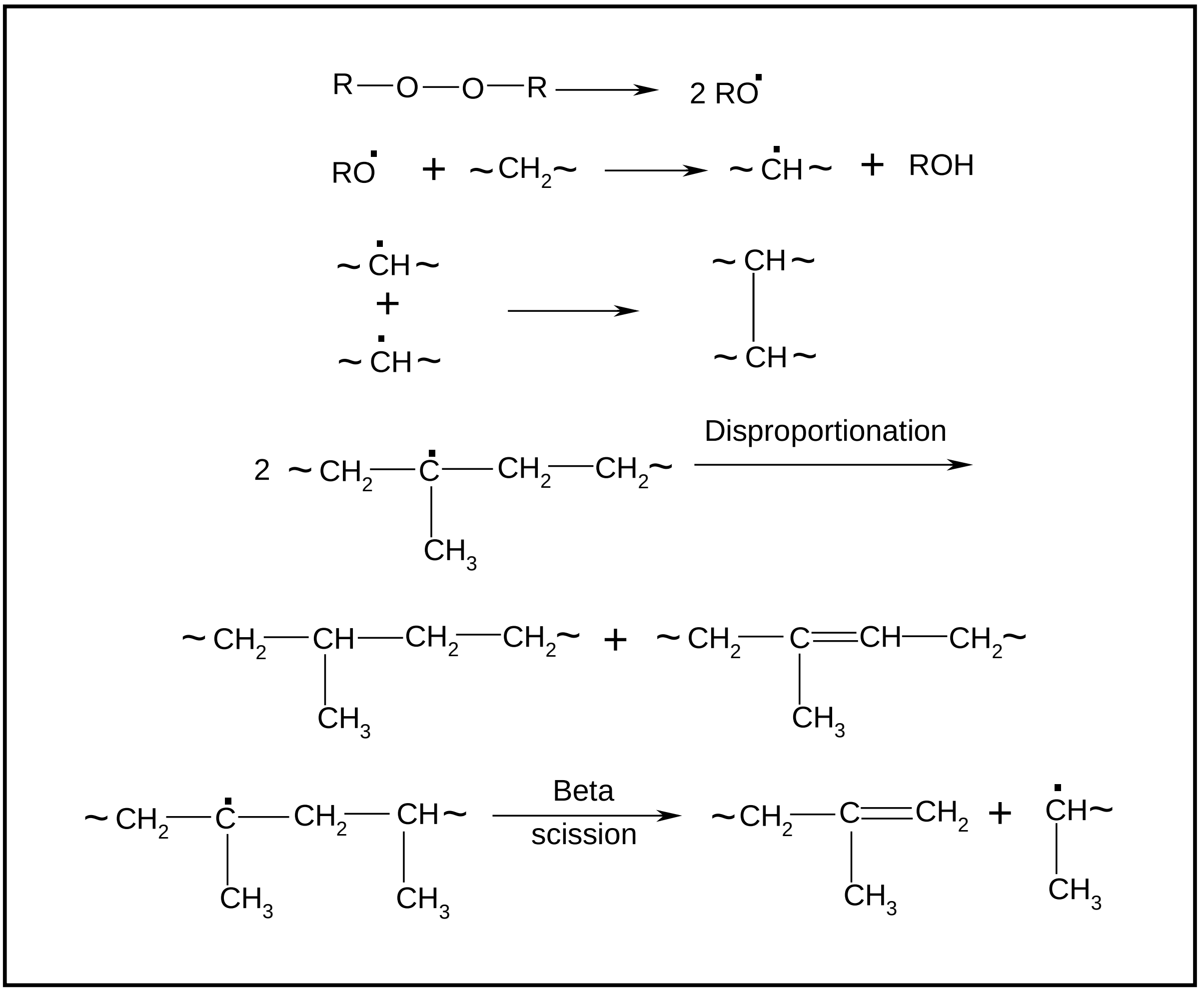

Figure 2.1: General crosslinking mechanism of a peroxide.

The crosslinking efficiency, ε_c, of a peroxides is defined as the number of moles of chemical crosslinks formed per mole of reacted peroxide. Normally for the peroxide vulcanization of some highly unsaturated elastomers like SBR and BR, ε_c-values higher than 10 are found, whereas for saturated elastomers generally values of ε_c less than 1 are observed. For instance, for the crossliking of ethylene propylene rubber (EPM) without any diene, crosslinking efficiencies of 0.1 to 0.8 were reported.[41,42] The overall crosslinking efficiency of a peroxide is the resultant of the efficiencies of all five reaction steps mentioned before.[43] Various types of side reactions may also interfere with the crosslinking process either by consuming the peroxide in non-productive ways or by simply degrading the polymer.[44] The efficiency of the total crosslinking reaction depends mainly on the type of peroxide and polymer radicals formed during the process. The relationship between peroxide structure and crosslinking efficiency has been described by Endstra.[43]

The main peroxide categories depending on their chemical nature, applied for crosslinking rubber-based compounds are[45,46]:

— Dialkyl peroxides;
— Alkyl-aralkyl peroxides;
— Diaralkyl peroxides;
— Peroxy-ketales and
— Peroxy-esters.

Compounds of the dialkyl peroxide class belong to the thermally most stable ones, whereas the peroxy-esters possess only a limited thermal stability: for a rubber compound that greatly restricts the practical suitability of those materials for crosslinking.

The advantages of peroxide crosslinking in comparison with sulfur-cure are already mentioned in Chapter 1. However, there exist some disadvantages of this type of crosslinking system as well. Those disadvantages of peroxide crosslinking in comparison with sulfur cure[47] are as follows:

(1) Sensitive to oxygen under curing conditions;

(2) Certain components of the rubber compounds, such as:

— extender oils, particularly aromatic and to a lesser extent naphthenic oils;[48,49]
— antioxidants and
— acidic fillers like silica (SiO_2) or clay; may, under certain conditions, consume peroxide free radicals and therefore reduce the crosslink efficiency. The influence of various mineral processing oils, widely varying in viscosity and chemical composition, on the peroxide crosslinking efficiency of EPDM rubber was extensively evaluated by Dikland et al.[50]

(2) Usually tensile and tear strength properties are reduced by about 15 % in comparison with a conventional sulfur-based crosslinking system and

(4) In some cases:

— acceleration and retardation, mainly influenced by temperature;
— occasionally an unpleasant smell and
— sometimes the need for post-cure to remove these unpleasantly smelly by-products by diffusion.

The most important characteristic of a crosslinking peroxide is its decomposition rate, which is generally expressed by half-life time ($t_{1/2}$) at a particular temperature. The latter is also a measure for the thermal stability of a peroxide. The half-life time is the time required for one half of the molecules of a given amount of peroxide to decompose at a certain temperature. Commonly, the half-life time is determined by differential scanning calorimetry – thermal activity monitoring (DSC-TAM) of a dilute solution of the peroxide in monochlorobenzene.[47] The dependence of the half-life time on temperature can theoretically be described by an Arrhenius equation:

$$k_d = A.e^{-\frac{E_a}{RT}} \qquad (2.2)$$

and $$t_{1/2} = \frac{\ln 2}{k_d} \qquad (2.3)$$

where, k_d = rate constant for the peroxide decomposition (s^{-1})
A = Arrhenius frequency factor (s^{-1})
E_a = activation energy for the peroxide decomposition (J/mole)
R = 8.3142, gas constant, (J/mole.K)
T = temperature (K) and
$t_{1/2}$ = half-life time (s)

As a rough estimation, the cure time needed for a peroxide-containing EPDM rubber compound corresponds with approximately seven times the half-life value at a specific temperature.[46] Other important considerations while selecting a peroxide for crosslinking are the minimum cure time, Self Accelerating Decomposition Temperature (SADT) and maximum storage temperature.

When peroxides are added to PP/EPDM blends, however, the PP tends to undergo degradation via β-scission of the polymer backbone under the action of the free radicals generated by the decomposition of the peroxide. This reaction occurs when two tertiary carbon atoms along the main polymer chain are separated by only one secondary carbon atom, as already mentioned and shown in Chapter 1. On the other hand, the EPDM phase of the blend can be crosslinked in the presence of the peroxide. The main factors which influence the peroxide crossslinking efficiency of EPM and EPDM are: type and amount of termonomer, ethylene/propylene ratio, randomness of monomer distribution, polymer molecular weight and molecular weight distribution.[51-54] For instance, the higher the ethylene/propylene ratio, the better is the crosslink density of EPM or EPDM. Baldwin et al.[42] studied about ten different kinds of dienes and concluded that methylene-norbornene (MNB) and vinylidene-norbornene (VNB) are most efficient for peroxide curing. Effects of termonomer type and content on peroxide crosslinking efficiency of EPDM was also studied by van Duin and Dikland[55] via the identification of the products formed upon peroxide decomposition in low-molecular weight model substrates (alkanes and alkenes) using gas chromatography with mass spectroscopy detection (GC-MS). They reported that EPDM containing termonomers with terminal unsaturations are more reactive than those with internal unsaturations. Advances were made recently to further increase the crosslinking density of TPVs, cured with peroxide/co-agent through the use of a reactive VNB-containing EPDM rubber.[56]

The damaging effects of β-scission of propylene-rich sequences in EPDM can be partially avoided and consequently the crosslinking efficiency of a peroxide enhanced, by the addition of a suitable co-agent. Co-agents are basically multifunctional reactive compounds, in most cases possessing multiple allylic groups. Several mechanisms for the increase of the crosslinking efficiency in the presence of co-agents with unsaturated moieties have been proposed. In most cases, a fast reaction is supposed to take place between the co-agent and the labile tertiary macro-radical, thereby suppressing the unwanted side reactions like β-scission and disproportionation.[39,57-59] According to Dikland,[60-62] polar co-agents do not dissolve in the non-polar polyolefin EPDM matrix. Upon peroxide decomposition, the co-agent domains become rapidly crosslinked via free radical addition and cyclo-polymerization reactions, resulting in small vitrified thermoset particles. Consequently, they act as multifunctional crosslinkers for EPM or EPDM. However, the solubility of the co-agent in the rubber is also an important issue, for instance, low molecular weight compounds with large differences in solubility parameter values may still dissolve, while, polymers with small differences in solubility parameter values do not. So, Dikland's model depends on the nature of the actual co-agents being used.

Some of the benefits that co-agents afford are[44,54,63,64]:

(1) Improved heat aging;
(2) Higher modulus;
(3) High tensile and tear strength;
(4) Higher hardness;
(5) Improved compression set and
(6) Increased abrasion resistance.

Co-agents are generally classified into two main categories, based on their effects on the nature of cure.[39,44,65] The first type includes acrylates, methacrylates, bismaleimides etc., which increase the rate of cure. Most of them contain readily accessible unsaturation without allylic hydrogens and therefore react only via addition reactions. Examples of the second category are triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), triallyl phosphate (TAP), divinyl benzene (DVB) and also a small amount of sulfur. Unlike the co-agents of the first category, most of the co-agents of the second type contain both readily accessible vinyl unsaturation and sites for radical addition and an ample amount of easily abstractable allylic hydrogens. Addition is their most important mechanism, but hydrogen-abstraction can also be expected to take place to a considerable extent. 1,2-polybutadiene resins as co-agents are also found to improve the heat, chemical and solvent resistance of EPDM and EPM.[66]

2.7.1.2 Phenolic resins

Phenolic resins are the polycondensation products of phenols and aldehydes. Phenolic resins are generally classified into two main classes: resols and novolacs. They have different chemical structures and reactivity, because of the variations in the phenol to aldehyde molar ratio and different pH levels applied for their preparation.[67] Resols are generally characterized by the presence of reactive methylol-groups and dimethylene-ether units, whereas novolacs do not contain any reactive methylol functionalities and thereby can not act as crosslinking agents. The typical structure of a resol-resin, containing a substituted alkyl group at the para position is shown in Figure 2.2.

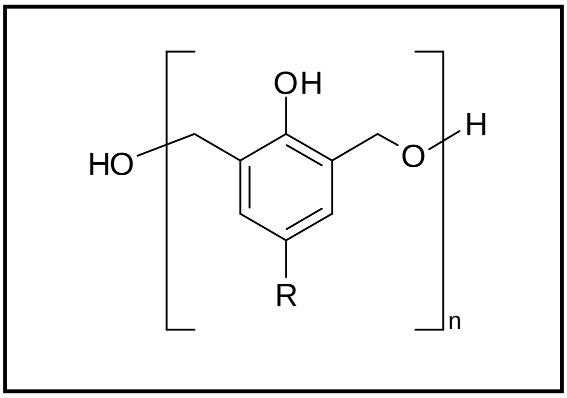

Figure 2.2: Typical structure of resol (R= iso-octyl and n=1-3).

The application of resols as crosslinking agents for TPVs is gaining importance due to the good high temperature properties of the corresponding products. The reaction mechanism of resol curing of ENB-containing EPDM was extensively investigated by van Duin et al.[40,68,69] via a low molecular weight model compound study; 2-ethylidene norbornane (ENBH) was used as the model. A mixture of crosslink precursors, crosslinks and side products with either an unsaturated methylene bridged structure or a saturated chroman ring was found to form, as shown in Figure 2.3.

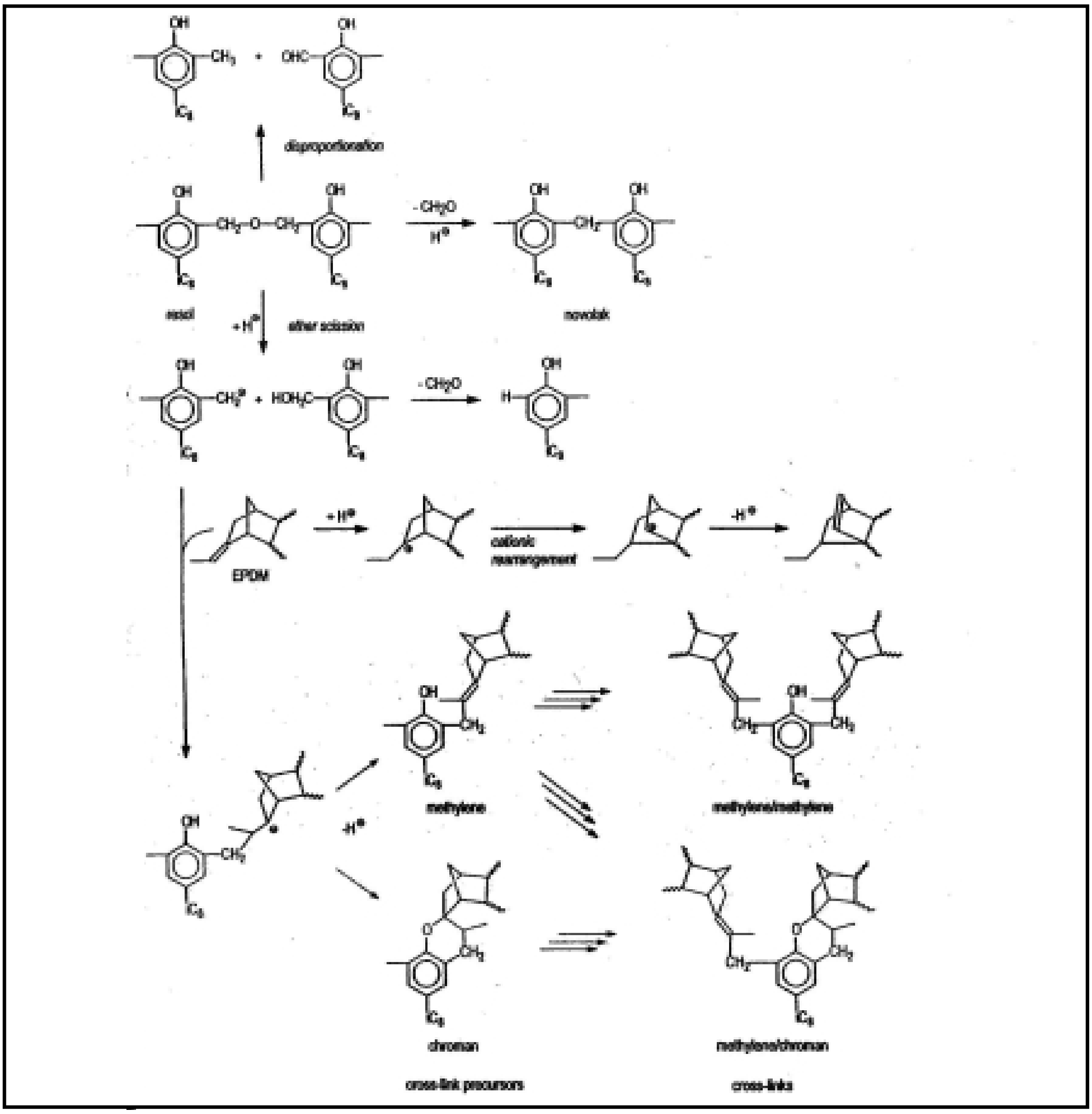

Figure 2.3: Products and reaction mechanism of activated resol cure of EPDM.[40]

Resols are used extensively for the crosslinking of EPDM in the production of TPVs. The EPDM phase is generally crosslinked with reactive alkylphenolic resins (e.g., Schenectady® SP 1045) and halogen containing compounds. Metal halides from Bronsted acid complexes like hydrated stannous chloride, ferric chloride or zinc chloride have been proposed as catalysts for this crosslinking system. During the crosslinking reaction, first ether bridges are split, yielding mono-phenolic units having benzylic cations. These benzylic cations then react with the unsaturation of EPDM rubber to accomplish the crosslinking.[40,68,69]

Abdou-Sabet and Fath[70] demonstrated that the rubber-like properties of PP/EPDM TPVs could be improved by using dimethylol octyl phenol curing resin. Improvements in compression set, oil resistance and processing characteristics of the material were achieved. These improvements were beyond those expected from the state of cure, and are probably due to in-situ formation of a graft copolymer between the rubber particles and the PP matrix. The graft copolymer was assumed to be generated through the functionalization of PP with dimethylol octyl phenol, which then reacts with the EPDM. Phenolic resin curatives having a majority of dibenzyl-ether linkages were unexpectedly found to be effective in curing the rubber in a blend of a crystalline polyolefin and EPDM.[71] Their effectiveness exceeds that of conventional phenolic resin for many TPV compositions.

TPVs cured with conventional phenolic resins often stain painted surfaces, when in contact. This has resulted in the exclusion of TPVs cured with phenolic resins in many applications where the elastomer will have extended contact with a painted surface such as the body of cars, structural moldings and glass to metal laminates. When the phenolic resin curatives are esterified (e.g., acetylated, tosylated, silylated or phosphorylated) before use as a curative, the amount of staining is reduced or even eliminated.[72]

2.7.1.3 Silane grafting

PP/EPDM blend can also be crosslinked by silane grafting in presence of a small amount of peroxide. Fritz et al.[73] studied the tension set and repeated tensile-stress to characterize the elastic properties of organosilane crosslinked PP/EPDM TPV. Grafting, hydrolysis and condensation crosslinking reactions are carried out in a single stage process. There are several patents claiming hydrosilane in presence of a catalyst as a curative for the preparation of TPVs.[74,75]

2.8 Morphology of PP/EPDM TPVs

The morphology of a material is its organization on a supra-molecular scale, i.e., the form, size and orientation of crystallites, domains, the structure of groups of molecules of the components and of their boundaries, and the degree of crystallinity. The morphology of polymer blends is understood as the mostly qualitative description of the spatial arrangement of the blend-component phases.

Several studies have been carried out on the morphology of polymer blends[76-80], which depends primarily on:

(1) The viscosity of individual components;
(2) The ratio of the components;
(3) The interfacial tension between the two polymeric components;
(4) Other ingredients such as extenders, stabilizers, lubricants, etc. and
(5) Processing conditions such as shear rate, temperature, type of flow during processing etc.

The morphology of an immiscible polymer blend can be visualized by an emulsion in which one liquid is dispersed in another. When the fraction of the dispersed phase exceeds a critical value, a region of composition can exist where the blend exhibits phase co-continuity. This co-continuous morphology can be considered as the intermediate structure at which phase inversion takes place and the dispersed phase becomes the matrix phase and vice versa. The midpoint of the phase inversion region can be generally expressed[81] by:

$$\frac{\phi_1}{\phi_2}\frac{\eta_2}{\eta_1}=1 \qquad (2.4)$$

in which η_1 and η_2 represent the melt viscosities of the pure components, whereas φ_1 and φ_2 are the volume fractions of the components at phase inversion.

The level of mechanical properties depends not only on the types and the content of the components, but also the phase morphologies and the interactions between the phases. Morphology formation, thermodynamic compatibility between the polymeric components and the crosslinking parameters of the dispersed rubber phase determine the final properties level of TPVs.[82] Kresge[83] studied the morphology of dynamically sulfur-cured PP/EPDM blends and concluded, that the net result of crosslinking and chain cleavage during the mixing and blending could be the small gel particles of elastomer of around 0.5 to 5 μm in the continuous PP phase. Sabet Abdou-Sabet et al.[84] and later Radusch et al.[82] studied the morphology generation during the process of dynamic vulcanization for phenolic resin cured PP/EPDM TPVs. According to Radusch, the main aim of the dynamic vulcanization procedure is the generation of the TPV-typical phase morphology. Only a fine dispersion of the relatively high amount of rubber into small particles < 0.5 μm surrounded by the thermoplastic matrix, guaranties an elastomer-typical and high mechanical property level. Here the problem lies in the difficulty to disperse the rubber components, representing the higher amount and having the highest viscosity, in the low viscous thermoplastic component, which has to form the matrix at the end of the process. In binary systems, generally the major component forms the matrix phase and the minor component forms a droplet-like dispersed phase. Normally, only low viscous droplets in a high viscous matrix are able to disperse effectively. In shear flow fields it is impossible to destroy a droplet effectively if the viscosity ratio of the dispersed phase to the matrix phase is higher than 1. However, in the case of dynamic vulcanization it is necessary to realize an inverse phase morphology characterized by a matrix phase representing the minor content. Therefore, no shear deformation as the main mixing mechanism, but mainly elongational deformations are required as a precondition for an effective dispersion process.[85] Grace[86] reported that non-rotational, elongational flows appear to produce more effective break-up and dispersion than rotational shear flows. In this connection, it was found that a co-continuous phase morphology at the beginning of the mixing process is a prerequisite to generate the dispersed phase morphology at the end. With TPVs immediately after the start of the selective crosslinking process the viscosity of the rubber becomes very high and with this, the stresses in the material increase very strongly, leading to the break-up of the co-continuous rubber phase into small particles. The investigation[82] showed that the period of morphology transformation from a co-continuous blend morphology to the island (rubber) – matrix (thermoplastic) morphology is very short. The crosslinking of the rubber molecules increases the viscosity of the rubber particles and prevents the coalescence of the particles. The development of the dispersed phase morphology from the co-continuous phase is depicted in Figure 2.4.

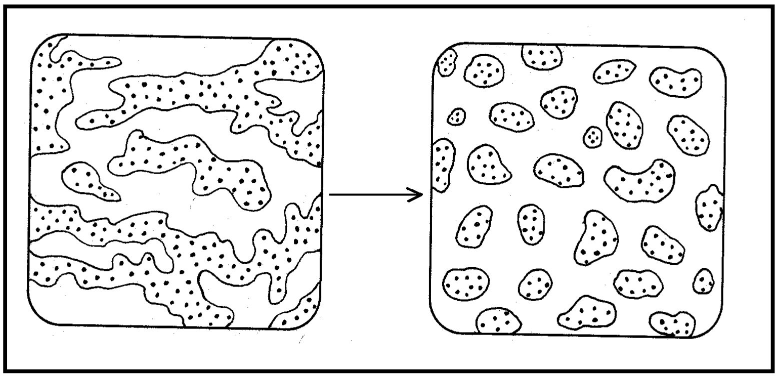

Figure 2.4: Development of morphology in a thermoplastic vulcanizate: from co-continuous to dispersed phase.[82]

It is generally accepted that one of the major advantages of the dynamically cured blends over unvulcanized blends is that the morphology is fixed on crosslinking and is not altered by subsequent melt processing.

Dispersed phase morphology can be proven with the help of combined electron microscopy and energy-dispersive microanalysis techniques.[84] According to Kanauzova et al.[87] at high temperature, PP crystallization in γ-modification results from intermolecular interaction of polymeric PP and EPDM chains in a boundary layer. The formation of the latter in PP/EPDM blends was determined by radiothermoluminescence method from the appearance of a new maximum in the relationship between intensity of luminescence and temperature. D′orazio et al.[88] studied the morphology of dynamically peroxide vulcanized iPP/EPM by means of DSC, by optical, scanning (SEM) and transmission electron microscopy (TEM), by wide angle (WAXS) and small angle X-ray scattering (SAXS). They observed that blends containing uncured EPM are characterized by the presence of iPP-domains randomly distributed in the EPM rubbery matrix, whereas in blends containing cured EPM, the iPP-phase becomes the continuous phase. The latter crystallizes in a structure that resembles a cobweb, tending to surround the EPM cured particles. Moreover, such an iPP-cobweb appears to be constituted by row structure of stacked lamellae. It was found that the addition of EPM-phase interferes dramatically with the crystallization process of the iPP, thus inducing drastic modification in its intrinsic morphology (size, neatness and regularity of spherulites, inner structure of spherulites, etc.). Such interference was found to be comparatively stronger, when the iPP phase crystallizes in presence of cured EPM. The elastic behavior of the thermoplastic elastomer material was accounted for by applying the ‘leaf spring model’ to the morphology and structure of the iPP-phase, crystallized in presence of cured EPM. Radusch et al.[89] have reported recently, that in case of sulfur-cured PP/EPDM TPV with increased curative concentration, tensile strength increases but storage modulus (E′) as obtained from dynamic mechanical analysis decreases. It may be due to thinning down of PP interstices for the finer dispersion of rubber particles in the PP-matrix. The morphology development, rheological behavior and viscoelastic properties of carbon black filled, dynamically vulcanized sulfur-cured thermoplastic elastomers based on PP/EPDM with varied blend-ratios, were studied and compared with similar but unfilled samples by Katbab et al.[90] Two phase morphology was observed at all different ratios of the dynamically cured samples, in which rubber particles were dispersed in the thermoplastic matrix. Carbon black distribution in each phase and damping behavior was found to be dependent on the mixing conditions and route of carbon black feeding. However, carbon black tends to stay mainly in the rubber phase, which leads to an increase in the viscosity difference and, therefore, increase in the rubber particle size. Tensile strength and rupture energy were found to increase with carbon black loading. Katbab et al.[91] also studied the morphology of the sulfur-cured PP/EPDM (40/60 w/w) blends. The morphology of those blends in the molten condition was dispersed: rubber particles dispersed throughout the PP matrix. The final morphology was controlled simultaneously by the rate of break-up and coalescece of the rubber droplets as two mutually counteracting mechanisms. However, when the molten samples of those blends were cooled to room temperature, a particulate co-continuous two-phase morphology was observed as coalescence of the rubber particles predominated. Ellul et al.[92] used a new microscopic technique, STEM (scanning transmission electron microscope) to characterize dynamically vulcanized TPEs. In recent years, atomic force microscopy (AFM) has also been widely used for high resolution imaging of polymer surfaces. Effects of compositions and processing conditions on morphology and final properties of saturated olefinic thermoplastic elastomer blends of PP/EPDM/oil and S-EB-S/PP/oil were compared by Sengupta et al.[93]

The understanding of the elasticity of TPVs is still a subject of debate, because the elastic recovery upon tension or compression at moderate temperatures seems to be in conflict with the low yield-strain of the thermoplastic component. Finite-element modeling studies have been published, but could not give a satisfactory explanation, mainly because the outcome of such calculations is strongly affected by the assumptions and by the description of the morphology and morphological changes upon deformation. Soliman et al.[94] studied the deformation mechanism of phenolic resin cured PP/EPDM TPV. According to them, during the stretching process of PP/EPDM TPV most of the PP acts as glue between the EPDM particles, which are deformed. Only a small fraction of the PP is irreversibly deformed: yielded. During the recovery process this PP fraction is partially pulled back by the recovery of the EPDM. Their model for the TPV deformation mechanism is shown in Figure 2.5.

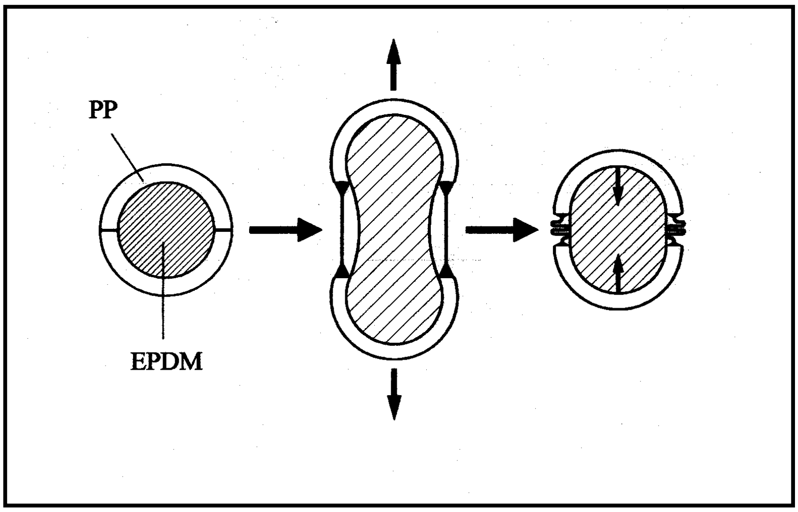

Figure 2.5: Model for TPV deformation mechanism.[94]

Sabet Abdou-Sabet[95] also gave another explanation. According to him, the PP-interstices between the rubber-particles are too small to render proper PP crystallization and so the PP-phase remains amorphous and therefore is deformable.

The stress-strain behavior of TPVs was also studied experimentally by Boyce et al.[96] A constitutive model for the behavior was proposed and found to successfully predict the important features of the observed stress-strain behavior. The micro-mechanisms of deformation and recovery in TPVs were also extensively studied by the same Boyce et al.,[97] using a series of micro-mechanical models. Application of a dynamic scaling model for analysis of the process of agglomerate formation between the cured rubber particles during dynamic vulcanization of TPVs was investigated by Goharpey et al.[98]

By the application of an experimental design, S. Datta[99] observed that the highest tensile strength of phenolic-resin cured PP/EPDM TPVs is achievable with high ethylene-content and high diene-content of the EPDM-phase; the viscosity of the EPDM-rubber is less significant in this case. On the other hand, better rubber-properties: e.g. set, impact strength and solvent-resistance, are achievable with low ethylene-content, low diene-content and low viscosity of the EPDM-rubber, smaller rubber particle size, uniform crosslinking density: shell to core of the EPDM particles and the kinetics of dispersion and curing.

2.9 Rheology and processing of TPVs

The processing of a rubber-plastic composite into a finished part is a function of the melt rheology of the composition. The melt rheology in turn is a function of temperature and shear rate. The processing of a TPV is determined primarily by the properties of its thermoplastic phase, yet the properties of the same TPV are determined by the nature of the crosslinked rubber phase. Thus a PP/EPDM TPV has essentially the same melting point as rigid PP and is processed in much the same manner as PP.

The rheological properties of TPVs have been studied by several research groups.[100-102] It was shown that fully cured thermoplastic vulcanizates behave similar to highly filled fluids in shear flow. They exhibit highly pseudoplastic behavior, lack of a viscosity plateau at low shear rate and low extrusion swell. Han and White[103] have studied the rheological behavior with various measurement techniques, including sandwich squeeze flow, cone-plate stress build-up, dynamic analysis and capillary rheometry. They concluded that the dynamically vulcanized blends show behavior, which is characteristic for materials with a rest state structure. From plots of the viscosity as a function of the shear stress, a critical stress or yield stress of flow was observed. Steeman and Zoetelief[104] showed that stress is the important factor, determining the rheological behavior of TPV-melts. At low stress, the materials mainly show elastic behavior, which is attributed to the presence of an interacting network of rubber particles. At intermediate stress, passing the yield stress, this network is broken and the materials behave as a melt of PP, filled with stiff rubber particles; the viscosity is heavily dependent on the rubber content. At high stresses, the viscosity of the TPVs increases with increasing hardness, i.e. with the PP-content.

High elasticity in PP/EPDM TPVs, as demonstrated by lower residual deformation upon release of deformation is highly desirable. Ellul[105] showed that this property could be achieved by the application of a PP-phase, having a high degree of long-chain branching. Thus, the TPV so obtained, behaves as a dual network material: one network being the chemically crosslinked rubber phase, whereas the other phase being the physical network arising from the high extent of long-chain branching in the PP.

The effects of degree of crosslinking on the rheological properties of PP/EPDM TPVs were studied by means of a rubber process analyzer, RPA 2000, by Marinovic et al.[106] Their results confirmed that stronger crosslinking contributes to the formation of more rigid EPDM domains dispersed in the continuous PP-phase. Heterogeneity of such systems, affecting molecular dynamics was also explored by electron spin resonance (ESR).

Processing methods and equipments for TPVs are essentially those of the thermoplastic in the material. The most widely used method is thermoplastic injection molding, which differs from vulcanizable rubber injection molding in that the final step in the fabrication process does not involve vulcanization.[70] Extrusion is also widely used to fabricate sheeting, intricate profiles, tubing, hose, and electrical insulation and jacketing from TPVs. It does not require the expensive vulcanization equipment commonly used with vulcanized rubbers. Recent developments have resulted in the generation of a foamed TPV[107] via extrusion with water as a foaming agent. Blow molding, thermoforming and heat welding are TPV fabrication methods, not feasible with vulcanized rubber. The generation of hollow TPV articles via blow molding has been found more efficient than forming similar articles from vulcanized rubber by injection molding.[70]

2.10 Oil-distribution over the two phases in TPVs

Solid state ^{13}C NMR spectroscopy and electron paramagnetic resonance (EPR) were employed by Winters et al.[108] to quantitatively determine the distribution of processing oil over the two phases in EPDM/PP/oil based TPVs in the melt, with and without talcum filler. The oil has a strong influence on both the processing and the mechanical properties of TPVs. ^{13}C NMR of the pure oil revealed that it closely resembles a low molecular weight EPM with M_n = 800 g/mole and an ethylene content of 70 wt %. They also determined the location of the oil in the melt. The NMR and EPR results provided evidence that in the melt about one third of the oil is neither mixed within the EPDM nor in the PP. The data also indicated that the oil might form a very thin layer around talcum filler particles.

Later, Sengers et al.[109] applied dielectric relaxation spectroscopy (DRS) as a new technique to determine the oil distribution in the melt as well as at room temperature. They studied the relaxation of molecular dipoles in terms of dielectric constants by measuring the capacitance. N,N-dibutyl amino nitrostilbene was used as a probe molecule. Contrary to the results of Winters et al., they decided that oil is equally distributed over the PP and EPDM phases, giving rise to a distribution coefficient value of 1.

2.11 End-use applications of TPVs

Potential and proven applications of recently developed thermoplastic elastomers and thermoplastic vulcanizates are as follows.[6,70]

For mechanical rubber goods applications: convoluted bellows, flexible diaphragms, gaskets, seals, extruded profiles, tubing, mounts, bumpers, housings, glazing seals, valves, shields, suction cups, torque couplings, vibration isolators, plugs, connectors, caps, rollers, oil-well injection lines, handles and grips.

For under-the-hood applications in the automotive field: air conditioning hose cover, fuel line hose cover, vacuum tubing, vacuum connectors, body plugs, seals, bushings, grommets, electrical components, convoluted bellows, steering gear boots, emission tubing, protective sleeves, shock isolators, and air ducts.

For industrial hose applications: hydraulic (wire braided), agricultural spray, paint spray, plant air-water, industrial tubing and mine hose.

For electrical application: plugs, strain relief, wire and cable insulation and jacketing, bushings, enclosures, connectors and terminal ends.

Furthermore, TPVs can also be used for consumer goods, for instance: floor and personal care, business appliances, sporting goods, portable kitchen appliances etc. Soft touch applications of TPVs are also becoming increasingly popular nowadays.

2.12 Summary and considerations for our research plan

This survey of the available literature reveals, that there is a growing interest for the use of thermoplastic vulcanizates (TPV) or dynamic vulcanizates (DV) for the last couple of decades. TPVs represent the second largest group of soft thermoplastic elastomers, after styrenic-based block copolymers. Commercialized dynamic vulcanizates are commonly based on blends of EPDM rubber and PP, and to a lesser extent on combinations of butyl or nitrile rubber with PP. Phenolic resins are extensively used commercially for the production of PP/EPDM TPVs. The use of peroxides for the same is still not well explored. For the selection of a peroxide as crosslinking agent for the preparation of TPVs, a good balance between EPDM-crosslinking and PP-degradation is an important criterion. Co-agents are often used to improve the crosslinking efficiency of a peroxide and also to diminish the PP-degradation. Only a few researches[110-117] in the field of peroxide/co-agent cured TPVs have been carried out inside the industry so far, but little is openly published because of commercial sensitivity.

Based on these conclusions, the research described in this thesis will basically focus on:

- A study of the behavior of various structurally differentperoxides in PP/EPDM TPVs at a fixed blend ratio;
- Study the effects of various peroxides in varied PP/EPDM ratios in order to get a better insight in structure-property relationships;
- To find a proper peroxide/co-agent combination for PP/EPDM-TPVs, in order to keep the extent of PP-degradation to a minimum and to maximize the degree of EPDM-crosslinking;
- Exploring the potentiality of recently developed multifunctional peroxides, having peroxide and co-agent functionality together in a single molecule for such systems as alternatives for conventional peroxide/co-agent combinations.
- To search for the formation of in-situ graft-links of PP with EPDM during the process of dynamic vulcanization in co-agent assisted peroxide-cured PP/EPDM blends.
- To observe the effects of pre-made compatibilizers like a PP/EPDM graft copolymer, to influence the morphology and final properties of TPVs.
- Study the effects of various kinds of thermal and processing stabilizers in peroxide-cured PP/EPDM TPVs.

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Chapter 3

The effects of different types of peroxides on the properties of TPVs

The effects of different types of peroxides as crosslinking agents on the properties of PP/EPDM TPVs were investigated at a fixed as well as at varied PP/EPDM blend ratios. The physical properties change significantly with the chemical nature of the peroxides, the extent of crosslinking of EPDM phase and the extent of degradation of PP phase. Three main parameters have been identified governing the final mechanical properties of TPVs: the solubility parameter of a peroxide relative to the polymers, PP and EPDM, the decomposition mechanism of the peroxide and the kinetic aspects of the peroxide fragmentation. Dicumyl peroxide (DCP) gives the best balance of all properties, since it complies the best of all with these parameters.

3.1 Introduction

Various crosslinking agents are employed to crosslink the EPDM phase in PP/EPDM TPVs.[1] The crosslinking agents most extensively used for the production of PP/EPDM TPVs are activated phenol-formaldehyde resins, commonly known as resol-resins. There are two major problems associated with this crosslinking system[1]: (a) hygroscopicity of the TPV produced with this system; the tendency to absorb moisture, even at ambient temperature, that must be removed through lengthy, high-temperature drying procedures before processing, to eliminate product defects and (b) appearance of a dark brown color, which is difficult to mask and sometimes necessitates the use of two different pigment systems to achieve a desired color. The above-mentioned disadvantages of the resol-resins as crosslinking agents were the driving force for searching other alternatives.

Part of this chapter was published in Rubber Chemistry and Technology, **76**, 1001 (2003) and Elastomer, **38**, 167 (2003).

Organic peroxides are frequently employed within industry for the crosslinking of elastomers and few thermoplastics.[2,3] When peroxide is added to a PP/EPDM blend, two competing processes take place simultaneously: EPDM crosslinking and polypropylene degradation by β-scission.[4-6] There is a need for a proper peroxide in combination with a suitable co-agent for PP/EPDM TPVs to diminish the extent of PP degradation and improve the degree of EPDM crosslinking. The main objective of this chapter is to investigate the effects of different types of peroxides on the properties of PP/EPDM TPVs at a fixed PP/EPDM blend ratio.[7]

The physical and mechanical properties of PP/EPDM TPVs can change drastically with the PP/EPDM blend ratio. In fact, a whole range of varying properties, for instance hardness is made available in the market by altering the PP/EPDM ratio and adding suitable quantities of an extender oil. The effects of composition on properties due to changes in PP/EPDM ratio in accelerator(s)/sulfur-cured TPVs were first studied by Coran and Patel.[8] They reported that, as the amount of PP-resin per amount of rubber increases, the composition becomes less rubbery and more plastic resin-like; modulus, hardness, tension set and tensile strength increase. Later, Sabet Abdou-Sabet et al.[9] studied the physical properties as well as the morphological features of phenolic resin-cured PP/EPDM TPVs, ranging from 80/20 EPDM/PP till 20/80 EPDM/PP. Dynamic vulcanizates based on PP/EPDM blends were also prepared by Radusch et al.[10,11] using different thermoplastic/rubber ratios e.g., 75/25 wt % to 20/80 wt % and various vulcanizing agents e.g., accelerator/sulfur, DCP/bismaleimide and phenolic resin. They characterized the properties of the products by tensile tests and determined the network parameters via cyclohexane solvent swelling. The morphology development, rheological behavior and viscoelastic properties of carbon black filled, dynamically sulfur-vulcanized thermoplastic elastomers based on PP/EPDM blends with the ratio in the range of 20/80 to 50/50 were studied and compared with similar but unfilled samples by Katbab et al.[12] A two-phase morphology was observed at all different ratios of the dynamically cured samples, in which rubber particles were dispersed in the thermoplastic matrix. The carbon black distribution in each phase and the rheological damping behavior were found to be dependent on the mixing conditions and the route of carbon black feeding. Carbon black tends to stay mainly in the rubber phase, which leads to an increase in the viscosity difference between the EPDM rubber and the PP-matrix and therefore, increase in the rubber particle size. Tensile strength and rupture energy were found to increase with carbon black loading.

Thus, it is also interesting to observe the influences of various peroxides at different PP-contents. Therefore, the second objective of the present chapter is to study the effects of various peroxides at varied PP/EPDM blend ratios in dynamically vulcanized blends.

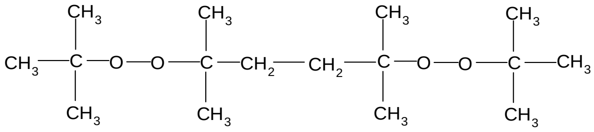
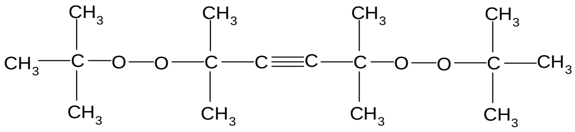
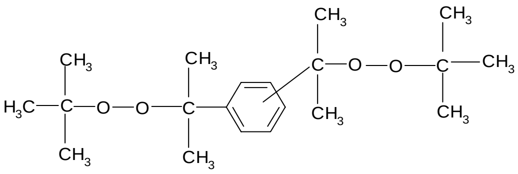
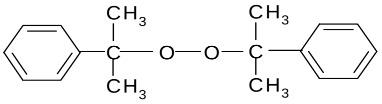
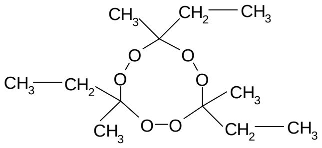
3.2 Experimental

3.2.1 Materials

Ethylidene norbornene (ENB)-containing EPDM rubber, which includes 50 wt % of paraffinic oil, was obtained from DSM Elastomers B.V., The Netherlands. The EPDM contains 63 wt % of ethylene and 4.5 wt % of ENB. It has a Mooney viscosity, ML (1+4) at 125°C, of 52. Polypropylene was obtained from DSM Polypropylenes B.V., The Netherlands. The melt flow index of the polypropylene, measured at 230°C and 2.16 kg is 0.3 g/10 min. Several types of peroxides, obtained from Akzo Nobel Polymer Chemicals B.V., The Netherlands, were employed for this study. The chemical and commercial names and structures of the five peroxides under investigation are given in

Table 3.1. A limited number of experiments could only be performed with 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane because of restricted availability. Triallyl cyanurate, TAC (50%) was used as the co-agent, also obtained from Akzo Nobel Polymer Chemicals B.V., The Netherlands. Two stabilizers, Irganox® 1076 and Irgafos® 168 were obtained from Ciba Geigy.

Table 3.1 Chemical/commercial names and structures of peroxides employed.

Chemical/commercial name	Chemical structure
2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DTBPH) (Trigonox® 101-40D) (40 %) (di-alkyl type)	
2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (DTBPHY) (Trigonox® 145-45B) (45 %) (di-alkyl type)	
di(tert-butylperoxyisopropyl)benzene (DTBPIB) (Perkadox® 14-40B) (40 %) (alkyl-aralkyl type)	
dicumyl peroxide (DCP) (Perkadox® BC-40B) (40 %) (di-aralkyl type)	
3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TTTP) (41 %) (cyclic type)	

3.2.2 Preparation of PP/EPDM TPVs

The TPV compositions employed are shown in Tables 3.2 – 3.4. The experimental variables are the concentration of peroxides and the PP/EPDM blend ratio. All TPVs were mixed by a batch process in a Brabender Plasti-Corder PL-2000, having a mixing chamber volume of 50 cm^3. The batch size was 36 g. The mixer temperature was kept at 180 – 200°C. A constant rotor (cam type) speed of 80 rpm was applied. Polypropylene, stabilizers (Irganox 1076 and Irgafos 168) and EPDM rubber were first mechanically melt-mixed. After 4 min of mixing, the co-agent (TAC) was added, followed by the peroxide. The mixing was continued for another 5 min to accomplish the dynamic vulcanization process. Immediately after mixing, the composition was removed from the mixer and while still molten, passed once through a cold two-roll mill to achieve a sheet of about 2 mm thickness. The sheet was cut and pressed in a compression molding machine (WLP 1600/5*4/3 Wickert laboratory press at 200°C, 4 min and 125 bar pressure). Aluminum foil was placed between the molded sheet and the press plates. The sheet was then cooled down to room temperature under pressure. The dimensions of the sheets were 90x90x2 mm thick. Test specimens were die-cut from the compression molded sheet and used for testing after 24 hrs of storage at room temperature.

Table 3.2 TPV composition (phr) at a fixed PP/EPDM blend ratio.

Material	Phr[#]
EPDM[*]	200.0
PP	50.0
I 1076	0.4
I 168	0.4
Peroxide	Varying doses (0.0 - 7.0)
Co-agent	4.0

[#] Phr is parts per hundred rubber

[*] Including 50 wt % paraffinic oil

Table 3.3 **TPV compositions (phr) at varied PP/EPDM blend ratios with peroxide-concentrations of 9 milli-equivalents and corresponding properties.**

Component	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20
EPDM*	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
PP	25	50	75	100	125	25	50	75	100	125	25	50	75	100	125	25	50	75	100	125
Peroxide:																				
DTBPH	3.3	3.3	3.3	3.3	3.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DTBPHY	–	–	–	–	–	2.9	2.9	2.9	2.9	2.9	–	–	–	–	–	–	–	–	–	–
DTBPIB	–	–	–	–	–	–	–	–	–	–	3.8	3.8	3.8	3.8	3.8	–	–	–	–	–
DCP	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	6.1	6.1	6.1	6.1	6.1
Co-agent:																				
TAC	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stabilizers:																				
I. 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
I. 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Physical properties																				
Tensile Strength (MPa)	2.2	4.2	5.7	6.7	7.8	2.8	3.9	5.2	6.2	7.3	2.3	4.5	5.5	6.5	6.3	2.4	4.7	6.5	7.4	8.9
Elongation at break (%)	401	455	482	419	420	443	401	450	387	391	326	440	427	416	270	419	472	428	375	401
Young's Modulus (MPa)	2.0	13.8	35.1	58.6	89.9	1.8	13.8	36.8	63.6	110.2	2.7	13.9	36.1	67.1	113.6	2.4	14.0	40.8	71.2	108.7
Modulus 300 % (MPa)	1.8	3.3	4.4	5.9	6.9	1.9	3.5	4.4	5.7	6.8	2.2	3.5	4.6	5.6	6.7	1.8	3.4	4.5	5.5	6.8
Hardness (Shore A)	39	61	78	85	92	43	61	79	86	91	44	63	78	87	93	39	61	79	88	93
Overall crosslink density $(\nu+PP)x10^5$ (mol/ml)	5.7	9.9	13.5	18.6	21.2	5.7	12.0	14.7	16.3	19.0	7.7	8.9	15.4	17.5	21.8	6.6	13.5	15.6	19.3	22.4

* Including 50 wt % paraffinic oil

Table 3.4 TPV compositions (phr) at varied PP/EPDM blend ratios with peroxide-concentrations of 15 milli-equivalents and corresponding properties.

Component	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20
EPDM*	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
PP	25	50	75	100	125	25	50	75	100	125	25	50	75	100	125	25	50	75	100	125
Peroxide:																				
DTBPH	5.5	5.5	5.5	5.5	5.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DTBPHY	–	–	–	–	–	4.8	4.8	4.8	4.8	4.8	–	–	–	–	–	–	–	–	–	–
DTBPIB	–	–	–	–	–	–	–	–	–	–	6.4	6.4	6.4	6.4	6.4	–	–	–	–	–
DCP	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	10.0	10.0	10.0	10.0	10.0
Co-agent:																				
TAC	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stabilizers:																				
I. 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
I. 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Physical properties																				
Tensile Strength (MPa)	2.5	5.1	6.5	6.7	7.4	2.6	4.6	5.8	7.1	7.1	2.3	5.2	6.1	7.2	7.8	1.9	5.1	6.6	7.4	7.1
Elongation at break (%)	278	419	442	351	362	294	357	410	436	380	274	369	386	371	356	264	427	429	400	291
Young's Modulus (MPa)	2.5	13.1	34.4	61.4	111.3	2.9	12.5	33.3	63.1	107.1	2.3	12.2	31.9	61.8	111.2	2.3	14.1	32.2	62.2	121.2
Modulus 300 % (MPa)	3.0	4.2	5.0	6.0	6.7	2.8	4.1	5.2	6.2	7.0	2.6	4.5	5.3	6.6	7.4	–	4.2	5.3	6.4	7.2
Hardness (Shore A)	45	67	81	87	92	44	67	79	87	90	40	67	78	87	91	42	68	80	87	92
Overall crosslink density $(\nu+PP)x10^{5}$ (mol/ml)	10.2	15.5	18.6	21.0	24.6	11.7	17.6	19.5	20.8	21.9	10.5	18.0	21.2	24.9	26.9	10.9	18.4	20.0	24.5	28.9

* Including 50 wt % paraffinic oil

3.2.3 Testing procedures

Tensile tests were carried out according to ISO 37 on dumb-bell shaped specimens (type 2) using a Zwick tensile testing machine Z020 at a constant cross-head speed of 500 mm/min. The Young's modulus was determined from the initial slope of the stress-strain curve (0.1 to 0.25 % strain) at a cross-head speed of 50 mm/min.

Compression set tests were performed at 70°C for 22 hrs (ISO 815).

Hardness of the samples was measured by a Zwick Hardness-meter (Shore A type, ISO R868).

The overall crosslink density of the EPDM phase in presence of PP was determined on the basis of equilibrium solvent-swelling measurements in cyclohexane at 23°C, by application of the well known modified Flory-Rehner equation, as shown in the equation 3.1 for tetrafunctional networks.[13,14] A 2-mm thick sample was submerged in cyclohexane. After 24 hrs, the cyclohexane was refreshed to remove the extracted oil and organic stabilizers. After another 24 hrs, the swollen sample was weighed, dried and weighed again. From the degree of swelling an overall crosslink density was calculated relative to the (EPDM+PP) phases as expressed by (ν+PP). The latter was done in order to avoid the need to correct for a part of the PP, being extracted as amorphous PP.

$$(\upsilon + PP) = -\frac{1}{V_s} \times \frac{\ln(1-V_r) + V_r + \chi(V_r)^2}{(V_r)^{1/3} - 0.5 \times V_r} \quad \text{(mol/ml)} \qquad 3.1$$

where, V_s = molar volume of cyclohexane, χ = polymer-swelling agent interaction parameter, or Flory-Huggins parameter, which in this case is 0.315[15] and V_r is the volume fraction of EPDM-rubber in the swollen network, which is expressed by

$$V_r = \frac{1}{A_r + 1} \qquad 3.2$$

where, A_r is the ratio of the volume of absorbed cyclohexane to that of EPDM after swelling.

A rubber process analyzer, RPA-2000 (Alpha Technologies), which is a torsional dynamic rheometer, whose test cavity design is similar to that of a moving die rheometer, was used to measure the cure-characteristics of the compounds containing different types of peroxides, at a fixed concentration of 9 milli-equivalents relative to 100 g of pure EPDM compound (no PP added) at a temperature of 180°C according to ISO 6502.

3.3 Results

3.3.1 Influence of various peroxides at a fixed PP/EPDM blend ratio

3.3.1.1 Influence of different types and concentrations of peroxides on the physical properties

Figure 3.1 shows the tensile strength as a function of concentration of the peroxides (milli-equivalents per 100 g of pure EPDM rubber) for the different types of peroxide-cured PP/EPDM TPVs. In most cases it is observed that with increasing concentration of peroxide the tensile strength first increases, then reaches a plateau. Dicumyl peroxide (DCP) reaches the earliest and highest plateau, whereas 2,5-

dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (DTBPHY) stops at the lowest level. 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TTTP) is the overall lowest, does not reach a plateau and keeps on increasing.

Figure 3.2 shows the elongation at break as a function of concentration of the peroxides. With increasing concentration the elongation at break decreases, although overall little difference between the various peroxides is noticed; except for TTTP, which shows a very high elongation at break compared to the others.

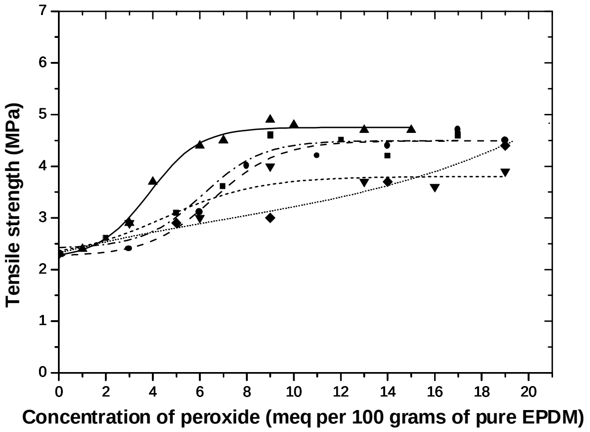


Figure 3.1: Tensile strength as a function of concentration for different types of peroxides: (▲—— ▲): DCP; (■----■): DTBPIB; (●--- ●): DTBPH; (▼... ▼):DTBPHY; (◆·······◆): TTTP.

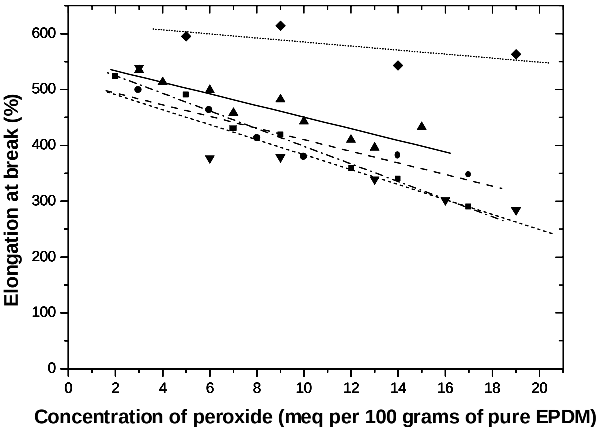


Figure 3.2: Elongation at break as a function of concentration for different types of peroxides; symbols as in Fig. 3.1.

In Figure 3.3 the Young's modulus is shown as a function of concentration of the peroxides. In most cases, the Young's modulus increases with increasing concentration of the peroxide and reaches a plateau at a concentration of 7 – 9 milli-equivalents of peroxide. Overall little difference is observed between the various peroxides; TTTP is overall the lowest, does not reach a plateau and keeps on increasing.

Compression set (70°C/22 hr) as a function of concentration of peroxides is shown in Figure 3.4. With increasing concentration of peroxide, the value of the compression set decreases linearly indicating better elastic recovery. DCP clearly gives the lowest compression set values, whereas TTTP gives the highest. No significant difference is seen for the other three.

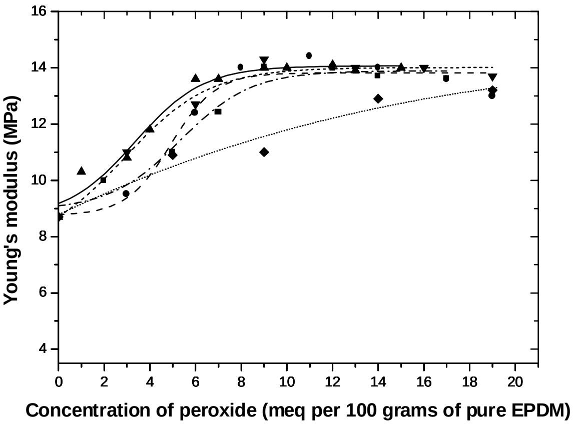


Figure 3.3: Young's modulus as a function of concentration for different types of peroxides; symbols as in Fig. 3.1.

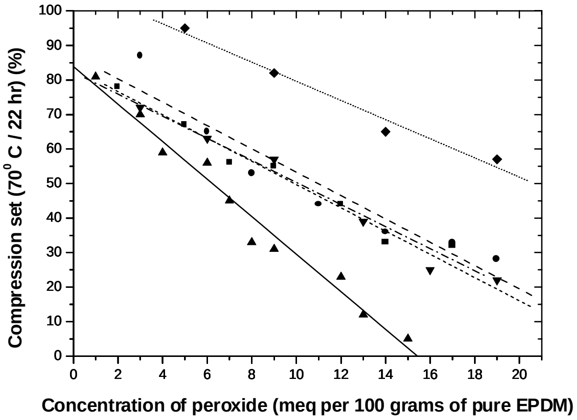


Figure 3.4: Compression set as a function of concentration for different types of peroxides; symbols as in Fig. 3.1.

Figure 3.5 shows Shore A hardness versus the concentration of peroxides. Only a small increase in the hardness values is noticed in all cases. The average values of the hardness vary in between 60 – 65 Shore A. DCP tends to show a small increase at higher peroxide concentrations, whereas TTTP is more or less in the same line with the other peroxides.

3.3.1.2 Overall crosslink density

The overall crosslink density, (ν+PP) as a function of the concentration of various peroxides is shown in Figure 3.6. With increasing concentration of peroxides, the value of the overall crosslink density increases. DCP is found to give the highest crosslink densities, whereas TTTP is the lowest. Only small differences are seen for the other three.

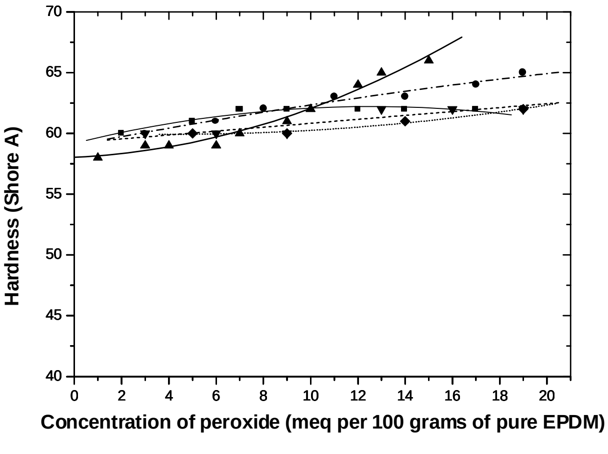


Figure 3.5: Hardness as a function of concentration for different types of peroxides; symbols as in Fig. 3.1.

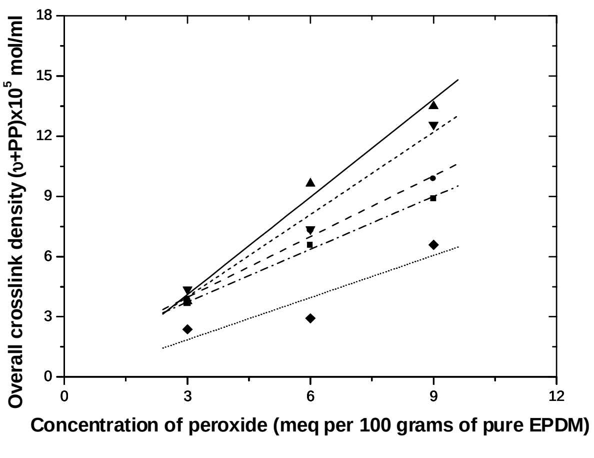


Figure 3.6: Overall crosslink density as a function of concentration for different types of peroxides; symbols as in Fig. 3.1.

3.3.1.3 Kinetic aspects

An attempt was made to interprete the results of the Young's modulus in terms of the crossslink densities, as obtained from the delta torque values (maximum torque – minimum torque) in RPA rheograms, taken on 'equivalent' pure vulcanized EPDM-compounds with 9 milli-equivalents of peroxides added. A compound with TTTP could not be measured because of restricted availability of this peroxide. Figures 3.7 and 3.8 show the rheograms of the 'equivalent' EPDM vulcanizates taken at 180° and 200°C, respectively. DCP shows fastest rate of cure, whereas DTBPHY shows a relatively slow rate of cure at either temperature.

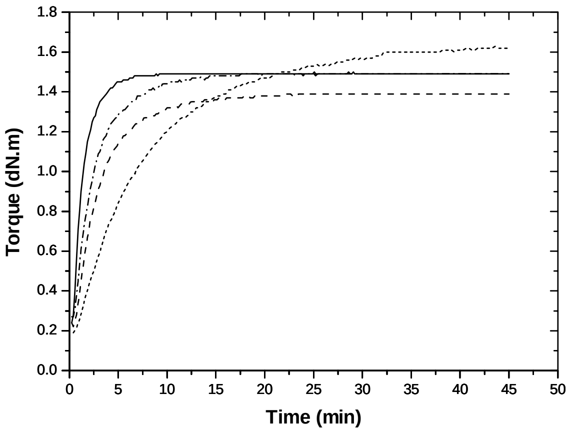


Figure 3.7: Rheograms for 'equivalent' thermoset EPDM-compounds with 9 meq of various peroxides at 180°C:(——): DCP; (-.-.): DTBPIB; (- - -): DTBPH; (..........): DTBPHY.

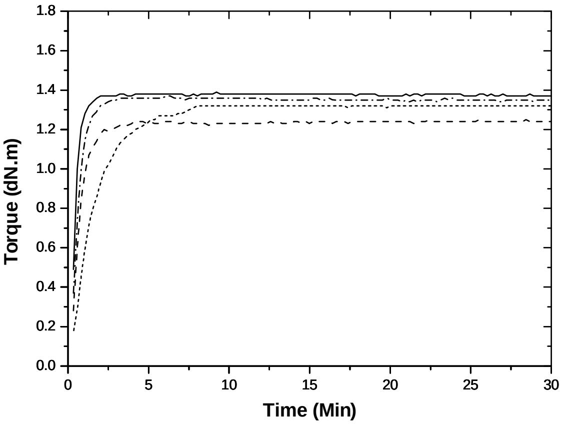


Figure 3.8: Rheograms for 'equivalent' thermoset EPDM-compounds at 200°C; symbols as in Fig. 3.7.

Figure 3.9 shows the comparison of delta torque obtained at 180°C and 200°C for the different peroxides. With increasing vulcanization temperature, the values of delta torque decrease. At 200°C, little difference remains left between the various peroxides.

Figure 3.10 shows a comparison of the different peroxides on tensile strength of TPVs, as obtained after different temperatures and total times of mixing. With increasing temperature and/or with increasing total time of mixing the tensile strength decreases. Although at mixing temperature 180°C and time 10 min, large differences are observed between the various peroxides as also shown in Figure 3.1, at extended mixing time (15 min) or higher mixing temperature (200°C) much of the differences between the various peroxide are leveled off.

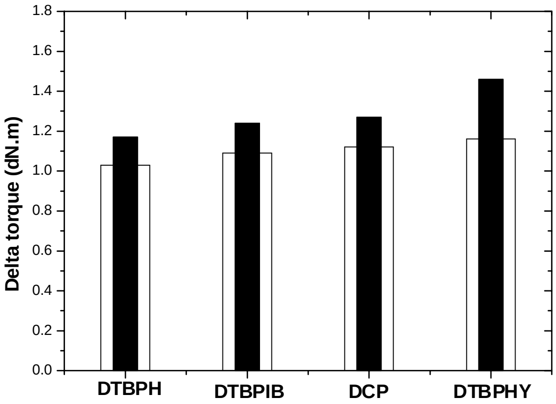


Figure 3.9: Delta torque for different types of peroxide-cured EPDM vulcanizates at (■): 180°C; (□): 200°C.

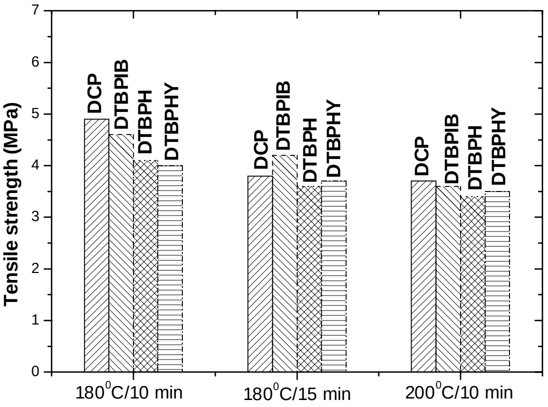


Figure 3.10: Tensile strength of TPVs for different types of peroxides as a function of different temperatures and total times of mixing.

Figure 3.11 shows the performance of peroxides on elongation at break of the TPVs. A similar argument as for the tensile strength does apply. The performance of the different peroxides on Young's modulus of the TPVs is shown in Figure 3.12. With increasing temperature or with increasing total times of mixing, in most of the cases, the Young's modulus decreases. No big differences between various peroxides are seen at 180°C/10 min of mixing and 200°C/10 min of mixing, but significant differences are observed at 180°C/15 min.

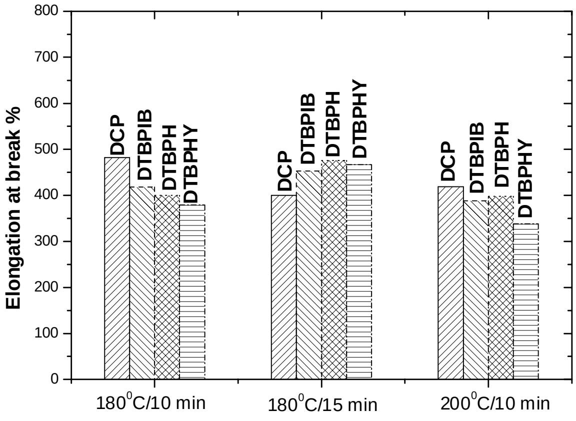


Figure 3.11: Elongation at break of TPVs for different types of peroxides as a function of different temperatures and total times of mixing.

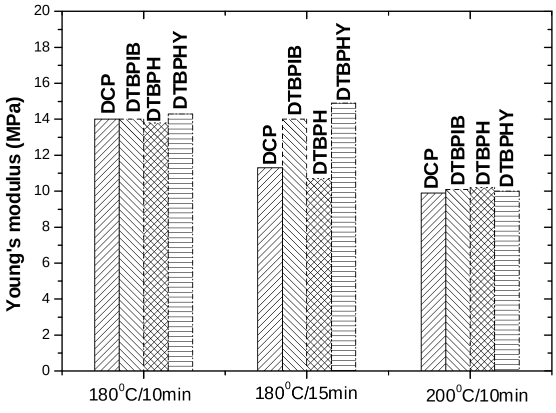


Figure 3.12: Young's modulus of TPVs for different types of peroxides as a function of different temperatures and total times of mixing.

3.3.2 Influence of various peroxides at varied PP/EPDM blend ratios

Figures 3.13 and 3.14 show the tensile strength of the PP/EPDM TPVs as a function of the amount of PP, at fixed concentrations of 9 and 15 milli-equivalents of the different peroxides per 100 g of pure EPDM rubber. With increasing concentration of PP, the tensile strength increases; but different types of peroxides show different behavior. At 9 milli-equivalents concentration, DCP shows the highest values irrespective of the PP-contents. DTBPH and DTBPHY give more or less similar values; whereas, DTBPIB shows the lowest values. At 15 milli-equivalents concentrations, all the peroxides except DCP give somewhat higher values of tensile strength as compared to 9 milli-equivalents. Furthermore, at 15 milli-equivalents concentrations, the values of tensile strength are the same amongst all different kinds of peroxides.

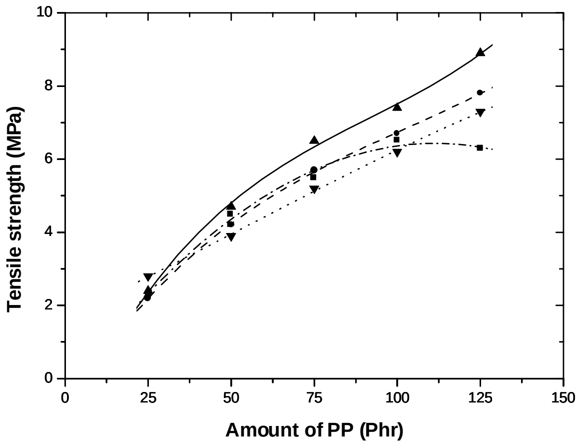


Figure 3.13: Tensile strength as a function of amount of PP for 9 milli-equivalents of different types of peroxides: (●–– ●): DTBPH; (▼… . ▼):DTBPHY; (■–·–· ■): DTBPIB; (▲ ——▲): DCP.

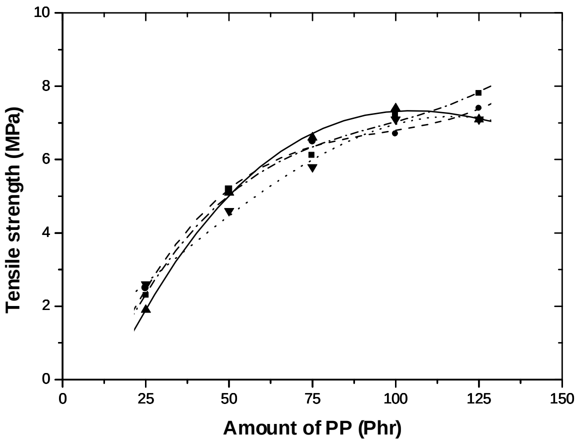


Figure 3.14: Tensile strength as a function of amount of PP for 15 milli-equivalents of different types of peroxides; symbols as in Fig. 3.13.

Young's moduli as a function of concentration of PP for various peroxides are depicted in Figures 3.15 for 9 milli-equivalents peroxide-concentration, and 3.16 for 15 milli-equivalents peroxide-concentration. With increasing contents of PP, the Young's moduli of the TPVs increase. At 9 milli-equivalents concentration, in most cases, DCP and DTBPIB exhibit higher values irrespective of PP-contents. On the other hand, DTBPH gives the lowest values. At 15 milli-equivalents concentrations, DCP shows the highest values irrespective of the concentration of PP, whereas the other three peroxides deliver more or less comparable values.

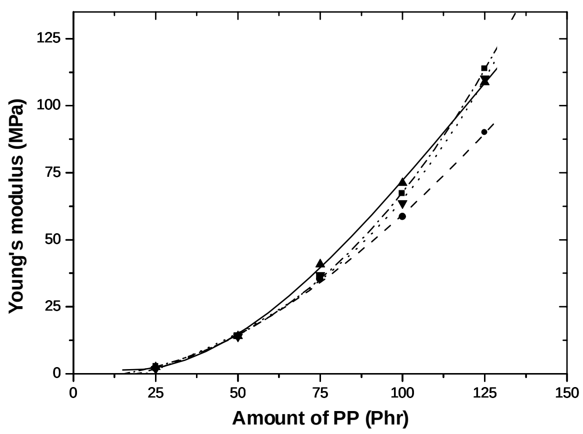


Figure 3.15: Young's modulus as a function of amount of PP for 9 milli-equivalents of different types of peroxides; symbols as in Fig. 3.13.

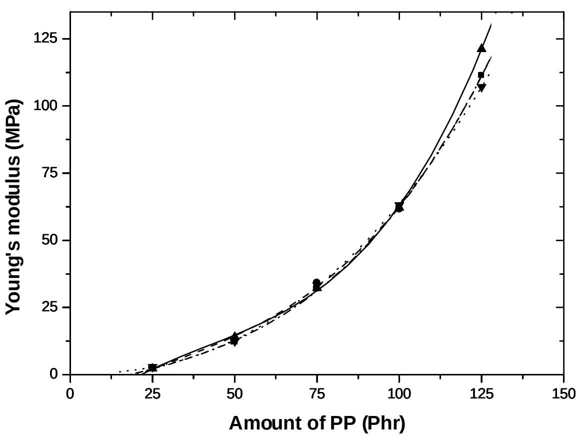
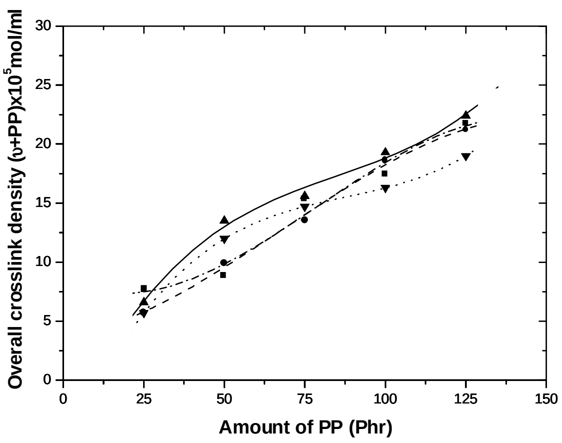


Figure 3.16: Young's modulus as a function of amount of PP for 15 milli-equivalents of different types of peroxides; symbols as in Fig. 3.13.

The values of the moduli at 300 % of the TPVs also increase with increasing amounts of PP, as seen in Tables 3.3 and 3.4. Both at 9 and 15 milli-equivalents concentrations, all the peroxides give more or less similar values.

Tables 3.3 and 3.4 also show the Shore A hardness values of the TPVs as a function of the concentration of PP. An increase in the hardness (~ 40 to 90 Shore A) takes place with increasing amount of PP. DCP shows slightly higher values as compared to the other peroxides. Overall little difference is seen between the various peroxides, irrespective of the PP-content. However, in most cases, at 15 milli-equivalents concentrations, all the peroxides give relatively higher values as compared to 9 milli-equivalents.

The overall crosslink density, (ν+PP) as obtained from the cyclohexane solvent swelling method, for different types of peroxides at different PP concentrations is shown in Figures 3.17 for 9 milli-equivalents peroxide-concentration and 3.18 for 15 milli-equivalents peroxide-concentration. The values are higher for 15 milli-equivalents peroxide-concentrations in comparison to those for 9 milli-equivalents. Moreover, with increasing amounts of PP, the overall crosslink density values of the TPVs increase. In this test the PP-content of the TPV is included in the value of the crosslink density, and therefore, only a comparison of values for the same PP-content is of value. In most cases, DCP shows the highest values amongst all the various peroxides, irrespective of the PP-contents, followed by DTBPIB. DTBPH and DTBPHY give more or less comparable values.



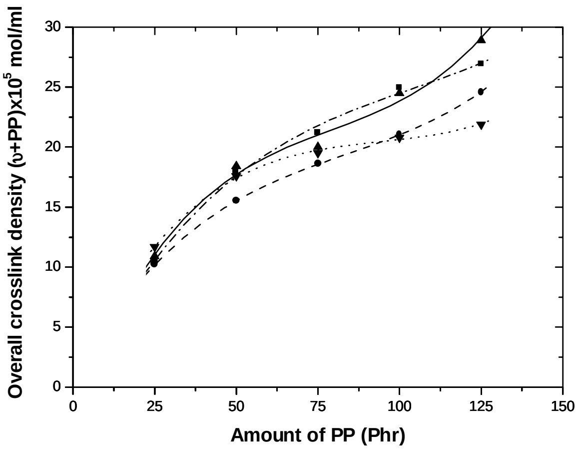


Figure 3.17: Overall crosslink density as a function of amount of PP for 9 milli-equivalents of different types of peroxides; symbols as in Fig. 3.13.

Figure 3.18: Overall crosslink density as a function of amount of PP for 15 milli-equivalents of different types of peroxides; symbols as in Fig. 3.13.

3.4 Discussion

There are many explanations possible for the difference in the physical properties related to the various peroxides used. It is amongst others well known that the morphology[16,17] and rheology[18,19] of the TPV has a strong influence on properties. Furthermore, the extent of degradation of PP-degradation versus crosslinking of the EPDM phase may differ for various types of peroxides investigated. In this context, the effects of decomposition mechanism, solubility aspects and kinetic factors of the various peroxides on the properties are mainly highlighted.

3.4.1 Decomposition mechanism

The decomposition rate of a peroxide depends on the bond strength of the weakest bond, being the O–O bond. This bond strength in turn depends on the chemical nature of hydrocarbon group attached and the polarity of the substrate, in which the peroxide is dispersed. The influence of the chemical nature of the hydrocarbon group depends on structural effects such as resonance stabilization of the free radicals generated upon decomposition of the peroxide, respectively steric and inductive effects. The chemical nature of the resulting free radicals from the peroxides plays another important role in determining the final properties. The most useful peroxides are those, of which the primary free radicals are sufficiently reactive to abstract hydrogen atoms from the polymer chain, to form the corresponding macro-radicals. The relative reactivity or stability of the free radicals generated is again related to the hydrogen bond dissociation energy of the parent compound. From the values of bond dissociation energy, it can be deduced that radicals such as phenyl, methyl, tert-butoxy and alkoxy are highly reactive and are good hydrogen-abstractors. On the other hand, radicals such as ethyl, isopropyl and tert-butyl are lower in energy and are poor hydrogen-abstractors.[20,21]

The relative amounts of decomposition products, as indicative of the types and quantities of radicals generated from the thermal decomposition of the various peroxides in pentadecane, are shown in Table 3.5.[3] For TTTP this data is not available. DCP primarily generates cumyloxy radicals, which further undergo β-cleavage to form acetophenone and methyl radicals. Both the cumyloxy and methyl radicals have sufficient energy to abstract hydrogen atoms from most sites available in a polymer. In addition, the methyl radical is not as sterically hindered as the initial cumyloxy radical and may more efficiently involve in reactions where steric hindrance is a limitation.[21] Most of other peroxides under investigation form tert-butoxy radicals, which further decompose into methyl radicals and other products. The sum of the relative amounts of methane and tert-butanol per peroxide provides a good indication of their respective abilities to form good hydrogen-abstractors.

The highest efficiency of DCP as observed in Figures 3.1 – 3.6 can therefore be interpreted in terms of the nature, reactivity and amount of generated radicals, as obtained from the fragmentation of the peroxide. In particular, the relatively large amount of methane per mole of DCP is indicative of a high level of highly reactive methyl radicals generated by this peroxide.

Table 3.5 Relative amounts of decomposition products from various peroxides.

Name of peroxide	Experimental temperature (°C)	Decomposition products	Relative amount (mol/mol peroxide)
DCP	160	methane	0.91
		acetophenone	0.91
		2-phenylpropanol-2	1.06
		α-methylstyrene	0.01
		water	0.01
DTBPIB	155	tert-butanol	1.83
		acetone	0.13
		methane	1.10
		di-(hydroxy-i-propyl) benzene	0.30
		acetyl hydroxy-i-propyl benzene	0.54
		diacetyl benzene	0.14
DTBPH	145	methane	0.31
		ethane	0.40
		acetone	1.62
		tert-butanol	1.65
		tert-amylalcohol	0.23
DTBPHY	180	methane	0.57
		carbon dioxide	0.02
		acetone	0.57
		tert-butanol	1.39
		2,5-dimethyl-2,5-dihydroxyhexyne-3	0.79

3.4.2 Solubility aspects

EPDM/PP blends essentially are a two-phase system, where the EPDM-phase has a slightly different solubility parameter from PP. At the temperature where the addition of the peroxide is made, the solubility parameter of the latter is of great importance for which of the two phases it shows the highest preference: the EPDM-phase to perform crosslinking or the PP-phase, where degradation of the PP will mainly occur. Therefore, it is an important point with the series of peroxides investigated in this paper to obtain an impression about their distribution over the two phases.

The solubility parameters (δ) of non-electrolytes can be determined from their cohesive energy density (CED) or their heat of vaporization as follows:

$$\delta = (\mathrm{CED})^{1/2} = \left\{\frac{H_v - RT}{V}\right\}^{1/2} \qquad (3.3)$$

where, H_v = molar heat of vaporization, R = gas constant, T = absolute temperature and V = molar volume.

However, as it is very difficult to measure the solubility parameters of the different components at the mixing temperature, an attempt was made to calculate those. The solubility parameter can be calculated using group contribution methods, which are based on the assumptions that the contributions of different functional groups to the thermodynamic property are additive.[22] The energy of vaporization of a solvent or polymer is:

$$\Delta E_V = \sum_j n_j \Delta e_j \qquad (3.4)$$

where, ΔE_V is the total energy of vaporization of the solvent or polymer, Δe_j is the energy of vaporization contribution of group j, and n_j the number of groups of type j in the molecule. The solubility parameter is thus obtained from equation 3.4:

$$\delta = \left(\frac{\Delta E_V}{V}\right)^{1/2} = \left(\frac{\sum_j n_j \Delta e_j}{V}\right)^{1/2} \qquad (3.5)$$

Small[23] defined the molar attraction constant as:

$$F_j = \left(\Delta E_V V\right)^{1/2} \qquad (3.6)$$

where, F_j is the molar attraction constant for group j.
Equations 3.5 and 3.6 can be used to calculate the solubility parameter by:

$$\delta = \left(\frac{\Delta E_V V}{V^2}\right)^{1/2} = \frac{\sum_j F_j}{V} = \frac{\rho \sum_j F_j}{M} \qquad (3.7)$$

where, ρ is the density and M is the molecular weight.

Using the values of molar attraction constants given by Small[23], the solubility parameters of different peroxides were calculated by Hogt.[24] The solubility parameters were also experimentally determined by Hogt from the molar heats of vaporization of various peroxides using a differential scanning calorimeter. For most peroxides, an excellent correlation was found between the solubility parameters determined experimentally and those calculated according to Small's group contribution method for a temperature of 25°C: Table 3.6.

Table 3.6 Molar volume, heat of vaporization and solubility parameter of peroxides and polymers.

Type of polymer/ peroxide	Molar volume, (cm^3/mole)	Heat of vaporization, (kJ/mole)	Solubility parameter at 25°C (Exp.) $(J/cm^3)^{1/2}$	Solubility parameter at 25°C (Calc.) $(J/cm^3)^{1/2}$	Solubility parameter at 180°C (Calc.) $(J/cm^3)^{1/2}$
EPDM				17.2	16.6
PP				16.6	15.1
DCP	260	84.1	17.7	17.7	14.6
DTBPIB	358	79.3	14.6	15.5	12.8
DTBPH	335	66.5	13.8	14.1	11.6
DTBPHY	324	76.8	15.1	13.9	11.5

On basis of Small's method, the values for PP and for EPM copolymer (70 – 80 wt % ethylene)[24], also at 25°C were calculated, as shown in Table 3.6 as well. In order to correlate these values at 25°C now with the mixing temperature, the solubility parameter values of the peroxides (at the liquid-state) at a mixing temperature of 180°C were calculated using the following equation:[25]

$$\ln \delta_T = \ln \delta_{298} - 1.25\alpha\,(T-298) \qquad (3.8)$$

where, α = the coefficient of linear thermal expansion of the peroxides. These were estimated from density measurements up to 80°C and were about 10^{-3} K^{-1}.[24] The solubility parameter values of PP and EPDM (at the molten-state) at the higher temperature of 180°C were calculated using the following equation:[26]

$$\ln \delta_T = \ln \delta_{298} - \alpha\,(T-298) \qquad (3.9)$$

as the coefficient of linear thermal expansion for PP a value of 6.3×10^{-4} K^{-1} was taken[27] and 2.3×10^{-4} K^{-1} for EPDM.[28] Table 3.6 gives the values of the experimental as well as calculated solubility parameters of the polymers and peroxides at 25 and 180°C. For all peroxides, their solubility parameters are lower than for PP and even more so for EPDM. Consequently, there is the tendency for the peroxide to preferably partition towards the PP phase. Higher solubility parameters of the peroxides correlate with a decreased difference with the solubility parameters of EPDM and correspondingly a higher tendency to partition towards EPDM. Hogt[24] showed a plot of the partition coefficient of peroxide in PP/NBR as a function of solubility parameter, resulting in an increased partitioning of the peroxide towards the NBR phase for a higher solubility parameter.

The decreasing order of the solubility parameters of the peroxides parallels the same order in the tensile strength of PP/EPDM TPVs, as shown in Figure 3.19. The higher extent of crosslinking in the EPDM phase results in a better elastic recovery and therefore lowers the compression set. Figure 3.20 shows the correlation between the compression sets of the PP/EPDM TPVs and the solubility parameters of the peroxides. The higher the solubility parameter of the peroxide, the better is the compression set property. DCP has a solubility parameter the closest to EPDM, therefore, it is more strongly partitioned away from PP into the rubber, resulting in less PP degradation. This is another explanation for the efficiency of DCP in giving the highest level of properties.

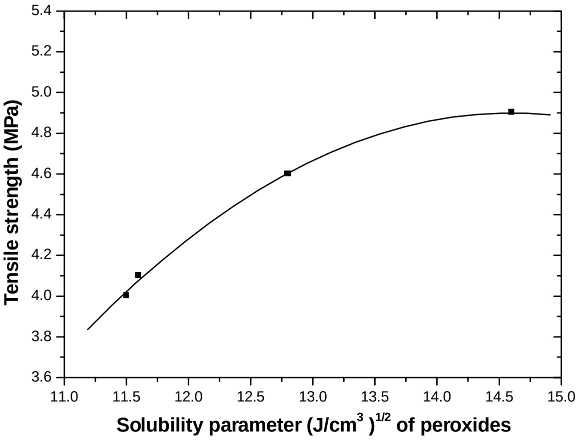


Figure 3.19: Tensile strength of PP/EPDM TPVs as a function of solubility parameter of the peroxides.

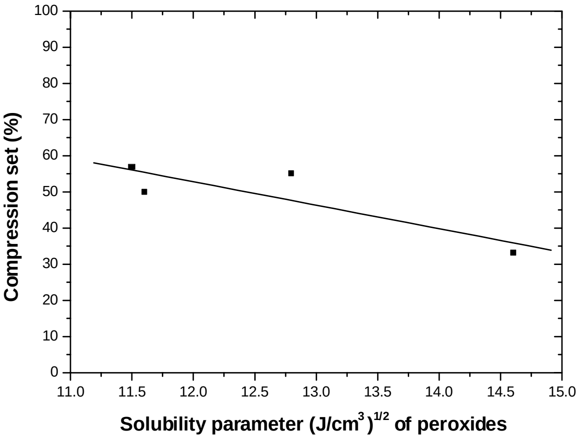


Figure 3.20: Compression set of PP/EPDM TPVs as a function of solubility parameter of the peroxides.

3.4.3 Kinetic factors

It is generally accepted that the degradation of PP proceeds through β-chain scission by abstraction of tertiary hydrogen atoms off the main chain. Generally, the activation energy for fragmentation is much higher than that for recombination of radicals, so the peroxide efficiency is influenced by temperature. Higher temperature increases the rate of fragmentation vs. that of macroradical recombination. The increase in β-scission is found to be approximately two orders of magnitude between 120 (solid state) and 170°C (melt).[29] With the progressing degradation, the average molecular weight of the PP decreases and the molecular weight distribution becomes narrower. The effect of different peroxides towards PP degradation is generally expressed in terms of the melt flow index (MFI). The MFI of degraded PP increases linearly with the peroxide concentration.[30] On the other hand, the MFI of PP itself also depends on the temperature. It has been observed that the increase in MFI is approximately two orders of magnitude between 100 and 140°C, which means that the increase in the MFI and the rate of β-scission are proportional.[29] Hogt[24] reported the change of MFI, measured at 190°C at 2.16 kg load for PP with 1 milli-equivalent of different peroxides. The peroxides tested were slightly different as to their reactivity towards the induction of chain scission in PP. It was observed that DCP and DTBPIB are less prone towards PP degradation as compared to DTBPHY.

The delta torque obtained from the RPA rheograms correlates with the crosslinking efficiency of the peroxides, which is defined as the number of moles of chemical crosslinks formed per mole peroxide. Normally, for the peroxide vulcanization of highly unsaturated elastomers (e.g., SBR and BR) efficiency values higher than 10 were found, whereas for saturated elastomers values of less than 1 were observed. For instance, for the crossliking of EPM, crossslinking efficiencies of 0.1 to 0.8 were reported.[4,31] The effect of different types of peroxides at a fixed concentration of peroxide on the Young's modulus of PP/EPDM TPVs can only be correlated with the delta torque values to a limited extent. As shown in Figures 3.21 and 3.22, the effect is more pronounced at 180°C and hardly left at 200°C. It should be noted however, that the latter was measured by static vulcanization in absence of PP. This is not exactly a one-to-one equivalence to dynamic vulcanization, due to the lack of high shear and the longer time scales, which translate to different crosslinking efficiency as shown in Figure 3.12. The decrease of delta torque for EPDM vulcanizate with increasing temperature can be explained in terms of the decreasing viscosity of EPDM and the decreasing efficiency of a peroxide with increasing temperature. Kawashima et al.[32] reported the dependence of the peroxide crosslinking efficiency on the reaction temperature of several unsaturated polyolefins: the efficiency gradually increased up to a certain temperature and then decreased abruptly. This decrease of efficiency was considered to be due to a decrease in the hydrogen abstraction efficiency and an increase in the termination rate in a chain reaction.

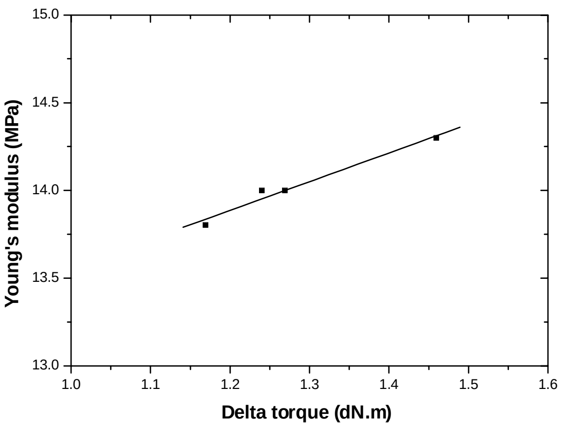


Figure 3.21: Young's modulus of PP/EPDM TPVs mixed at 180°C as a function of delta torque measured on 'equivalent' EPDM compounds at 180°C.

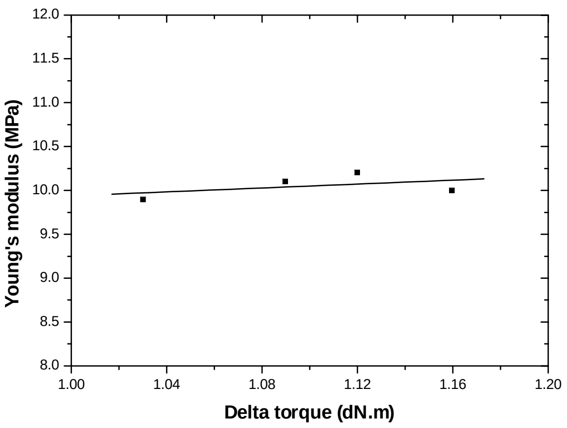


Figure 3.22: Young's modulus of PP/EPDM TPVs mixed at 200°C as a function of delta torque measured on 'equivalent' EPDM compounds at 200°C.

The decrease of the tensile strength and Young's modulus of TPVs with increasing temperature or total time of mixing as obtained from Figures 3.10 and 3.12 is therefore ascribed to the following factors: prolonged degradation of PP and decreased efficiency of the peroxides at higher temperature, resulting in a lower level of crosslinking.

Different rates of cure for different types of peroxides can be explained in terms of the half-life time of the corresponding peroxides. The half-life decreases with increasing temperature. The Arrhenius factor (A) and the activation energy (E_a) of the peroxides used are given in the Table 3.7.[33] The half-life times of the peroxides at 180 and 200°C, calculated from A and E_a values are also given in Table 3.7. The values of $t_{0,90} - t_{S2}$, (min) for different types of peroxide-cured EPDM vulcanizates, as obtained from RPA at 180 and 200°C, are given in Table 3.8. This can be taken as a measure of cure rate. DCP, having the shortest half-life time of all peroxides investigated, shows the fastest rate of cure. Therefore, the kinetic aspect is another reason for the highest level of physical properties obtained with DCP.

Table 3.7 Arrhenius factor (A), activation energy (E_a) and half-life of peroxides at 180 and 200°C.

Peroxide type	A (s^{-1})	E_a (kJ/mole)	Half-life (min) at 180°C	Half-life (min) at 200°C
DCP	9.24 E + 15	152.67	0.50	0.09
DTBPH	1.68 E + 16	155.49	0.58	0.10
DTBPIB	7.65 E + 15	152.69	0.61	0.11
DTBPHY	1.90 E + 15	150.67	1.54	0.26

Table 3.8 Cure rate index for different types of peroxide-cured EPDM vulcanizates at 180 and 200°C.

Peroxide type	Cure rate index (min) at 180°C	Cure rate index (min) at 200°C
DCP	3.20	0.75
DTBPH	7.53	1.42
DTBPIB	6.42	1.18
DTBPHY	20.89	4.12

The reason for the increased tensile strength, modulus, hardness and overall crosslink density of TPVs with increasing amount of PP in PP/EPDM blends, as seen in Tables 3.3 and 3.4, is obviously the result of the higher amount of thermoplastic hard component in the blends. However, the dependence of tensile strength, modulus and overall crosslink density on PP-content shows minor differences, depending on the nature of peroxide, particularly at high PP-amounts. These differences are to be interpreted in terms of different crosslink densities obtained with the various peroxides and at the varied PP/EPDM blend ratios. For that purpose a test-method for crosslink density is required, which excludes effects of the varied PP/EPDM blend ratios. The latter is generally acknowledged to be a major problem for TPVs.

In the present study, two methods were attempted to determine the crosslink density: cyclohexane solvent swelling and the boiling xylene-gel method. The first, cyclohexane solvent swelling, obviously does not comply with the requirement that it excludes effects of the PP/EPDM blend ratios. As explained before, the (ν+PP) includes the PP-content of the blend in the gel-count. The boiling xylene-gel method comprises two successive extractions: first, extraction of oil and organic stabilizers from TPV film by boiling acetone (20 hrs) and determining the dry weight of the acetone residue; then exhaustive extraction of the acetone residue by means of boiling xylene (20 hrs) and determining the dry weight of the xylene residue. The xylene-gel method would be grossly preferred over the solvent swelling measurement with cyclohexane, because in this method, the PP-matrix does dissolve and is not included in the gel-count. However, it was observed that the values obtained from the solvent swelling method are far more accurate and reproducible than those of the xylene gel test. The differences to be measured in the ultimate yield are in the order of milligrams: particularly at high PP-amounts, the xylene-gel is the difference of two large numbers, each with their own relative weighing errors, resulting in an excessively large relative error in the final result. Furthermore, extra attention needs to be paid to the xylene-extraction, which is found to be not always exhaustive. For these reasons, it is generally acknowledged that gel-contents below 80 % cannot be accurately measured by this xylene gel method.[34] In the context of this study, mostly xylene-gel counts less than 80 % were found, suffering from above inaccuracies. This test was therefore not further pursued.

It was tried to correlate the changes in physical properties of peroxide-cured TPVs e.g., tensile strength and Young’s modulus as a function of the changes in overall crosslink density values. Unfortunately, it did not really show a good correlation either, which is most probably because of the different extents of degradation caused by the different types of peroxides. The latter also contributes to the final properties of the TPVs.

Overall, the study at varied PP/EPDM blend ratios turned out to be an evidence and further justification in favor of the results as already obtained with the fixed PP/EPDM blend ratios.

3.5 Conclusions

The physical properties of peroxide-cured TPVs at a fixed as well as at varied PP/EPDM ratio change significantly with the chemical nature of peroxides, the extent of crosslinking of the EPDM phase and the extent of degradation of PP-phase. The reason of increased tensile strength, modulus and hardness with the increasing amount of PP is the increased thermoplastic hard component in the blends. Three parameters have been identified, which are of paramount importance on the final properties of TPVs: the solubility parameter of a peroxide relative to the polymers PP and EPDM, the decomposition mechanism of the peroxide and the kinetic aspects of the peroxide fragmentation. The tensile strength and compression set of the TPVs with the various peroxides can be correlated with the solubility parameters of the various components: the closer the solubility parameter of the peroxide to that of the EPDM, the higher is the tensile strength and the better is the compression set property. The Young’s modulus of peroxide-cured TPVs shows a slight correlation with the delta torque values of RPA measurements on ‘equivalent’ pure EPDM vulcanizates. The latter corresponds to the crosslinking efficiencies of the peroxides. Dicumyl peroxide (DCP), out of five different types of peroxides investigated for PP/EPDM TPVs, gives the best overall balance of properties. This peroxide complies the best of all with the parameters described above.

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Chapter 4

Multifunctional peroxides as potential alternatives for conventional peroxide/co-agent combinations in TPVs

Dicumyl peroxide in combination with triallyl cyanurate as crosslinking agent provided a good overall balance of physical properties of PP/EPDM TPVs. However, commonly used peroxides like dicumyl peroxide generally produce volatile decomposition products, which provide a typical smell or show a blooming effect. In the present chapter, multifunctional peroxides are described, which reduce the above-mentioned problems. They consist of a peroxide and co-agent-functionality combined in a single molecule. The multifunctional peroxides provide performance-properties of TPVs, which are comparable with commonly employed co-agent assisted peroxides. The solubility and kinetic aspects of the various peroxides are mainly highlighted, as well as the decomposition products of the multifunctional peroxides with respect to the avoidance of smelly by-products. Particularly 2,4-diallyloxy-6-tert-butylperoxy-1,3,5-triazine turns out to be a good alternative for the dicumyl peroxide/triallyl cyanurate combination.

4.1 Introduction

In Chapter 3 it was demonstrated, that the application of a proper peroxide in combination with a suitable classical co-agent provides a good overall balance of physical properties of PP/EPDM TPVs. Besides the advantages of peroxides, there are also some disadvantages. Depending on the composition of the peroxide applied, the decomposition products are more or less volatile. The latter often provide a typical smell, show a blooming effect or can be extracted from the crosslinked compound by solvents. For instance, the typical sweet smell of acetophenone, one of the decomposition products of dicumyl peroxide (DCP) is well known, as shown in Figure 4.1.

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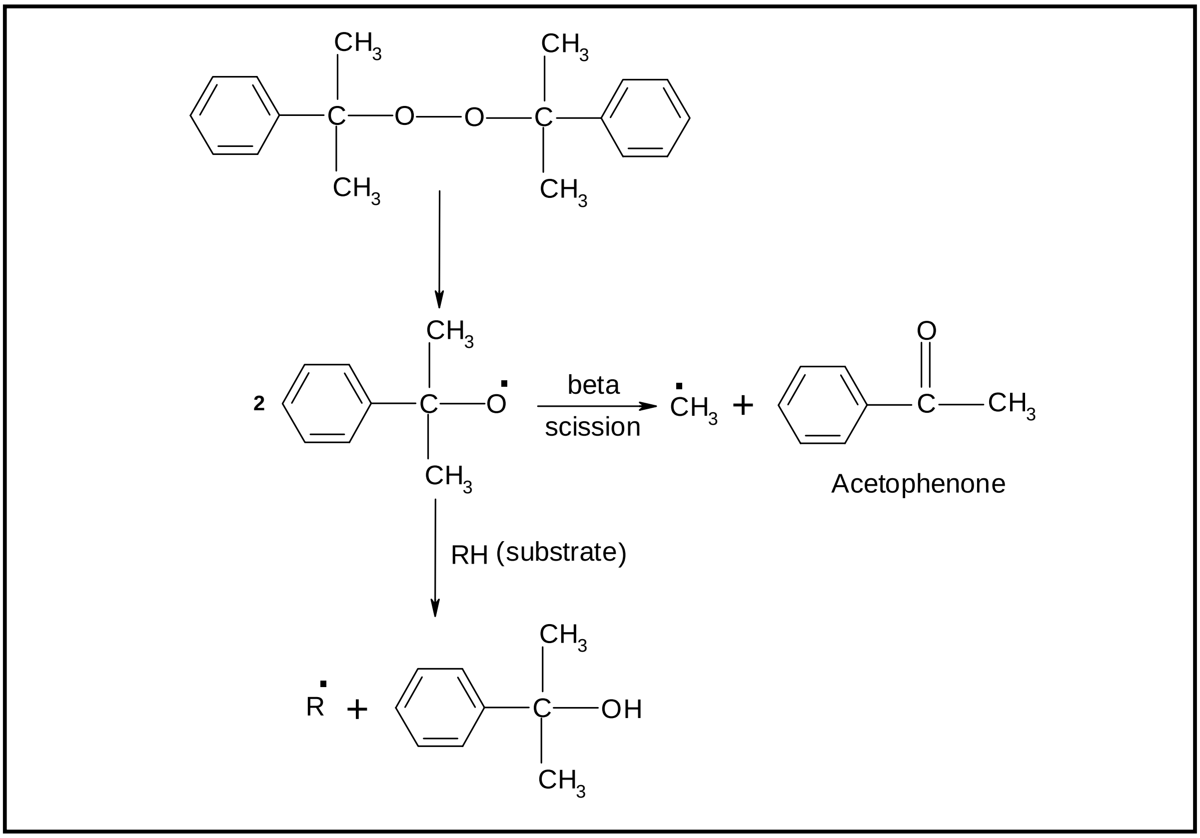


Figure 4.1: Decomposition mechanism of dicumyl peroxide (DCP).

Blooming phenomena can also take place due to the formation of dihydroxy isopropyl benzene from the decomposition of di(tert-butylperoxyisopropyl)benzene, because of its limited solubility in the rubber matrix.[1] The decomposition mechanism of that peroxide is shown in Figure 4.2.

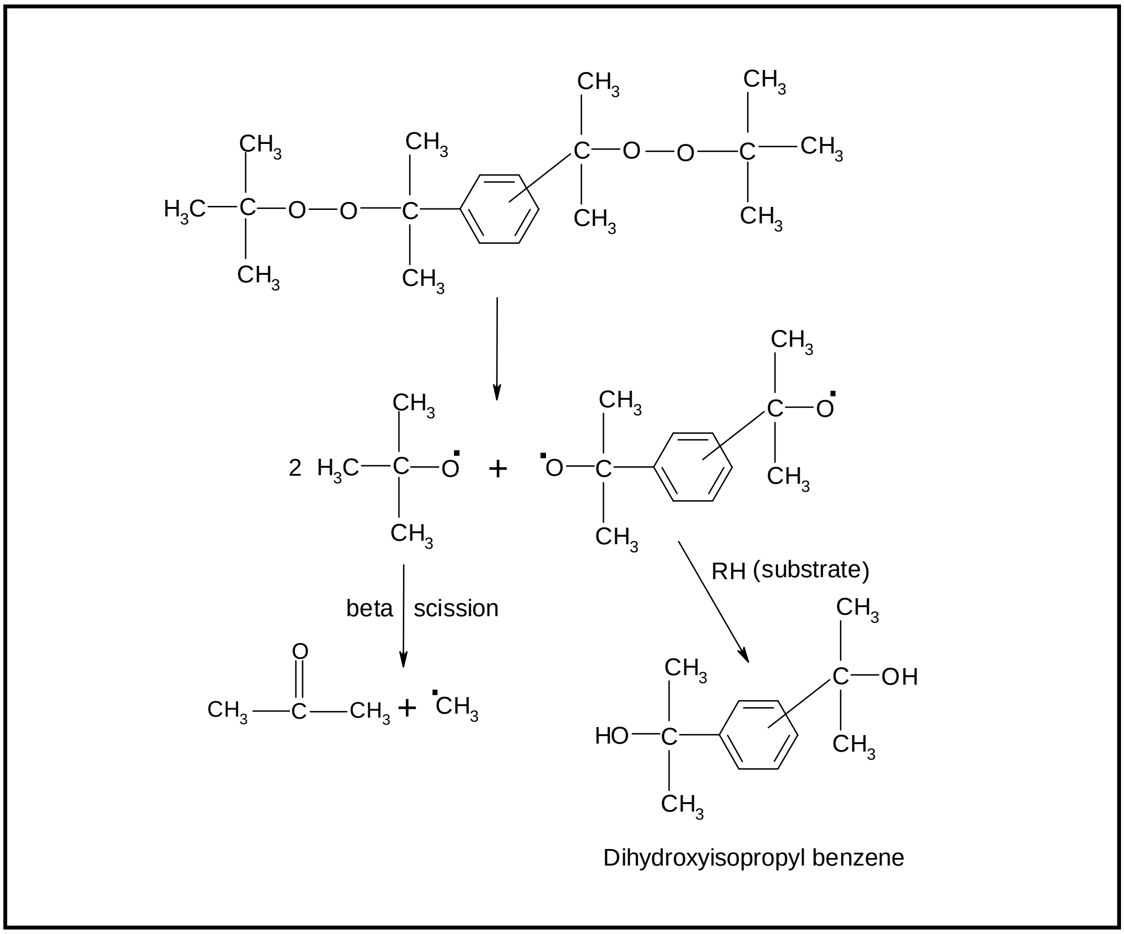


Figure 4.2: Decomposition mechanism of di(tert-butylperoxyisopropyl)benzene.

Multifunctional peroxides were recently developed to overcome the above mentioned drawbacks of the commonly used peroxides. They contain functional unsaturated groups in addition to a peroxide group. In this manner, part of the decomposition products is no longer volatile, nor gives rise to smell or blooming phenomena.[1]

Only a few studies on multifunctional peroxides have been performed, but little is openly published because of commercial sensitivity.[2-4] These multifunctional peroxides were mainly applied to crosslink EPM, EPDM, chlorinated polyethylene rubber and low density polyethylene.[4]

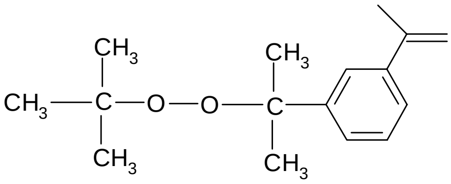
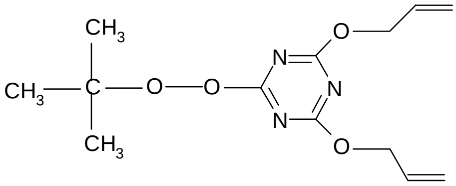
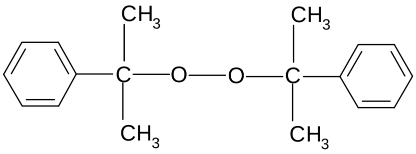
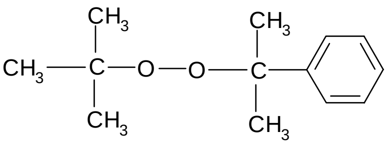
There were basically two main objectives for the study described in the present chapter: the first was to show the efficiency of multifunctional peroxides as curing agents for TPVs, at a fixed as well as at varied PP/EPDM blend ratios; the second objective was to limit the formation of unpleasant or smelly by-products from the decomposition of peroxides. Obviously, the main scope of this chapter was to find potential alternatives for conventional peroxide/co-agent combinations in PP/EPDM TPVs.

4.2 Experimental

4.2.1 Materials

Materials used in this chapter were the same as mentioned in Chapter 3. The chemical names and structures of the four peroxides investigated in this chapter are given in Table 4.1, as well as their decomposition temperatures corresponding to a half-life time of 1 hr, as determined in chlorobenzene solution.[1,5] The two types of multifunctional peroxides were synthesized at Akzo Nobel Polymer Chemicals, The Netherlands. They combine peroxide and co-agent functionality in a single molecule. The two conventional peroxides DCP and TBCP were employed as references due to their structural similarity with the multifunctional peroxides. They were also obtained from Akzo Nobel Polymer Chemicals, The Netherlands. Triallyl cyanurate (TAC), 50 % and α-methyl styrene (α-MeS), 99 % were used as references for the co-agents. For DCP, TAC was used as co-agent because of the structural similarity with DTBT; where as for TBCP, α-MeS was applied as co-agent due to the structural similarity with TBIB.

Table 4.1 Chemical/commercial names, temperature corresponding to a half-life time of 1 hr, and structures of peroxides studied.

Chemical/commercial name	T (^oC) for $t_{½}$ = 1 hr	Chemical structure
1-(2-tert-butylperoxyisopropyl)-3-isopropenyl benzene (TBIB) (71 %): multifunctional	138	
2,4-diallyloxy-6-tert-butylperoxy-1,3,5-triazine (DTBT) (95 %): multifunctional	132	
dicumyl peroxide (DCP) (Perkadox BC-40B) (40 %)	128	
tert-butyl cumyl peroxide (TBCP) (Trigonox T) (50 %)	131	

Syntheses of multifunctional peroxides:

(A) Synthesis of TBIB: TBIB was synthesized following the process as described in the patent.[4] To a mixture of equimolar amounts of tert-butyl hydroperoxide (32 g) and

1-(α-hydroxyisopropyl)-3-isopropenylbenzene (57 g) stirred at 30°C, 1.32 ml of an aqueous solution of 20 % by weight of perchloric acid was added. Over a period of 30 min magnesium sulfate ($MgSO_4.H_2O$) was added portion-wise up to a total amount of 26.3 g, after which the reaction mixture was stirred for 2 hrs at 35°C. Then sufficient water was added to dissolve all of the magnesium sulfate. The organic phase was separated, washed with aqueous NaOH and finally with water. 80 g of the colorless liquid peroxide was obtained. The structure of the peroxide was confirmed by NMR and IR analyses.

(B) Synthesis of DTBT: DTBT was synthesized following another process as described in the patent.[6] To a mixture of 14 g of an aqueous solution containing 70 % by weight of tert-butyl hydroperoxide and 40 g of an aqueous solution containing 11 % by weight of sodium hydroperoxide, a solution of 19 g of 2-chloro-4,6-diallyloxy-1,3,5-triazine in 30 ml of dichloromethane was added, after which the reaction mixture was stirred for 4 hrs at 35°C. Subsequently, the organic phase was separated and successively washed with dilute aqueous sodium hydroxide and water, after which the dichloromethane was removed by distillation under reduced pressure. 23 g of peroxide in the form of a colorless liquid was obtained. The structure of the peroxide was confirmed by NMR and IR analyses.

4.2.2 Preparation of PP/EPDM TPVs

The PP/EPDM TPV compositions employed for the study are given in Table 4.2 and 4.3. The experimental variables were the concentrations of peroxide and co-agent: Table 4.2 and the PP/EPDM blend ratio: Table 4.3. In order to make a comparison among the various peroxides, care has to be taken, that with equal amounts of peroxides added per 100 g of pure EPDM rubber, the amounts of the co-agent functionality per 100 g of pure EPDM differ, depending on the amount of co-agent functionality provided by the peroxide itself. For example, if 15 milli-equivalents of peroxide was used, DTBT by its nature having two pendant allylic groups, provides 30 milli-equivalents of co-agent functionality. This level of 30 milli-equivalents of co-agent functionality was then taken as reference and a correction was applied to make up the lack of co-agent functionality in the other recipes by adding either TAC or α-MeS, as shown in Table 4.4.

The method of preparation of All TPVs used in this chapter was the same as mentioned in Chapter 3.

Table 4.2 **TPV compositions (phr) and corresponding properties, variation of peroxide and co-agent concentrations.**

Component	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12
EPDM[#]	200	200	200	200	200	200	200	200	200	200	200	200
PP	50	50	50	50	50	50	50	50	50	50	50	50
Peroxide:												
TBIB	1.7(5)[*]	3.4(10)	5.1(15)	–	–	–	–	–	–	–	–	–
DTBT	–	–	–	1.5(5)	3.0 (10)	4.5(15)	–	–	–	–	–	–
DCP	–	–	–	–	–	–	3.4(5)	6.8(10)	10.1(15)	–	–	–
TBCP	–	–	–	–	–	–	–	–	–	2.1(5)	4.2(10)	6.3(15)
Co-agent:												
TAC	–	–	–	–	–	–	1.7(10)	3.4(20)	5.1(30)	–	–	–
α-MeS	0.6(5)	1.2(10)	1.8(15)	–	–	–	–	–	–	1.2(10)	1.8(15)	3.6(30)
Stabilizers:												
I 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
I 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Physical properties												
Tensile strength (MPa)	4.0	4.1	4.3	3.0	4.3	5.2	4.7	5.5	5.1	3.4	5.1	5.3
Elongation at break (%)	685	629	550	412	593	504	548	419	368	567	617	587
Young's modulus (MPa)	10.1	11.1	12.7	13.2	14.0	18.4	16.6	19.0	21.1	11.8	15.9	19.2
Modulus 300 % (MPa)	2.3	2.4	2.9	2.7	2.9	3.6	3.2	4.4	4.4	2.4	2.9	3.4
Hardness (Shore A)	60	62	64	66	67	68	63	66	68	59	63	65
Overall crosslink density $(\nu+PP)x10^{5}$ (mol/ml)	2.3	2.9	5.5	2.1	4.5	8.4	7.5	16.0	17.5	2.8	4.7	7.8

[#] Includes 50 wt % paraffinic oil

[*] Numbers between brackets represent milli-equivalents of peroxides and co-agents per 100 parts of pure EPDM rubber, see Table 4.4

Table 4.3 TPV compositions (phr) at varied PP/EPDM blend ratios and corresponding properties.

Component	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20
EPDM[#]	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
PP	25	75	100	125	25	75	100	125	25	75	100	125	25	75	100	125	25	75	100	125
Peroxide:																				
TBIB	5.1	5.1	5.1	5.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
DTBT	–	–	–	–	4.5	4.5	4.5	4.5	–	–	–	–	–	–	–	–	–	–	–	–
DCP	–	–	–	–	–	–	–	–	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	–	–	–	–
TBCP	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	6.3	6.3	6.3	6.3
Co-agent:																				
TAC	–	–	–	–	–	–	–	–	5.1	5.1	5.1	5.1	–	–	–	–	–	–	–	–
α-MeS	1.8	1.8	1.8	1.8	–	–	–	–	–	–	–	–	–	–	–	–	3.6	3.6	3.6	3.6
Stabilizers:																				
I 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
I 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Physical properties																				
Tensile strength (MPa)	2.6	6.9	7.0	7.3	2.3	5.3	6.8	8.6	2.2	6.2	7.8	8.1	2.2	5.6	5.8	6.8	3.4	6.2	6.7	7.9
Elongation at break (%)	440	579	453	367	482	465	415	453	235	377	405	337	419	475	419	329	512	520	464	444
Young's modulus (MPa)	2.9	45.6	93.2	115.0	1.9	43.0	80.4	134.0	3.2	54.0	90.0	123.0	2.0	30.3	49	78	3.5	44.8	81.1	120.8
Modulus 300 % (MPa)	2.0	4.7	6.1	6.9	1.6	4.4	6.1	7.4	–	5.4	6.6	7.8	1.8	4.3	5.1	6.6	2.2	4.7	5.7	7.1
Hardness (Shore A)	37	76	85	90	34	76	86	90	42	80	87	91	40	77	86	90	38	76	85	90
Overall crosslink density $(\nu+PP)x10^5$ (mol/ml)	5.8	12.0	14.1	17.9	4.3	11.6	15.3	19.5	13.4	22.1	25.3	29.2	5.1	13.9	15.1	17.0	5.0	12.7	14.0	20.0

[#] Includes 50 wt % paraffinic oil

Table 4.4 Correction for co-agent functionality.

Name of peroxide	Amount of peroxide (mmol)	Peroxide functionality (meq)	Co-agent functionality (meq)	Co-agent added extra (meq)
TBIB	15	15	15	15 (α-MeS)
DTBT	15	15	30	—
DCP	15	15	—	30 (TAC)
TBCP	15	15	—	30 (α-MeS)

4.2.3 Testing procedure

All the tensile and hardness tests were carried out according to the procedures, as described in Chapter 3.

The overall crosslink density of the EPDM phase in presence of PP was determined on the basis of equilibrium solvent-swelling measurements (cyclohexane at 23°C) by application of the well known modified Flory-Rehner equation for tetrafunctional networks.[7,8] A 2-mm thick sample was submerged in cyclohexane. After 24 hrs, the cyclohexane was refreshed to remove the extracted oil and organic stabilizers. After another 24 hrs, the swollen sample was weighed, dried and weighed again. From the degree of swelling an overall crosslink density was calculated, as expressed by (ν+PP).

4.2.4 Curing characteristics

A rubber process analyzer, RPA-2000 (Alpha Technologies) was used to measure the cure-characteristics of the different types of peroxide/co-agent combinations in pure EPDM-rubber at 180°C according to ISO 6502. The recipes employed for that purpose are given in Table 4.5: C1 – C5. The samples were prepared by mixing at 30 – 40°C on a two-roll mill. The concentrations of the different crosslinking agents were set at 15 milli-equivalents of peroxide functionality with 30 milli-equivalents of co-agent functionality per 100 g of pure EPDM rubber, similar to the dosages defined in Table 4.4.

Table 4.5 **Pure EPDM vulcanizate compositions (phr) and RPA 2000 rheometer data.**

Component	C1	C2	C3	C4	C5
EPDM	200	200	200	200	200
Peroxide:					
TBIB	5.1 (15)	—	—	—	—
DTBT	—	4.5 (15)	—	—	—
DCP	—	—	10.1 (15)	10.1 (15)	—
TBCP	—	—	—	—	6.3 (15)
Co-agent:					
TAC	—	—	5.1 (30)	—	—
α-MeS	1.8 (15)	—	—	—	3.6 (30)
RPA Data					
Minimum torque (dN.m)	0.24	0.23	0.18	0.25	0.24
Maximum torque (dN.m)	0.96	1.27	1.79	1.22	0.87
Maximum torque – Minimum torque (dN.m)	0.72	1.04	1.61	0.97	0.63
t_{S2} (min)	0.48	0.44	0.35	0.30	0.40
$t_{0,90}$ (min)	5.44	4.55	3.45	3.64	4.76

4.3 Results

4.3.1 Influence of different types and concentrations of crosslinking agents on the physical properties of TPVs at a fixed PP/EPDM blend ratio of 50 phr of PP

The physical properties of the PP/EPDM TPVs cured with various crosslinking agents at their different concentrations are given in Table 4.3. Figure 4.3 shows the tensile strength of the PP/EPDM TPVs as a function of concentration of crosslinking agents (peroxides and co-agent) per 100 g of pure EPDM rubber for the recipes A1 – A12. At low concentration levels of the crosslinking agents, TAC assisted DCP gives the highest tensile strength, followed by TBIB. Whereas, TBCP and DTBT give comparatively low values. On the other hand, at high concentration levels of the crosslinking agents, DCP, TBCP and DTBT give more or less equivalent values of tensile strength, whereas TBIB gives a relatively low value. For DTBT and TBCP, there is a clear trend of increasing tensile strength with more crosslinking agent added, while for DCP and TBIB no significant effect of the concentration of crosslinking agent is observed.

Figure 4.4 shows the elongation at break as a function of concentration of crosslinking agents. In this figure the trends are exactly the opposite: for DCP+TAC and TBIB the elongation at break decreases, while for the other two it either remains constant or shows a sort of maximum at intermediate dosage of crosslinking agent.

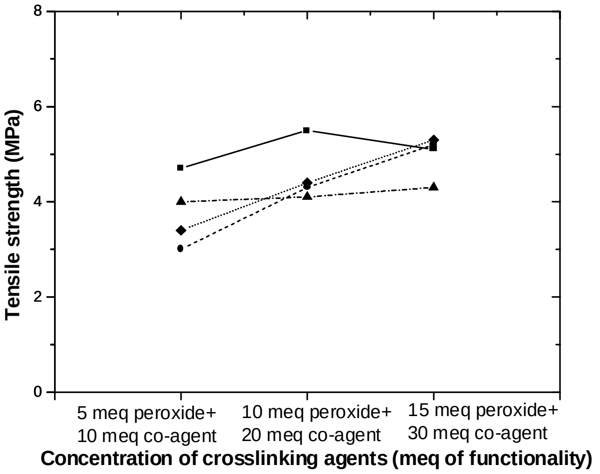


Figure 4.3: Tensile strength as a function of concentration of crosslinking agents for different types of peroxides for recipes A1-A12; (▲-·-▲):TBIB+αMeS; (●- - - ●): DTBT; (■——■): DCP+TAC; (◆······ ◆): TBCP+αMeS.

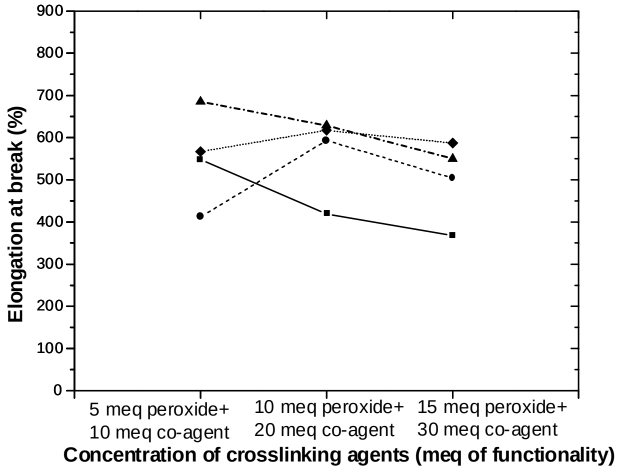


Figure 4.4: Elongation at break as a function of concentration of crosslinking agents for different types of peroxides for recipes A1- A12; symbols as in Fig. 4.3.

In Figure 4.5, the Young's modulus is shown as a function of the amount of crosslinking agents. The Young's modulus increases with increasing amount of crosslinking agent. DCP+TAC is observed to give the highest values of Young's modulus, irrespective of the concentrations of crosslinking agents, whereas TBIB shows relatively low values. Only small differences are seen for the other two, taking an intermediate position. Table 4.2 also shows the values of modulus at 300 % strain (M_{300}) for the various TPVs. The ranking of the results is more or less similar to that shown in Figure 4.5.

An increase in the hardness values is noticed in all cases with increasing dosage of crosslinking agent: Table 4.3. The average values of the hardness vary between 60-70 Shore A. The crosslinking system DTBT, without extra co-agent added, tends to give somewhat higher values than the others, followed by DCP+TAC.

The overall crosslink density, (ν+PP), as a function of the concentration of the crosslinking agents is shown in Figure 4.6. TAC assisted DCP is found to give by far the highest overall crosslink densities irrespective of the concentrations of crosslinking agents. TBIB shows relatively low values. Only small differences are seen for the other two peroxides.

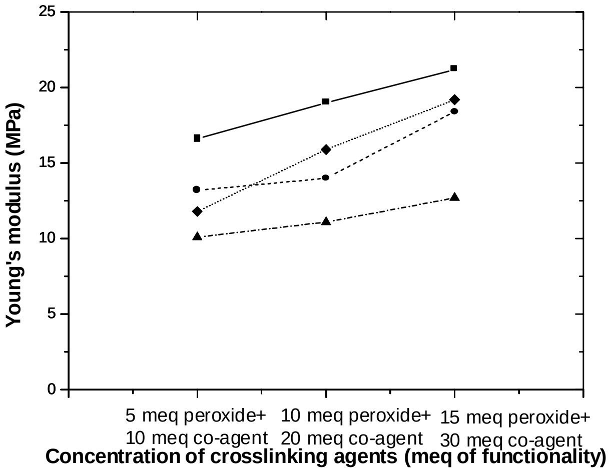


Figure 4.5: Young's modulus as a function of concentration of crosslinking agents for different types of peroxides for recipes A1 - A12; symbols as in Fig. 4.3.

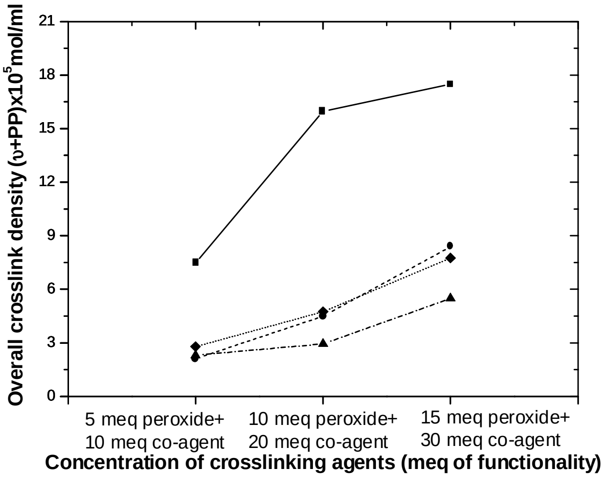


Figure 4.6: Overall crosslink density as a function of concentration of crosslinking agents for different types of peroxides for recipes A1 - A12; symbols as in Fig. 4.3.

4.3.2 Influence of different types of crosslinking agents at fixed concentrations on the physical properties of TPVs with varied PP/EPDM blend ratios

The physical properties of the PP/EPDM TPVs cured with various crosslinking agents with varied blend ratios (recipes B1 – B20) are given in Table 4.3. The properties corresponding to 50 phr PP were already given in Table 4.2. For better understanding of the contribution from co-agent TAC in the case of DCP in the recipes B9 – B12, additional experiments have also been performed taking DCP without the addition of TAC: recipes B13 – B16.

The data show that the tensile strength increases with increasing amount of PP, but the different peroxides exhibit varied responses. At 25 phr of PP, TBCP gives the highest tensile strength, while the other three peroxides with co-agent functionality show more or less comparable values. At 125 phr of PP, the multifunctional peroxide, DTBT exhibits the highest tensile strength as shown in Figure 4.7, followed by DCP+TAC, TBCP and TBIB; whereas DCP without TAC gives the lowest value.

The Young's modulus increases with increasing amount of PP, but at 125 phr of PP, some difference is seen: DTBT exhibits the highest value of Young's modulus as shown in Figure 4.8, followed by DCP+TAC, TBCP and TBIB. DCP without TAC always shows the lowest value, irrespective of the PP-content. M_{300} also increases with increasing amount of PP. TAC-assisted DCP shows the highest values of M_{300} irrespective of the PP-contents, whereas DCP without TAC exhibits the lowest values. An increase in the values of hardness takes place with increasing PP-content. Overall little difference is noticed amongst the various peroxides.

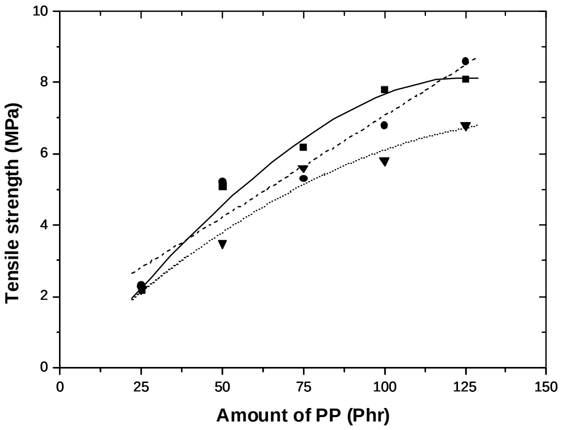


Figure 4.7: Tensile strength for different types of peroxides as a function of amount of PP; (■——■): DCP with co-agent;(▼ ....▼): DCP without co-agent;(●- - - ●): DTBT.

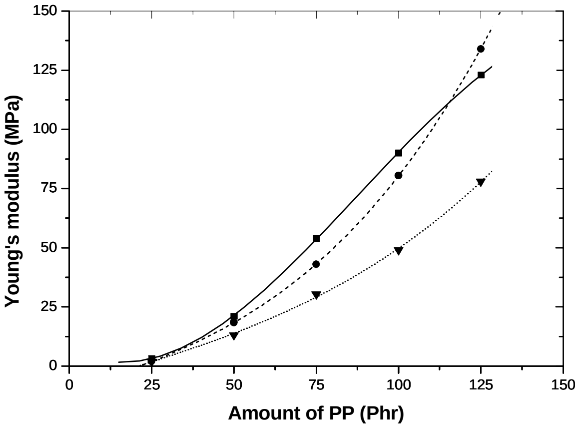


Figure 4.8: Young's modulus for different types of peroxides as a function of amount of PP; symbols as in Fig. 4.7.

The values of overall crosslink density (ν+PP), for the different types of peroxides at different PP-contents is also given in Table 4.3. In all cases, DCP+TAC gives by far the highest values of crosslink density, irrespective of the amount of PP, whereas the other three peroxides and DCP without TAC show more or less comparable values at corresponding PP-contents. It is important to stress for this series, that the difference in the values of (ν+PP) to a large extent also reflects the different PP-contents. The higher the amount of PP in the blend, the more it constrains swelling and hence, the higher is the apparent value of crosslink density. However, a relative comparison between blends with the same EPDM/PP ratios can be made.

4.3.3 Kinetic aspects

For a proper interpretation of the data obtained, it is important to know the vulcanization characteristics of the peroxide/co-agent combinations in pure EPDM gum-compounds, with the PP omitted. Table 4.5 shows the recipes as well as the RPA 2000 rheometer data at 180°C. The latter are also depicted in Figure 4.9. Three different sets are observed in the delta torque values: maximum – minimum torque. DCP in presence of co-agent TAC gives by far the highest value. DCP without co-agent and DTBT are found to show intermediate delta torque values. The delta torque values for TBIB and TBCP are relatively low.

The values of $t_{0,90} - t_{S2}$, can be taken as an indication of rate of cure. Figure 4.10 shows the cure rate indices for the different recipes C1 – C5. DCP with co-agent TAC shows the fastest rate of cure, followed by DCP without TAC. TBIB clearly shows the slowest rate of cure at 180°C.

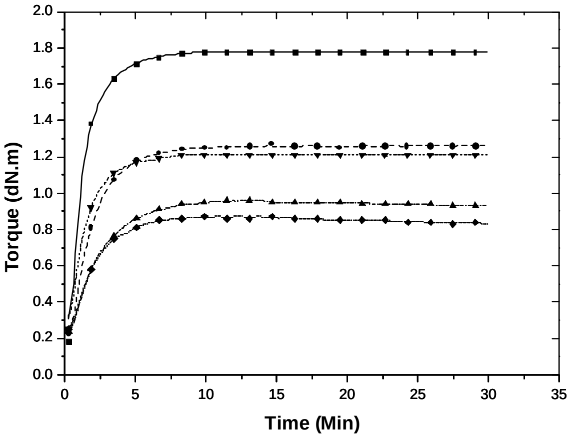


Figure 4.9: Rheograms for different types of peroxides-cured pure EPDM vulcanizates at 180℃; (▲_._.▲): TBIB+α-MeS; (●- - - -●): DTBT, (■——■): DCP with co-agent; (▼. . . .▼): DCP without co-agent; (◆·········◆): TBCP+α-MeS.

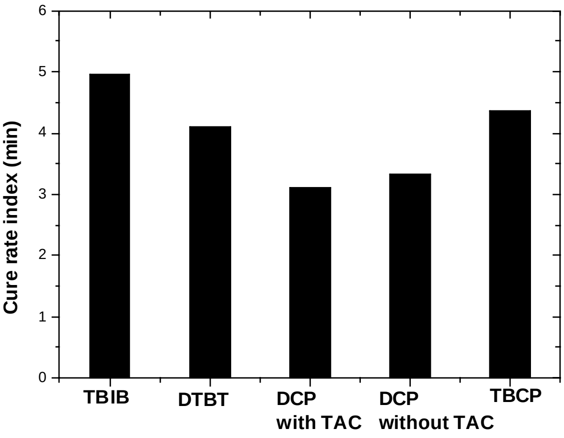


Figure 4.10: Cure rate indices for different types of peroxides-cured pure EPDM vulcanizates at 180℃.

4.4 Discussion

Co-agent TAC assisted DCP overall still gives the best combination of physical properties of the TPVs. On the other hand, the multifunctional peroxides DTBT and TBIB, respectively co-agent assisted TBCP do provide properties, that come close to those of DCP+TAC and are better than the properties obtained with DCP without TAC. Depending on specific requirements, in particular the demand for absence of smelling by-products of the peroxide DCP, the other combinations may preferably be employed.

There are many possible reasons for the differences in physical properties of the TPVs cured with the various peroxide/co-agent combinations. In line with the objectives of this chapter, the interpretation of the similarities or differences observed between the different peroxide/co-agent combinations, in terms of their respective solubilities in the EPDM and the PP-phases, the kinetic aspects of the various peroxides, and their tendency to form unpleasantly smelling by-products, will be mainly focused on.

4.4.1 Solubility aspects of the respective components in the PP- or EPDM-phases

The solubility parameters, δ-values at the mixing temperature of 180°C, calculated using the Hildebrand equation[9-11] for DCP, DTBT, TBCP and TBIB are 14.6, 19.6, 13.8 and 12.7 $(J/cm^3)^{1/2}$ respectively, whereas those of EPDM and PP are 16.6 and 15.1 $(J/cm^3)^{1/2}$.[12-14] The δ-values of the co-agents TAC and α-MeS are 30.7 and 14.7 $(J/cm^3)^{1/2}$.[9] The ranking of these δ-values is graphically depicted in Figure 4.11.

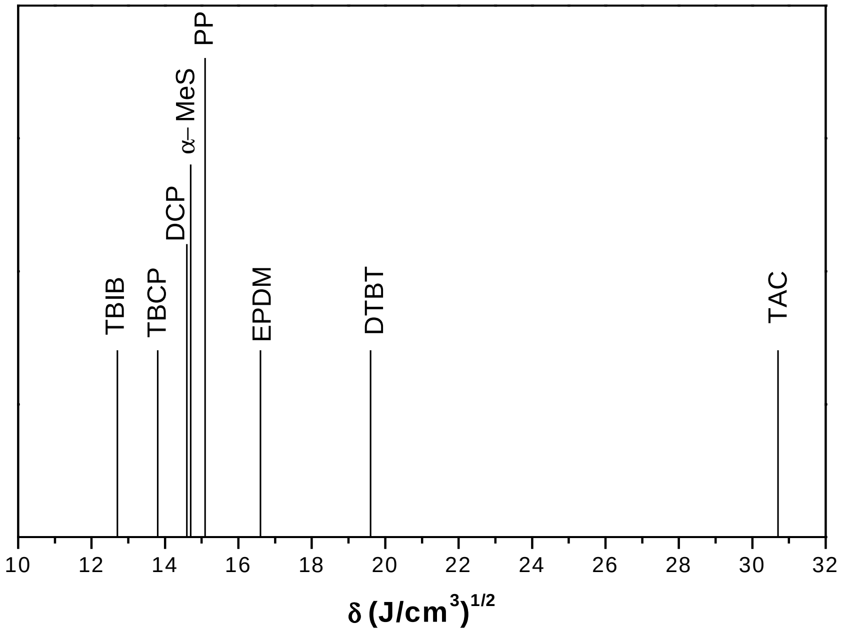


Figure 4.11: Relative ranking of solubility parameters of the various compounds investigated at 180℃.

From these δ-values it can be deduced, that there is a tendency for TBIB, TBCP and DCP to preferably partition towards the PP phase, as compared to DTBT, which will show a preference towards the EPDM-phase. Further, of the three: TBIB, TBCP and DCP, the last one has a solubility parameter, which comes closest to that of EPDM; therefore, DCP is relatively most preferentially partitioned away from the PP-phase into the rubber phase, resulting in a higher degree of crosslinking of the EPDM phase. TAC with its very high δ-value, added as a co-agent to DCP, preferably ends up in the EPDM-phase anyway and therefore boosts the effect of EPDM-crosslinking by DCP. This is seen as a large effect in the overall crosslink density, Figure 4.6, but a much smaller effect in the mechanical properties: Figures 4.3 – 4.5. DCP alone, without TAC, performs after all hardly better than any of the other peroxide/co-agent combinations.

The experiments done with varied PP/EPDM blend ratios: the B-series, show further evidence of the effects observed. At first sight, it looks like the tensile strengths, moduli and hardness are largely determined by the varying PP contents in these blends, overshadowing the differences between the various curing systems. Also the higher overall crosslink density of the TPVs with increasing amounts of PP, as seen in Table 4.3, is obviously due to the fact that the hard PP-phase is included in the gel-count. The relative rankings in gel-measurement remain the same relative to the differences seen in series A, irrespective of the PP/EPDM blend ratios. However, a closer look at the three series: DTBT, DCP and DCP+TAC, shows significant differences in the physical properties, particularly at the high PP-contents. Where the compounds based on DTBT perform nearly equal to those based on DCP+TAC, the compounds based on DCP alone tend to lower tensile strength and moduli as shown in Figures 4.7 and 4.8. There is even a slightly lower overall crosslink density observed for DCP relative to DTBT at the highest PP-content of 125 phr. This is obviously a sign of the tendency of the peroxide to degrade the PP. The lower the solubility parameter of the peroxide on the PP-side, the more it will tend to end up in the PP-phase, where it degrades the PP.

DTBT, because of its high solubility parameter on the EPDM-side, preferably ends up in the EPDM-phase to perform its proper role as a crosslinker.

In summary, the peroxide/co-agent combination in DTBT has two advantages: the solubility parameter of this compound is on the EPDM-side, and the two functionalities are forcibly coupled, thereby jointly moving to the EPDM-phase. This is one of the explanations for the efficiency of DTBT to give high levels of physical properties relative to the others, and close to the DCP+TAC combination.

4.4.2 Kinetic aspects

In the rheograms in Figure 4.9 taken on pure EPDM-compounds, the DCP+TAC combination gives the highest torque value, corresponding to the highest crosslinking efficiency. The higher values of modulus and overall crosslink density for co-agent assisted DCP, as observed in the TPVs for this system, thus tally with the delta torque values as obtained from these rheograms.

It can also be observed from the delta torque values taken from the rheograms in Figure 4.9, that the multifunctional peroxide DTBT shows a comparable performance to that of DCP without co-agent, and a better performance compared to those of co-agent assisted TBCP and TBIB. It proves that DTBT indeed performs best as peroxide and as co-agent, of the products investigated.

The relative amounts of decomposition products, as indicative of the types and quantities of radicals generated from the thermal decomposition of the various peroxides in pentadecane, are shown in Table 4.6.[1] For DTBT this data is not available. However, DTBT basically consists of a di-tert-butyl peroxide (DTBP) fragment at one side and diallyl cyanurate at the other end. The decomposition products obtained from DTBP are known, as shown in Table 4.6 as an indication of what may be expected from DTBT, except that for DTBT only half the quantities of the decomposition products of DTBP can be expected.

The high efficiency of DCP as observed in the Tables 4.2 and 4.3 can be interpreted in terms of the nature, reactivity and amount of generated radicals, as obtained from the fragmentation of the peroxides. In particular, the relatively large amount of methane per mole of DCP is indicative of a high level of highly reactive methyl radicals generated by this peroxide. The relatively good crosslinking ability of DTBT, as seen in Figure 4.9, and the good TPV-properties obtained with this new multifunctional peroxide in the absence of further co-agent can be partly interpreted on the basis of the decomposition products from DTBP. The latter indicates the formation of some methane and a higher amount of tert-butanol per mole of the peroxide, indicative of the generation of highly reactive tert-butoxy radicals. An attempt to correlate the rheometer data in Figure 4.8 with the amounts of active species obtained after the decomposition of peroxides does not work, as the role of the co-agents cannot be included. However, the good performance of DTBT may also be taken as an indication that the co-agent functionality in this compound really works as such.

Table 4.6 Relative amounts of decomposition products from various peroxides in pentadecane.

Name of peroxide	Experimental temperature (°C)	Decomposition products	Relative amount (mol/mol peroxide)
DCP	160	methane	0.91
		acetophenone	0.91
		2-phenylpropanol-2	1.06
		α-methylstyrene	0.01
		water	0.01
TBCP	155	methane	0.57
		acetone	0.13
		tert-butanol	0.79
		acetophenone	0.44
		2-phenylpropanol-2	0.53
TBIB	155	methane	0.31
		acetone	1.62
		tert-butanol	1.65
		1-(2-isopropanol)-3-isopropenyl benzene	<0.01
		1-acetyl-3-isopropenyl benzene	<0.01
		water	0.04
DTBP	152	methane	0.24
		acetone	0.36
		tert-butanol	1.63
		dimer of pentadecane	0.40

Different rates of cure for various peroxides as obtained from the rheograms can be explained in terms of the half-life temperatures of the corresponding peroxides, as given in Table 4.1. A correlation between cure rate and decomposition temperature for $t_{½}$ = 1 hr is made in Figure 4.12. DCP, whether or not in presence of TAC, has the lowest decomposition temperature of all peroxides investigated, which in turn implies the fastest rate of cure of the TPVs. Figure 4.12 also shows a second advantage of the bifunctional DTBT over TBIB: a lower decomposition temperature, closer to that of DCP, and therefore a higher crosslinking speed.

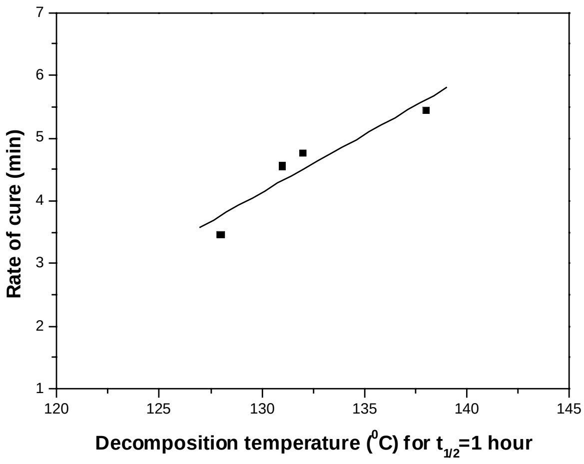


Figure 4.12: Rate of cure as a function of the decomposition temperature of the peroxides investigated.

4.4.3 Avoidance of unpleasantly smelling by-products

From Table 4.6 it can be deduced that DCP primarily generates cumyloxy radicals, which further decompose into highly reactive methyl radicals and acetophenone, having a typical sweet smell. Similarly, TBCP forms large quantities of acetophenone, as this compound still half resembles DCP. From the decomposition products of TBIB, it can be deduced that the amount of aromatic alcohol and aromatic ketone are below the detection limit (< 0.01 mol/mol decomposed peroxide); further no traces of other decomposition products could be identified. This implies that most likely the initially formed aromatic decomposition products reacted with the substrate by the formation of adducts. In addition, unlike DCP, there is no possibility in TBIB, because of its chemical structure, to form acetophenone. As DTBT contains the same basic tert-butyl peroxide unit as TBIB, it may be anticipated that their primary decomposition products will be similar. This also explains why the decomposition products obtained from the multifunctional peroxides do not provide unpleasant smell, unlike DCP.

4.5 Conclusions

Multifunctional peroxides, DTBT and TBIB, having both peroxide and co-agent functionalities in a single molecule, provide TPV-properties, which are grossly comparable with those obtained with commonly employed co-agent assisted peroxides. With co-agent TAC assisted DCP taken as reference for the overall combination of physical properties in PP/EPDM TPVs, particularly DTBT performs better of the two. DTBT has a solubility parameter on the high side of the spectrum, which directs this peroxide/co-agent combination preferably to the EPDM-phase during mixing. The co-agent functionality of this compound helps to improve the crosslinking effect, so as to be comparable with DCP. DTBT further shows a decomposition temperature related to a $t_{½}$ = 1 hr close to DCP, which results in a vulcanization rate, which is grossly comparable. The multifunctional peroxides investigated do provide by-products after their decomposition, but without unpleasant smell unlike DCP.

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Chapter 5

Characterization of the multifunctional peroxides in EPDM

The characterization of peroxide-cured PP/EPDM TPVs using various spectroscopic techniques is difficult, because these techniques are most suited for analysis of solutions, while the PP-phase does not dissolve in common organic solvents at room temperature. In order to obtain more in-sight into the chemistry and reactivity involved between the multifunctional peroxides and EPDM rubber, several characterization techniques were employed. In the present chapter, FTIR, GC-(FID+MS) and HP-SEC were used to characterize the functionalities present in the multifunctional peroxides, TBIB and DTBT, before and after the dynamic curing of the EPDM-phase. The decomposition products obtained from these multifunctional peroxides are demonstrated to be grafted onto the EPDM-rubber, thereby reducing their volatility and avoiding the common unpleasant smell.

5.1 Introduction

In Chapter 4, it was demonstrated that multifunctional peroxides were recently developed to overcome the drawbacks of the commonly used peroxides: in particular unpleasantly smelling by-products. They consist of a peroxide and co-agent-functionality combined in a single molecule. The multifunctional peroxides provide performance-properties of TPVs, which are comparable with commonly employed co-agent assisted peroxides.[1,2] For a proper understanding of the mechanistic aspects of these multifunctional peroxides, various analytical techniques can in principle be employed. However, the characterization of peroxide-cured PP/EPDM TPVs using various spectroscopic techniques is very difficult, because these techniques are most suited for analysis of solutions, and the PP-phase and the crosslinked EPDM-phase do not dissolve in common organic solvents at room temperature.

Part of this chapter has been submitted to Rubber Chemistry and Technology.

Solid-state nuclear magnetic resonance (NMR) is one of the powerful techniques for characterization of polymers without the need to dissolve. Important information about miscibility and compatibility, intermolecular interactions, and morphology of polymer blends at or near the molecular level can be obtained by examining NMR parameters such as chemical shifts, line widths, relaxation parameters and polarization transfer processes.[3-8] However, the desired high resolution is still a hallmark problem for the sensitivity of NMR.

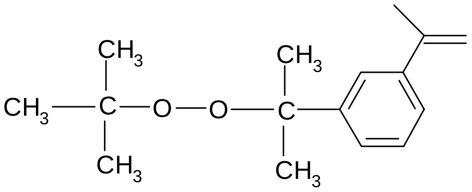
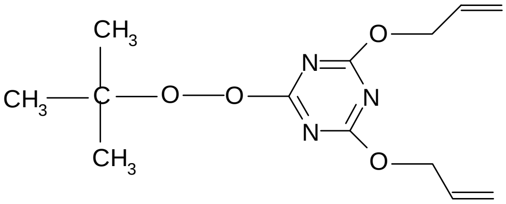
On the other hand, β-chain scission of the EPDM rubber-phase can occur to some extent with peroxide curing, resulting in the formation of low molecular weight oligomers of EPDM, which are generally soluble in the common organic solvents at room temperature. Therefore, in order to obtain more insight into the chemistry and reactivity involved between the multifunctional peroxides and EPDM rubber, several characterization techniques were employed making use of the soluble moieties generated by the chain-scission reactions. In the present chapter, FTIR, GC-(FID+MS) and HP-SEC are employed to characterize the functionalities of multifunctional peroxides, TBIB and DTBT before and after dynamic curing of the EPDM-phase.

5.2 Experimental

5.2.1 Materials

Ethylidene norbornene (ENB)-containing EPDM rubber, Keltan P597, which includes 50 wt % of paraffinic oil, was obtained from DSM Elastomers B.V., The Netherlands. The EPDM contained 63 wt % of ethylene and 4.5 wt % of ENB; it had a Mooney viscosity, ML (1+4) at 125°C of 52. The two types of multifunctional peroxides were synthesized at Akzo Nobel Polymer Chemicals, The Netherlands. They combine peroxide and co-agent functionality in a single molecule. The chemical names and structures of these multifunctional peroxides investigated are given in Table 5.1.

Table 5.1 Chemical names and structures of multifunctional peroxides studied.

Chemical name	Chemical structure
1-(2-tert-Butylperoxyisopropyl)-3-isopropenyl benzene (TBIB) (71 %)	
2,4-Diallyloxy-6-tert-butylperoxy-1,3,5-triazine (DTBT) (95 %)	

5.2.2 Preparation of the samples

Samples of TBIB+α-MeS+EPDM and DTBT+EPDM were prepared according to the recipes A1 and A2, as shown in Table 5.2, by mixing at 30 – 40°C on a two-roll mill and at 180 – 190°C in a Brabender Plasticorder by dynamic curing, using exactly the same procedure as mentioned before in this thesis, only except the addition of PP and stabilizers. The latter was possible, because of the fact that the EPDM itself contains plenty of oil for the material to remain sufficiently 'plastic'. α-MeS was added as co-agent to TBIB, in order to adjust the total co-agent functionality to be comparable with the peroxide and co-agent functionality of DTBT. The two-roll mill prepared samples will be referred to as the ones "before the dynamic curing" and the Brabender prepared samples as the ones "after the dynamic curing" in the following.

Table 5.2 Pure EPDM vulcanizate compositions (phr).

Component	A1	A2
EPDM[#]	200	200
Peroxide:		
TBIB	5.1 (15)[*]	—
DTBT	—	4.5 (15)
Co-agent:		
α-MeS	1.8 (15)	—

[#] Includes 50 wt % paraffinic oil

[*] Numbers between brackets represent milli-equivalents of peroxides and co-agent per 100 parts of pure EPDM rubber

5.2.3 Characterization of the multifunctional peroxides in EPDM phase

The following techniques were applied to characterize the multifunctional peroxides before and after the dynamic curing of EPDM-phase.

(A) Fourier transform – infra red (FT-IR): Is one of the most sensitive spectroscopic methods to analyze molecules containing functional groups such as C=C, C=O, etc. With the horizontal ATR golden gate, diamond probe accessory, FTIR measurements were carried out in a Perkin Elmer 2000 with the EPDM samples containing peroxide before and after the curing.

(B) Gas chromatography – flame ionization detection – mass spectroscopy (GC-FID-MS): To detect peroxide decomposition products after the curing step, 250 mg of the EPDM-peroxide blends, before and after the dynamic curing reaction, were extracted with 5 ml of dichloromethane (DCM) for 24 hrs at room temperature. Analysis of the clear DCM solutions was carried out using n-undecane as internal standard. These solutions were subjected to gas chromatography in the flame ionization detection mode, followed by mass spectrometry in a GC-FID: HP-6890 and GC-MS: HP-5890 respectively.

(C) High pressure – size exclusion chromatography (HP-SEC): To qualitatively test whether EPDM has reacted (crosslinked) with peroxide or not, high pressure size exclusion chromatography was carried out in a Waters 510 HPLC. Approximately 250 mg of samples containing EPDM-peroxide blends, before and after the dynamic curing reaction were extracted with 10 ml of tetrahydrofuran (THF) for 24 hrs at room temperature. A large part of the samples did not dissolve in the solvent. The clear THF solution was analyzed. A Waters 2414 was used as refractive index (RI) detector, whereas a HP Series 1050 was used as ultra violet (UV) detector.

5.3 Results and discussion

Figure 5.1 shows the FT-IR ATR-spectra of TBIB+α-MeS+EPDM before and after the curing reaction. Figure 5.2 shows the same after expansion of the carbonyl (C=O) region. A closer look at Figures 5.1 and 5.2 reveals that the characteristic peak of an acetophenone moiety: 1690 cm^{-1}, is present in the sample TBIB+α-MeS+EPDM after curing treatment (180 – 190°C). It implies that at high temperature TBIB decomposes into an acetophenone moiety to some extent.

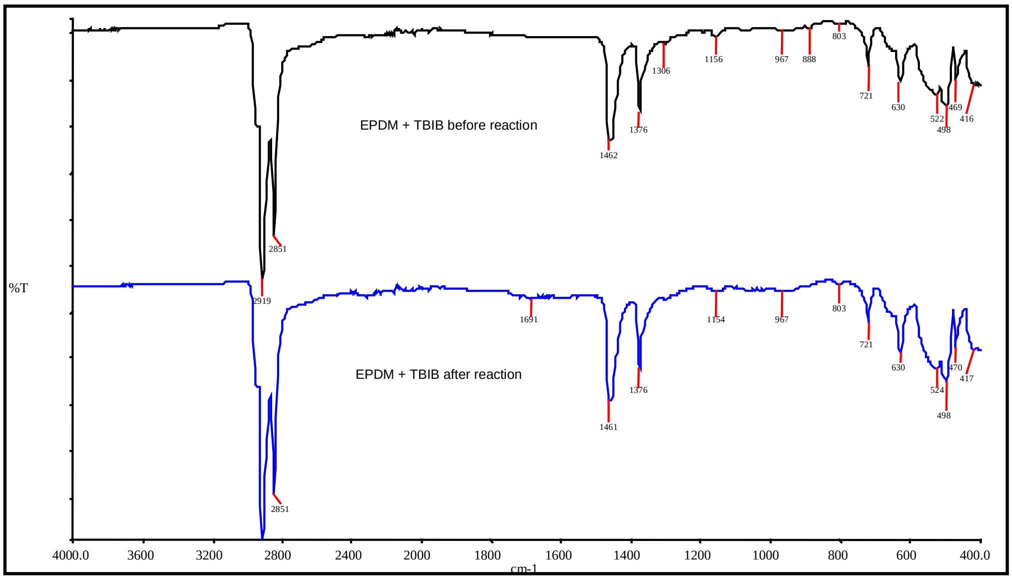


Figure 5.1: FT-IR ATR-spectra of TBIB+α-MeS+EPDM before and after dynamic curing reaction.

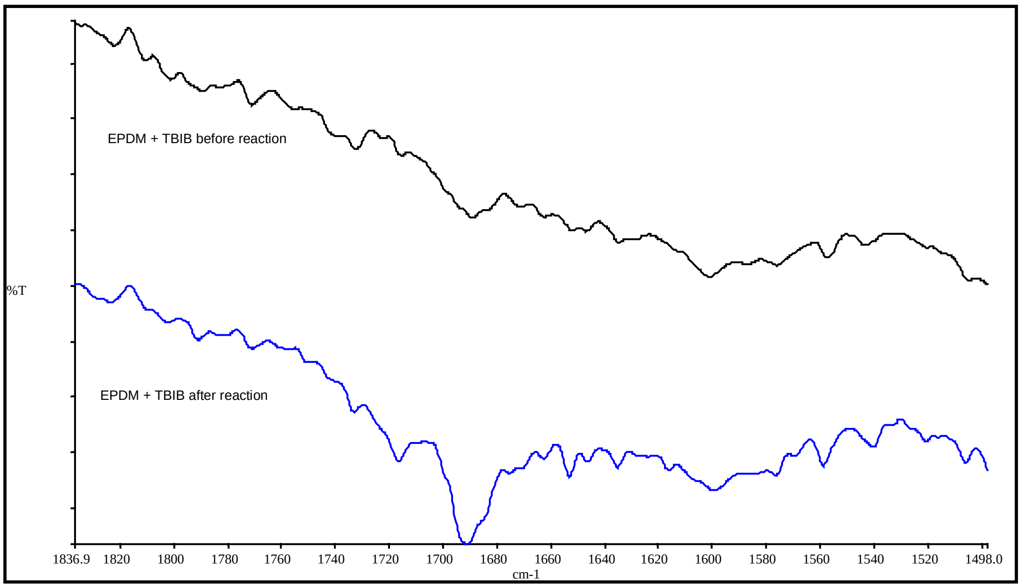


Figure 5.2: FT-IR ATR-spectra of TBIB+α-MeS+EPDM before and after curing reaction: expansion of the carbonyl region.

Figure 5.3 shows the GC chromatograms of TBIB+α-MeS+EPDM before and after curing reaction. GC analyses (FID+MS) reveals that before dynamic curing the undecomposed peroxide TBIB is basically present in the sample: peak number 7. However, after curing, TBIB can not be found back as such; only a few decomposition products can be detected at very low levels. It is likely, that the TBIB is consumed and grafted to the EPDM during the curing treatment.

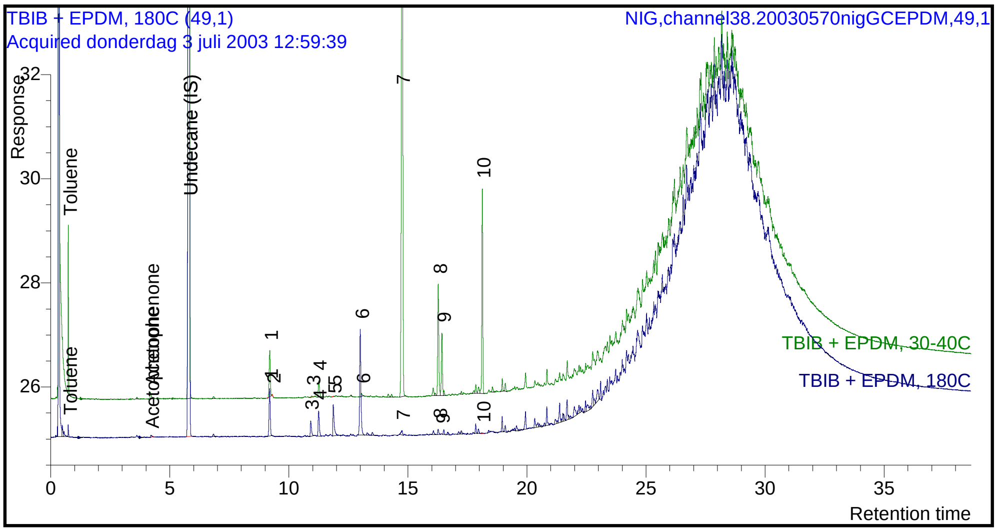


Figure 5.3: GC chromatograms of TBIB+α-MeS+EPDM before and after curing reaction.

To check this hypothesis, HP-SEC study was carried out. HP-SEC chromatograms, using a refractive index (RI) detector, are shown in Figure 5.4. The sample of EPDM+TBIB+α-MeS before curing, dissolves well in the solvent THF used for the HP-SEC analysis. The broad peak of retention time at approximately 9 min – 13 min, the position of high molecular weight components, in the chromatogram shows the presence of EPDM as such. After heat treatment, the sample is still only partly soluble in THF. This indicates that little or no free EPDM is available anymore: absence of a broad peak of EPDM in the chromatogram, and that peroxide cross-linked EPDM does not dissolve in THF. Only a very small amount of low molecular weight EPDM oligomer can still be noticed in the chromatogram.

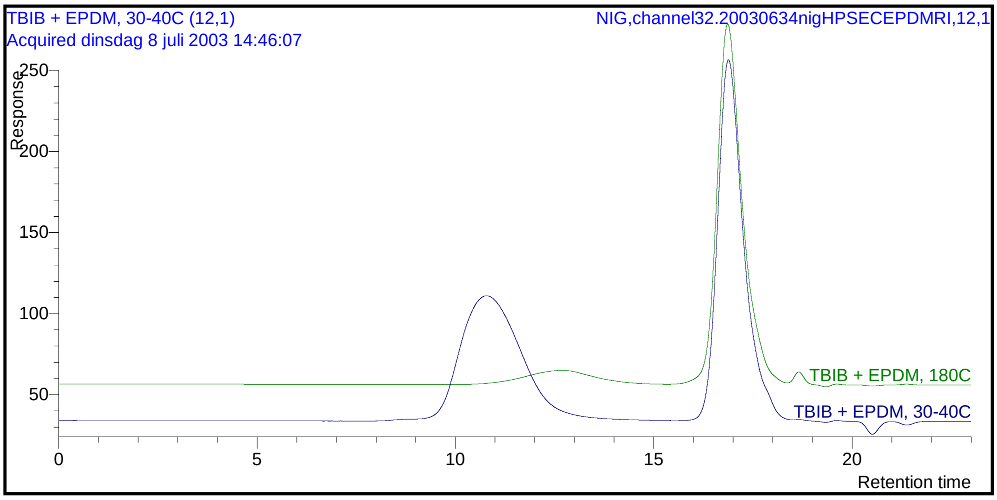


Figure 5.4: HP-SEC chromatograms of TBIB+α-MeS+EPDM before and after curing using RI detector.

HP-SEC analysis using an UV-detector at 275 nm wavelength was done to see whether peroxide is actually grafted to the EPDM, as shown in Figure 5.5. The uncured sample of TBIB+α-MeS+EPDM dissolves totally in THF and a small broad peak is observed by HP-SEC analysis using the UV-detector, as EPDM is slightly UV-active. However, the sample after curing shows a small increase in the peak area at the oligomer position. As already mentioned earlier, crosslinked EPDM does not dissolve in the solvent and so can not be analyzed. Only low molecular weight oligomers of EPDM can dissolve. Because TBIB, containing aromatic groups, is highly UV sensitive, even a small amount of TBIB grafted to EPDM of low molecular weight will show a larger peak when UV-detection is used. It can be taken as an indication, that the reaction products of TBIB are grafted to the EPDM.

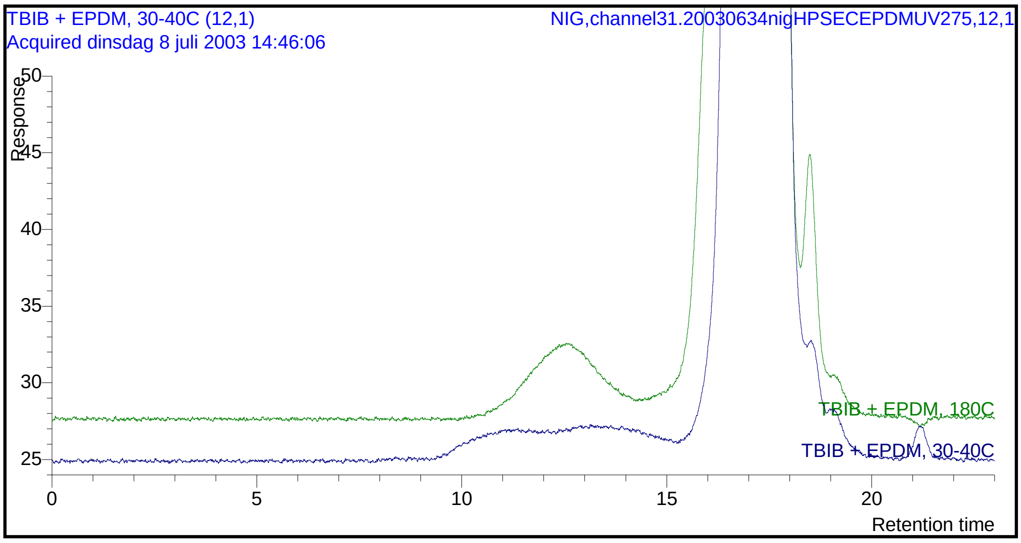


Figure 5.5: HP-SEC chromatograms of TBIB+α-MeS+EPDM before and after curing via UV detector.

The same sets of experiments were also carried out using the DTBT triazine peroxide. The FT-IR spectra of DTBT+EPDM before and after curing are shown in Figure 5.6, and Figure 5.7 shows the same after expansion of the region 1790 – 1250 cm^{-1}. From the expanded spectra, some significant changes can be noticed in the regions of 1600 cm^{-1} and 1400 cm^{-1}. It is clear that some kind of chemical reaction has taken place. However, it can not be concluded, whether the reaction products of the peroxide are grafted onto the EPDM polymer yet.

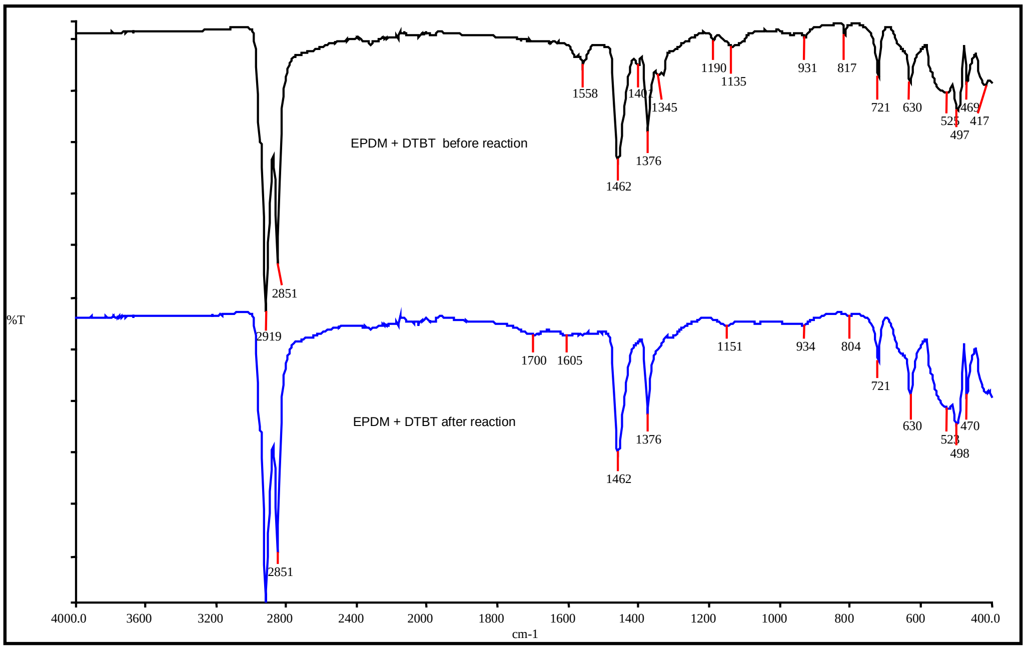


Figure 5.6: FT-IR spectra of DTBT+EPDM before and after curing reaction.

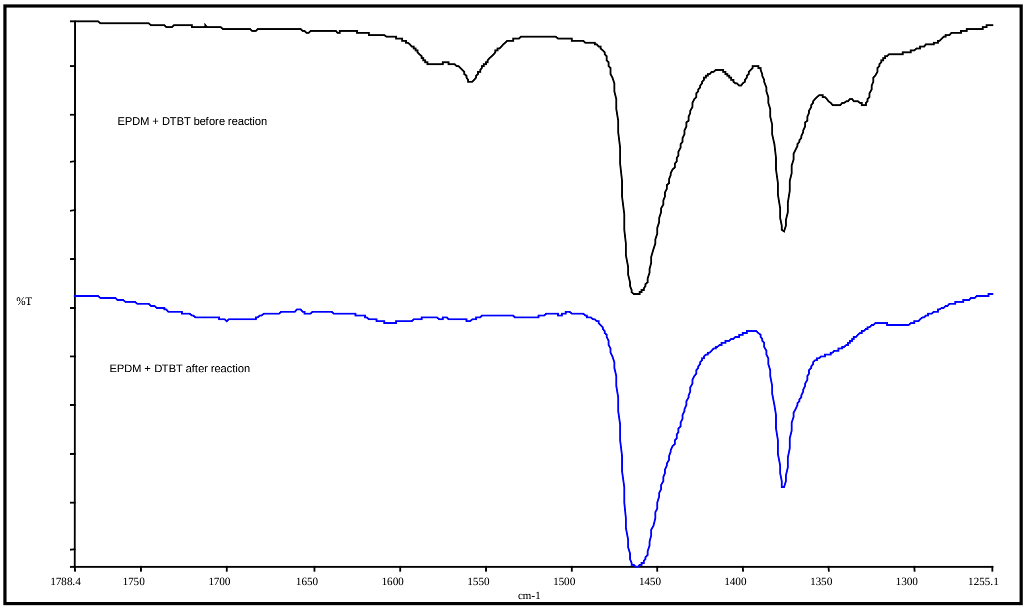


Figure 5.7: FT-IR spectra of DTBT+EPDM before and after curing: after the expansion of the region 1790 – 1250 cm^{-1}.

Figure 5.8 shows the GC chromatograms of DTBT+EPDM, before and after curing, along with the reference pure DTBT peroxide. It can be seen that DTBT shows very little response in GC-FID and probably decomposes to a large extent during analysis. Analyses of these two samples have again been carried out using a thin film column (Sil 5 CB column with fd: 0.1μm). These chromatograms are shown in Figure 5.9. Using this thin film column, DTBT appears as one peak but the response is still very low (ref. triazine Peroxide DTBT: approx. 10 %). It is seen that after curing no peroxide or decomposition products can be detected anymore. A probable explanation is, that either the decomposition products are very volatile and evaporate during thermal treatment, or that these decomposition products are totally grafted onto the EPDM polymer.

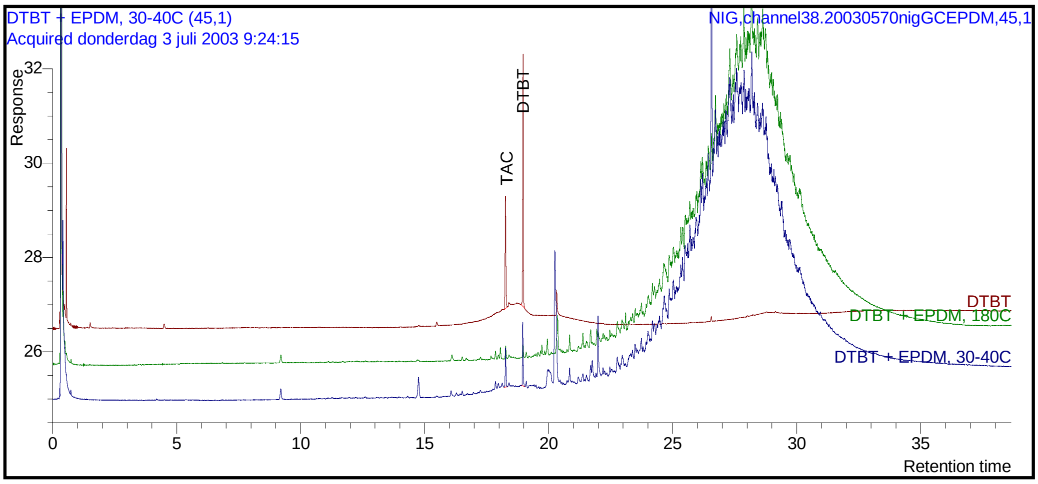


Figure 5.8: GC chromatograms of DTBT+EPDM before and after curing along with reference DTBT (Sil 5 CB column with fd: 0.4μm).

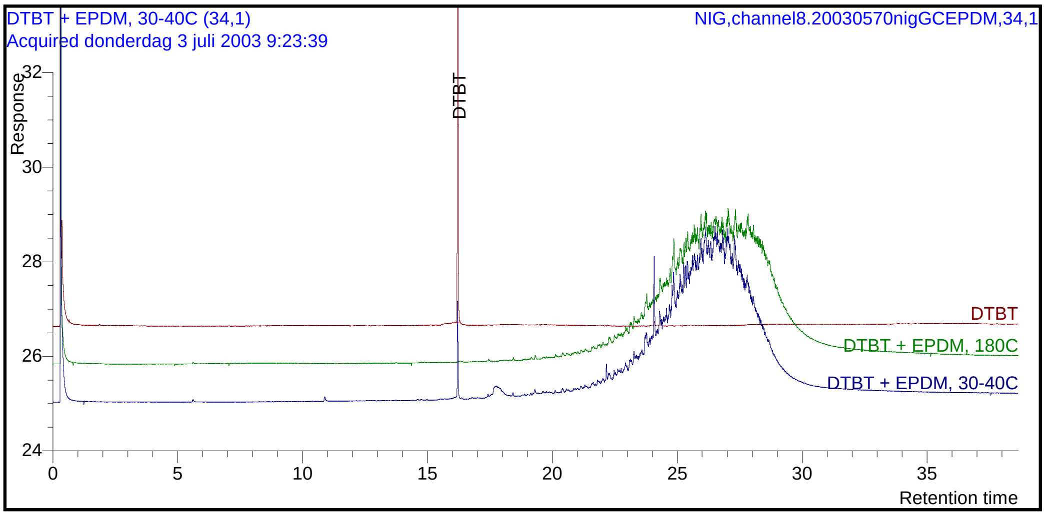


Figure 5.9: GC chromatograms of DTBT+EPDM before and after curing along with reference DTBT (Sil 5 CB column with fd: 0.1μm).

Again, to check this hypothesis, HP-SEC was performed. Also in this case the DTBT+EPDM, after curing only slightly dissolves in the solvent THF used for the HP-SEC analysis. HP-SEC chromatograms using a RI detector before and after curing are shown in Figure 5.10. Again, after curing the sample is only slightly soluble in THF and shows a very small amount of low molecular weight oligomer type of product, while the sample before curing dissolves completely in THF and shows the presence of EPDM at a retention time of 8.5 – 13 min.

HP-SEC analysis using an UV-detector was attempted to see whether peroxide is actually grafted to EPDM. HP-SEC chromatograms using the UV-detector are shown in Figure 5.11. The same phenomenon as already found before is again observed here. Most likely, the decomposition products of the DTBT peroxide are also grafted to the EPDM.

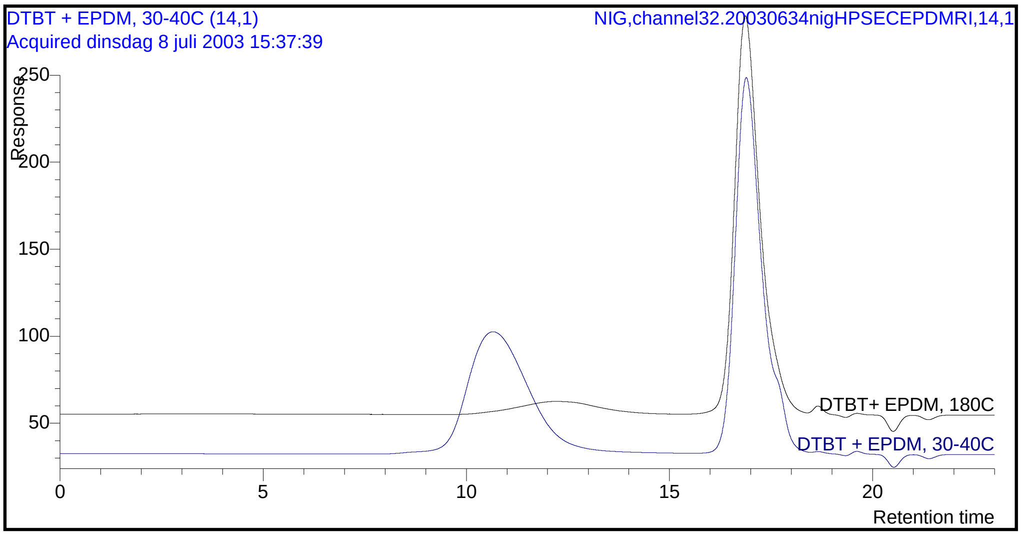


Figure 5.10: HP-SEC chromatograms of DTBT+EPDM before and after curing (RI-detector).

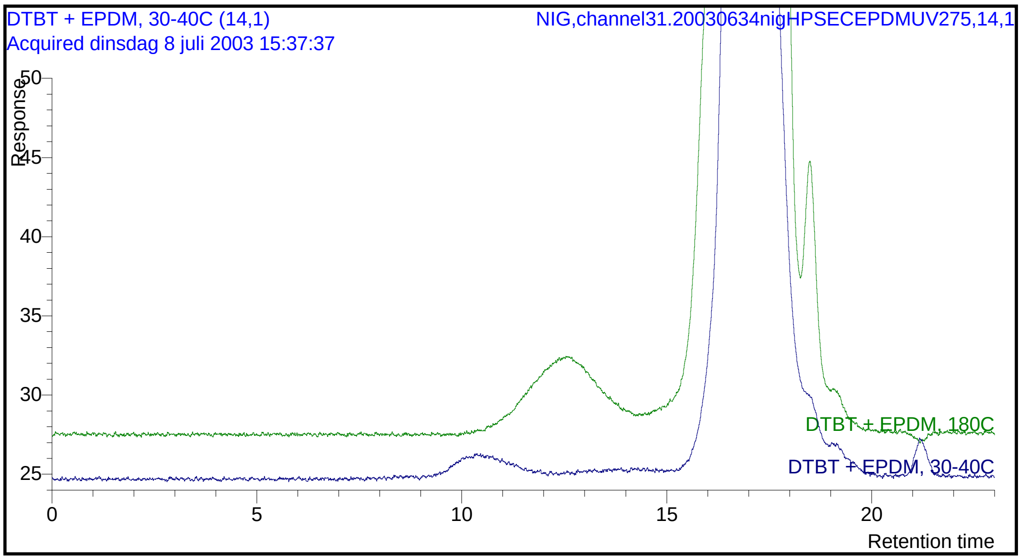


Figure 5.11: HP-SEC chromatograms of DTBT+EPDM before and after curing (UV-detector).

5.4 Conclusions

The experiments described in this chapter gave strong indications, that the decomposition products as obtained from the multifunctional peroxides, TBIB and DTBT, are grafted to the EPDM-phase, thereby reducing their volatility and consequently providing no significant smelly by-products. It was also demonstrated that the co-agent functionalities present in those peroxides are playing a role in the grafting reactions.

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Chapter 6

Influence of pre-made and in-situ compatibilizers in PP/EPDM TEOs and TPVs

During dynamic vulcanization of PP/EPDM blends with DCP/TAC, there is a possibility of generation of in-situ graft-links at the interface between both phases. Three potential compatibilizers for PP/EPDM blends were first investigated as references in order to obtain a quantified insight into the effects to be expected from in-situ graft-links: PP-grafted EPDM,
S-EB-S and TOR. Only the first one showed some compatibilizing action in straight, unvulcanized blends, as evidenced by a slight increase in tensile strength of the blend and somewhat smaller EPDM particle size within the PP-matrix. Also dynamic mechanical testing, in particular the glass transition temperatures of the PP and EPDM components showed some signs of compatibilization. The PP-grafted EPDM resembles most closely to the structures of PP and EPDM. On the other hand, when mixed into a dynamically vulcanized PP/EPDM-blend, all compatibilizers resulted in an overall deterioration of mechanical properties. The vulcanization step, particularly with peroxides, causes a complete reversal of the effects observed with straight blends.

From the spectra as obtained with high temperature solid state NMR, there is an indication that PP-EPDM graft links are generated during the dynamic vulcanization process, that still remain after the extraction of the free PP-phase from the TPV-film. NMR-relaxation experiments gave further evidence for the in-situ formed graft-links. In all cases only qualitative indications could be achieved, due to the extremely low amounts of graft-links formed.

Part of this chapter has been submitted to Journal of Applied Polymer Science.

6.1 Introduction

Polymer blends are an important class of materials, since they may exhibit synergistic effects with respect to useful properties. They may be generally categorized into two main classes: immiscible and miscible blends. Immmiscible blends are those which exist in two different phases, e.g., rubber-toughened plastics. On the other hand, miscible blends are those, which exist in a single homogeneous phase and may exhibit different properties, which are uncommon to both of the pure components. Apart from these two, there is a third category of blends, often quoted as technologically compatible blends or alloys. The latter are those which exist in two or more different phases on micro-scale, but exhibit macroscopic properties similar to that of a single phase material.[1,2] Unfortunately, most of the polymer blends are thermodynamically immiscible, resulting in poor interfacial adhesion and a gross phase-separated morphology, consequently leading to poor mechanical properties. It is already well known that the phase morphology of immiscible polymer blends can be influenced by the use of appropriate 'compatibilizers', block or graft copolymers, which can act as interfacial agents. The basic roles of the compatibilizers are: reduction of interfacial tension, enhancement of interfacial adhesion, finer dispersion and improvement of morphological stability.

The block or graft copolymer compatibilizers can be pre-made and added to the immiscible polymer blends, but can also be generated in-situ through covalent or ionic bonding (chemical reaction) during the reactive melt-blending process. The latter is a very effective means of compatibilization, since the compatibilizers are formed at the site, where they are required to be present: at the interface. In general, both polymers have to be functionalized with chemical groups, that show reactivity towards each other.[3]

There is a possibility of the formation of in-situ graft-link structures of PP with EPDM at the interface during the process of dynamic vulcanization in co-agent assisted peroxide-cured PP/EPDM blends. These in-situ graft-links can act as a compatibilizer in such a system, which in turn can improve final mechanical properties. Very recently, Isayev et al.[4] reported in-situ compatibilization of plastic/rubber and rubber/rubber blends through ultrasonically treating the blends during continuous mixing. However, from our preliminary study, it was found to be very difficult to prove the in-situ generation of graft-links formed during dynamic vulcanization, by conventional characterization techniques like Fourier transform infra-red (FTIR), differential scanning calorimetry (DSC) or dynamic mechanical thermal analysis (DMTA), due to the extremely low amounts of graft-links formed.

Extensive studies on PP/EPDM thermoplastic elastomeric olefins (TEOs) have been carried out by several authors, because a wide range of properties can be obtained just by changing the blend composition.[5-10] It is considered that PP and EPDM are incompatible, although their molecular structures are very similar. A number of studies have been carried out on the impact modification of polyolefins by the addition of various elastomers,[11-13] for instance, EPDM or S-EB-S.

However, only limited work has been published so far about the use of compatibilizers for PP/EP(D)M TEOs and for TPVs. The addition of 2 – 15 wt % of an ethylene-propylene block copolymer, containing 80 – 90 wt % of propylene, has been recently tried as compatibilizer to improve the dispersion of EPDM in PP for PP/EPDM TEOs.[14] Lohse et al.[15] reported, that the addition of a small amount: < 10 wt % of iPP-EPDM graft copolymer to an iPP/EPM TEO has a pronounced effect on its morphology and final mechanical properties. The miscibility between PP and EPDM was also found to improve through the introduction of specific interactions, for instance dipole-ion interaction: PP was modified by grafting maleic anhydride (MAH) onto the backbone, leading to MAH-grafted PP; on the other hand, sulfonated EPDM ionomer neutralized with bivalent zinc cations (Zn-SEPDM) was used as the other component. Ludwig et al.[16] observed an increase in low temperature impact strength and enhanced dispersion of EPDM in the PP matrix in presence of a peroxide initiator and a new multifunctional coupling agent, hexa (allylamino) cyclotriphosphonitrile (HAP). It has also been reported that the miscibility of PP/EPDM blends can be controlled by the addition of ethylene-co-methacrylic acid ionomer, followed by the application of dynamic vulcanization.[17] Coran and Patel[18] showed that the morphology of a nitrile rubber (NBR)/PP blend could be controlled by adding block copolymers, having compatibilizing segments for both the polymers. Enhanced solubility, partitioning and homogenizing effects can also be achieved by the incorporation of commercial and model phenol and hydrocarbon resins in rubbers and corresponding blends.[19,20]

The basic objective of this chapter is to search for in-situ compatibilization or graft-links formed during co-agent assisted peroxide vulcanization of PP/EPDM blends. For that purpose, the main focus was on NMR, knowing that other more common techniques would not lead to conclusive results, because of the very low amounts of graft-links expected to be formed. An attempt was made to search for the existence of in-situ formed graft-link structures by the CP-MAS NMR technique in terms of spectra and relaxation time, $T_{1\rho}$ (^{13}C). Various pre-made compatibilizers are also tested as references for PP/EPDM blends in order to obtain a quantified insight into the influences to be expected from in-situ formed PP-EPDM graft-links. Three potential compatibilizers for PP/EPDM blends were selected for that purpose: PP-grafted EPDM, S-EB-S and trans polyoctenamer (TOR). Apart from the PP-EPDM graft copolymer as described below, S-EB-S and (TOR) were tried as compatibilizers since they are having solubility parameters which are close to that of PP and EPDM respectively. S-EB-S acts as compatibilizer in PP/PC[21], PE/PS[22], PE/PA, PS/PET and PS/PA blends etc.[23] improving the impact strength. On the other hand, Schuster et al.[24] reported that 5 phr of TOR acts as a very good compatibilizer improving the tensile strength and elongation at break of peroxide-cured NBR/PP blends.

Solid-state nuclear magnetic resonance (NMR) is nowadays one of the most useful techniques for the characterization of polymers without the need to dissolve the polymers in suitable solvents. Important information about miscibility and compatibility, intermolecular interactions, molecular dynamics and morphology, crystal structures etc. of polymer blends can be obtained by examining NMR parameters such as chemical shifts, line widths, relaxation parameters and polarization transfer processes.[25-30] Until several decades ago, solid state NMR provided spectra containing only broad lines. The introduction of the CP-MAS (cross polarization, magic angle spinning) ^{13}C NMR technique created lots of interest in getting insight into the structures of polymers, carbohydrates, biopolymers etc. Generally, the ‘magic angle spinning’ refers to the combination of cross polarization (CP), the actual rotation of the sample at the magic angle of 54.7° (MAS) and dipolar decoupling (DD) of the ^{1}H nuclei from ^{13}C nucleus. With rigid solid substances, only the combination of all three experiments makes it possible and practicable to record spectra of rare nuclei (most commonly ^{13}C) and to resolve them in terms of chemical structure.[31]

The relaxation time in the rotating co-ordinate system, $T_{1\rho}$(^{13}C) is another special parameter for the investigation of polymers. The amplitude of the radio-frequency field which is applied during the relaxation and which is parallel to the magnetization determines the frequency of the spins within the rotating co-ordinate system. Molecular motions or dynamics having a spectral component at this frequency are of vital importance for the relaxation. However, the interpretation of $T_{1\rho}(^{13}C)$ data is complicated because the relaxation in the rotating coordinate system is caused by the fluctuating dipole fields of the protons.

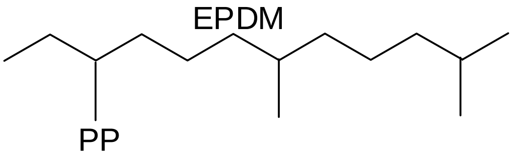
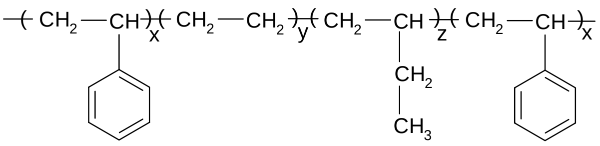
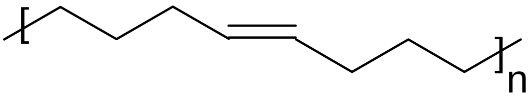
High-resolution ^{13}C NMR spectra of solid isotactic PP were extensively studied by Bunn et al.[32] They reported a dependence of the solid state spectra on the history of the physical treatment of the sample and secondly, a relationship of these spectra to the structure of the crystalline regions of the materials. Isotactic PP can exist in two different forms: the thermodynamically stable crystalline α-form, consisting of iPP chains in the helical conformation packed in a monoclinic unit cell and the metastable β-form, containing hexagonally packed helical chains. Normally, the β-form shows the chemical shifts at a little higher side as compared to the α-form. Investigations were carried out not only on the homopolymers, but also, for instance, on a polypropylene grafted with butadiene, in order to quantitatively determine the proportion of grafts via CP-MAS experiments.[33]

6.2 Experimental

6.2.1 Materials

The specifications of the EPDM, PP and the stabilizers used for this work were mentioned before in chapter 3. Dicumyl peroxide (DCP) (40 %) was used as the crosslinking agent and triallyl cyanurate (TAC) (50 %) was employed as the co-agent. The chemical/commercial names and structures of the three different types of compatibilizers under investigation are given in Table 6.1. PP-EPDM graft copolymer was synthesized in the laboratories of DSM Research B.V., whereas S-EB-S was a specially synthesized grade from Kraton Polymers.

Table 6.1 Chemical/commercial names and structures of compatibilizers employed.

Chemical/commercial name	Chemical structure
PP-EPDM graft copolymer	
Styrene-ethylenebutylene-styrene (S-EB-S), Kraton® G (Kraton Polymers): pure triblock copolymer with 35 wt % ethylene content and 20 wt % polystyrene content	
Trans polyoctenamer (TOR), Vestenamer® 8012 (Degussa)	

6.2.1.1 Synthesis of PP-EPDM graft copolymer

A graft copolymer with iPP arms pendant from an ethylene propylene copolymer backbone was synthesized according to the process as described by Lohse et al.[15] The synthesis involved a two-step process. In the first step, an ethylene propylene diene terpolymer (EPDM) was prepared using vinylidene-norbornene (VNB) as a diene so that there remained unreacted double bonds, well removed from the polymer backbone. In the second step, iPP chains were allowed to grow from these double bonds in order to form the graft copolymer.

VNB-containing EPDM polymer was first made as follows: A continuous flow stirred tank reactor (CFSTR) was used to synthesize VNB-containing EPDM. The temperature was kept at 35°C. A feed stream comprising hexane, ethylene, propylene and VNB was continuously fed to the CFSTR. The Ziegler-Natta catalyst system consisting of vanadium oxitrichloride ($VOCl_3$) and ethylaluminum sesquichloride (EASC) with an Al/V molar ratio of 5 was used to achieve a homogeneous polymer. The residence time in the reactor was 8 min. Hydrogen was added to act as a chain-transfer agent. The characteristics of the VNB-containing EPDM polymer were as follows:

— ethylene content: 54.3 wt % and propylene content: 42.4 wt %, as calculated from FTIR study, calibrated with ^{13}C NMR[34];

— FTIR spectra of a polymer film showed a band at 906 cm^{-1}, indicating the incorporation of VNB; VNB content: 3.2 wt %, as also obtained from the FTIR spectra calibrated with ^{1}H NMR[34];

— molecular weights, M_n: 37,000 g/mole, M_w: 105,000 g/mole, M_z: 280,000 g/mole with $M_w/M_n = 2.9$ and $M_z/M_w = 2.7$, indicating a relatively narrow molecular weight distribution, as measured by gel permeation chromatography (GPC) and

— Mooney viscosity, ML (1+8) at 100°C = 19.6.

The grafting of iPP on the EPDM polymer was achieved as follows:

(1) The above-mentioned VNB-containing EPDM was dissolved in 1000 ml of petroleum ether, and then passed through a column of activated aluminum oxide to remove previously used vanadium catalyst. After evaporation of part of the solvent, 900 ml petroleum ether solution of EPDM (2.1g/100 ml) was obtained.

(2) A 2 liter flask was then charged by 750 ml of the EPDM-containing petroleum ether and 3 ml of triethyl aluminum (7 M, 21 mmol) as co-catalyst and then heated to a constant reaction temperature of 50°C. 2 g of titanium trichloride (Stauffer AA) was added as catalyst. After that, gaseous propylene monomer was introduced to the flask at atmospheric pressure. After half an hour, the solution containing EPDM+iPP was then saturated by ethylene gas at atmospheric pressure. The latter was performed in order to initiate the grafting procedure: the catalyst used here can not effect a reaction between VNB and propylene, but can only catalyze a reaction between VNB and ethylene due to steric reasons: smaller size of ethylene as compared to propylene. The reaction mixture thus formed was stirred and allowed to react for 2 hrs. A suspension of white powder was obtained.

(3) To the above flask, 20 ml HCl/methanol mixture and 200 ml methanol were added respectively. A methanol layer containing the catalyst residue was first removed. 300 ml methanol was then added to the petroleum ether layer which already contained a white precipitate. Lots of precipitates were formed. After the separation, two fractions were obtained: one was white precipitate and the other one was the petroleum ether solution. The solvent was removed and two polymers were finally obtained: PP-EPDM graft copolymer 1 (90 g) and PP-EPDM graft copolymer 2 (24 g). PP-EPDM graft

copolymer 1 was selected as the compatibilizer. The specifications of the latter are as follows:

- ethylene content: 5.7 wt % and propylene content: 94.3 wt %, as calculated from FTIR analysis, calibrated with ^{13}C NMR;
- molecular weights, M_n: 16,000 g/mole, M_w: 390,000 g/mole, M_z: 2000,000 g/mole with M_w/M_n = 24.1 and M_z/M_w = 5.2, indicating a broad molecular weight distribution, as measured by GPC.
- FTIR-film spectra of the graft showed a sharp band at 899 cm^{-1}, indicating the presence of a high amount of iPP and at 721 cm^{-1}, indicating the presence of EPDM. On the other hand, absence of a band at ~ 906 cm^{-1} indicated the full reaction of VNB into the final grafted polymer.

6.2.2 Preparation of PP/EPDM TEOs and TPVs containing pre-made compatibilizers

The TEO and TPV compositions employed are shown in Tables 6.2 and 6.3. The experimental variable is the type and amount of the compatibilizers. All TPVs were prepared according to the procedures as described in Chapter 3. The TEOs were also prepared in the same way.

Table 6.2 TEO compositions.

Material	Phr
EPDM*	200
PP	100
Compatibilizer	0 – 25

* Including 50 wt % paraffinic oil

Table 6.3 TPV compositions.

Material	Phr
EPDM*	200
PP	100
Compatibilizer	0 – 25
DCP	10.1
TAC	5.0

* Including 50 wt % paraffinic oil

6.2.3 Testing Procedures

Tensile tests:

Tensile tests were performed on compression molded samples according to the procedure as described in Chapter 3.

Dynamic Mechanical thermal analysis (DMTA):

DMTA measurements were performed on compression molded samples (50x9x2 mm) using a Myrenne ATM3 torsion pendulum at a frequency of 1Hz and 0.1 % strain. The samples were first cooled to – 80°C and then subsequently heated at a rate of 1°C/min over a temperature range of – 80 to + 60°C. The tan delta-peak maxima were assigned to the glass transitions of the EPDM and the PP.

Morphological characterization:

The phase morphology of various PP/EPDM TEOs with the compatibilizers was investigated by low voltage – scanning electron microscopy (LV-SEM). For this study a blend composition of 67:33 w/w of PP and EPDM was chosen (different from Table 6.2) on purpose in order to achieve a well-dispersed phase morphology. The samples were quickly quenched in liquid nitrogen after taking them out of the hot mixer. Afterwards, they were cut cryogenically (at – 130°C) to very thin slices (~ 50 – 80 nm) using a diamond knife in a Leica Ultramicrotome EM FCS. The microtomed samples were vapor-stained with freshly prepared ruthenium tetroxide for 30 min to generate contrast between PP and EPDM phases. The stained surfaces were then examined under the LV-SEM. The images were obtained with a LEO 1550 FEG Scanning Electron Microscope at an operating voltage of 0.65 KV.

6.2.4 Search for in-situ graft links

6.2.4.1 Preparation of samples

Thin films of PP, EPDM rubber and DCP-cured PP/EPDM TPVs (following the same recipe as mentioned in Table 6.3, only excluding the compatibilizer) were first prepared in a compression molding machine: WLP 1600/5*4/3 Wickert laboratory press at 200°C, 2 min and 125 bar pressure. Aluminum foil was placed between the molded film in the press plates. The films were then cooled down to room temperature under pressure. Later on, PP-phase was extracted from the PP/EPDM TPV film by exhaustive hot xylene treatment in a soxhlet apparatus. The extraction was assumed to be complete. In situ formed graft-links together with degraded PP-oligomer branches were supposed to remain in the film even after the extraction. Only a limited number of experiments could be performed because of the restricted availability of the NMR technique.

6.2.4.2 Solid state NMR

First, solid state ^{13}C NMR spectra of the thin films were obtained at 70°C using a Chemagnetics CMX-400 Infinity Spectrometer, equipped with CMX 4 mm BB CP-MAS rotor. NMR spectra were recorded with cross polarization-magic angle spinning (CP-MAS) pulse sequence. In this sequence, the sample is rotated at very high speed (ca. 9 kHz) to average out the dipolar coupling and the chemical shift anisotopy (CSA). To gain sensitivity, proton magnetization is transferred to the carbons by means of cross polarization. During the sampling of the signal, the protons are decoupled.

Secondly, the relaxation times in the rotating co-ordinate system, $T_{1\rho}(^{13}C)$ were also measured at 70°C via the CP-MAS technique. The most intense signals as obtained from the first experiments were used to perform this relaxation experiment. The magnetization was spin-locked in the xy-plane and the relaxation in this plane was measured, which was carried out by an increasing spin-lock time and subsequent measurement of the signal intensity, as shown in Figure 6.1.

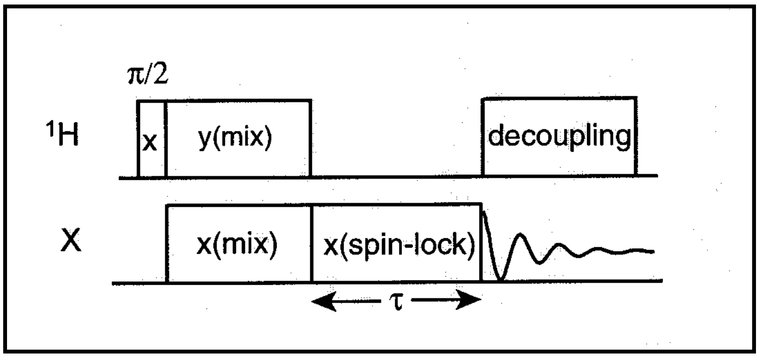


Figure 6.1. Measurement of $T_{1\rho}$ by cross polarization via spin locking.

The NMR signal intensity (M) was measured as a function of the spin-lock duration τ. The time constants ($T_{1\rho}$ relaxation times), which are characteristic of different rates of the magnetization decay, were obtained by performing a least square fit of the data with a Weibull function, or a linear combination of the Weibull function and exponential functions. Depending on the nature of system studied, one, two or three components can be used for the fit. Statistically, it was insignificant to use a series containing more than a three components-fit for this purpose. In case of two different relaxation times (short and long), the following equation was used:

$$M = M_\infty + (M_0 - M_\infty)e^{\frac{-\tau}{T_{1\rho}^s}} + (M_0 - M_\infty)e^{\frac{-\tau}{T_{1\rho}^l}} \qquad 6.1$$

where, M_0 is the initial magnetization, and M_∞ is the magnetization when the spin system and the lattice reach a quasi-equilibrium during the spin-lock ($M_\infty = 0$ at resonance). The $T_{1\rho}$ measurement is suitable to measure correlation times in the order of KHz, in our case ca. 80 KHz, because this value is particularly useful for probing molecular motions of polymers.

6.3 Results and discussion

6.3.1 Influence of various pre-made compatibilizers on the physical properties of TEOs

Figure 6.2 shows the tensile strength of TEOs with various pre-made compatibilizers as a function of their amounts. In case of the PP-EPDM graft copolymer, it is observed that with its increasing amount the tensile strength increases. On the other hand, for S-EB-S, the tensile strength decreases, whereas for TOR it first decreases and then reaches a plateau.

Figure 6.3 shows the elongation at break as a function of concentration of the compatibilizers. With increasing concentration the elongation at break decreases somewhat in all cases. Overall little differences between the various compatibilizers are observed, except for S-EB-S, which shows a relatively low elongation at break as compared to others at 25 phr concentration of the compatibilizer.

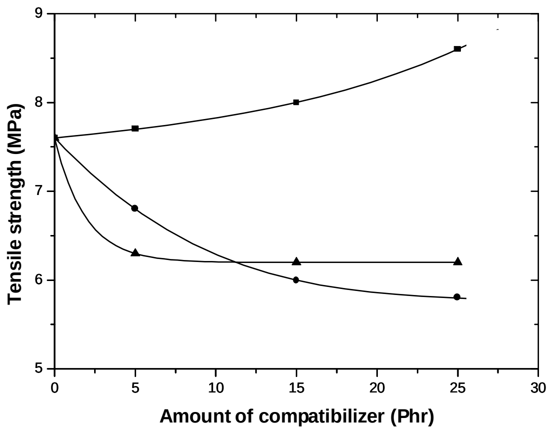


Figure 6.2: Tensile strength of PP/EPDM TEOs as a function of amounts of various compatibilizers: (■): PP-EPDM graft copolymer; (●): S-EB-S; (▲): TOR.

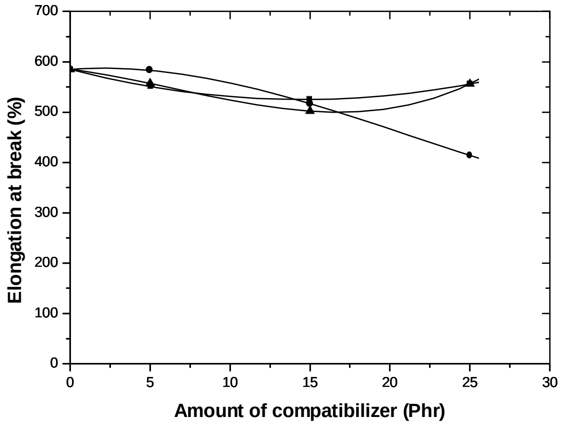


Figure 6.3: Elongaion at break of PP/EPDM TEOs as a function of amounts of various compatibilizers; symbols as in Fig. 6.2.

In Figure 6.4 the Young's modulus as a function of amount of the compatibilizers is shown. The Young's modulus increases with increasing concentration of the PP-EPDM graft copolymer. On the contrary, for S-EB-S and TOR a decrease is observed.

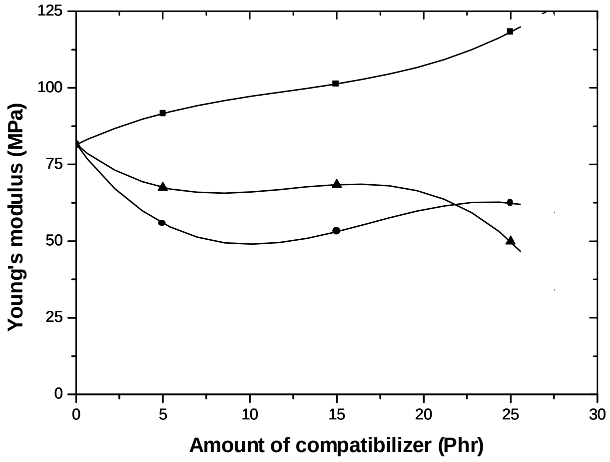


Figure 6.4: Young's modulus of PP/EPDM TEOs as a function of amounts of various compatibilizers; symbols as in Fig. 6.2.

All these results clearly indicate that the PP-EPDM graft copolymer acts as an effective compatibilizer in PP/EPDM TEOs, since its addition improves the physical properties like tensile strength and modulus to a considerable extent. In contrast, S-EB-S and TOR do not contribute to an improvement of the physical properties, thereby not acting as good compatibilizers in PP/EPDM blends. An obvious explanation for the better performance of the PP-EPDM graft copolymer is the fact that it structurally resembles most closely that of the two constituents of the blend: PP and EPDM.

6.3.2 Influence of various pre-made compatibilizers on the morphology of TEOs

Figures 6.5 and 6.6 show LV-SEM micrographs of PP/EPDM (67:33 w/w) TEOs without the addition of any compatibilizer: EPDM particles dispersed and distributed in the continuous PP-matrix. The structured EPDM-particle sizes mostly vary in between 3 – 5 µm. LV-SEM images of PP/EPDM TEOs after the addition of the compatibilizers PP-EPDM graft copolymer, S-EB-S and TOR are depicted in Figures 6.7 – 6.9, respectively. A slight reduction of EPDM particle size till mostly ~ 1.5 – 2 µm is noticed in all the cases, indicating some action of compatibilization.

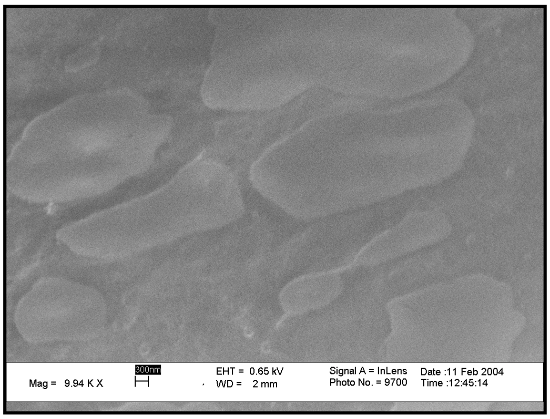


Figure 6.5: LV-SEM micrograph of PP/EPDM (67:33 w/w) TEOs at higher magnification (scale: 300 nm).

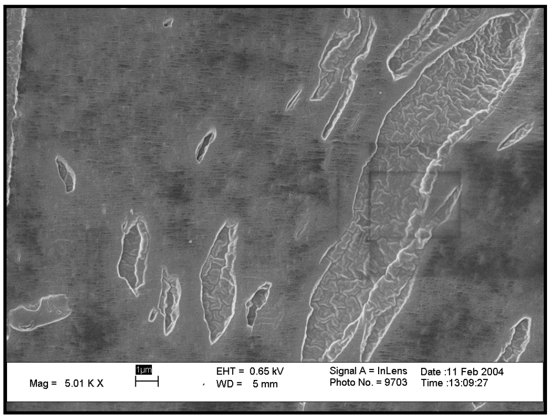


Figure 6.6: LV-SEM micrograph of PP/EPDM (67:33 w/w) TEOs at lower magnification (scale: 1 µm).

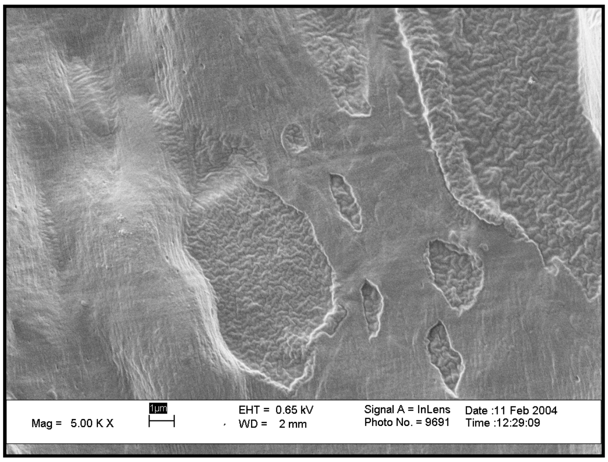


Figure 6.7: LV-SEM micrograph of PP/EPDM TEOs in presence of PP-EPDM graft copolymer (scale: 1 µm).

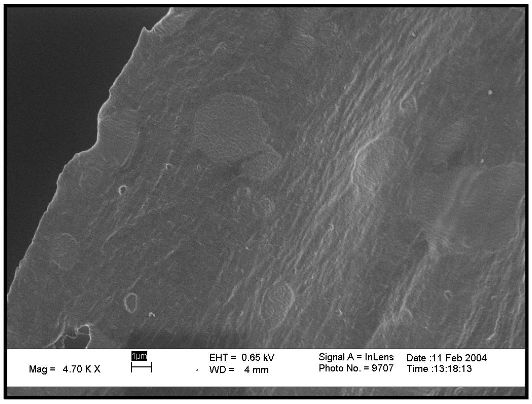


Figure 6.8: LV-SEM micrograph of PP/EPDM TEOs in presence of S-EB-S (scale: 1 µm).

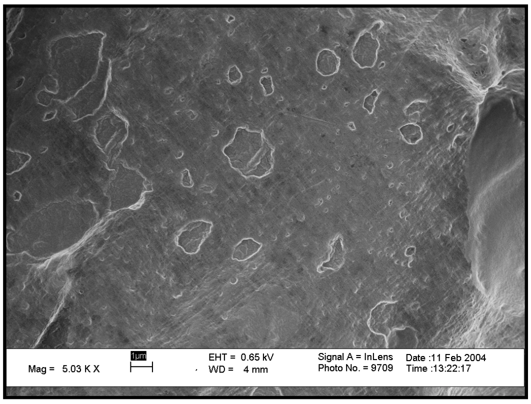


Figure 6.9: LV-SEM micrograph of PP/EPDM TEOs in presence of TOR (scale: 1 µm).

6.3.3 Influence of PP-EPDM graft copolymer as compatibilizer on the dynamic mechanical properties of TEOs

Figure 6.10 shows the DMTA results of PP/EPDM TEOs, with and without the addition of PP-EPDM graft copolymer. It can be observed from the plot of the loss angle tan delta as a function of temperature, that there are two major transitions: the glass transition (T_g) of EPDM at around – 56°C and that of PP at around – 10°C. After the addition of PP-EPDM graft copolymer to the PP/EPDM TEO, a slight decrease of the peak height of tan delta is observed for EPDM, a slight shifting of the T_g of PP towards lower temperature and broadening of the T_g-peak. These observations are an indication of a slight improvement of compatibility between PP and EPDM under the influence of PP-EPDM graft copolymer, in line with the mechanical properties.

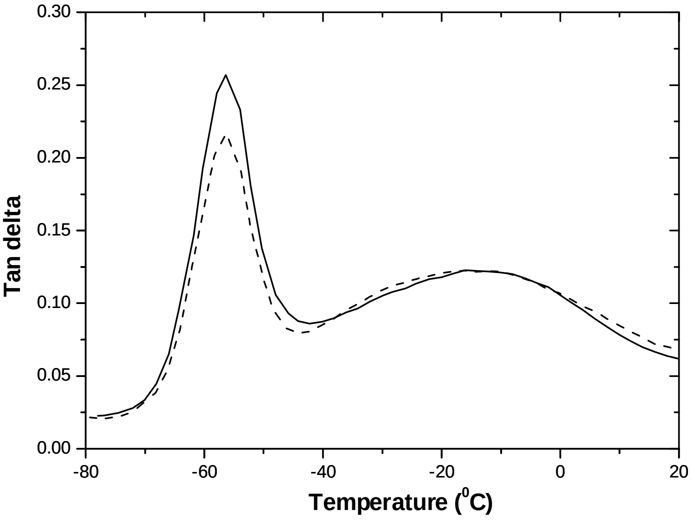


Figure 6.10: Tan delta as a function of temperature of PP/EPDM TEO:(——): without and (---): with the addition of 25 phr of PP-EPDM graft copolymer.

6.3.4 Influence of various pre-made compatibilizers on the physical properties of TPVs

Figure 6.11 shows the tensile strength versus the concentration of pre-made compatibilizers. In all cases, tensile strength decreases with increasing amount of compatibilizers. In most cases, the values of the tensile strength of the PP/EPDM TPVs are even lower than those of corresponding TEOs, irrespective of the nature of compatibilizer. S-EB-S exhibits the lowest values, whereas TOR still shows the highest. The values obtained for the PP-EPDM graft copolymer vary in between TOR and S-EB-S.

Figure 6.12 depicts the elongation at break as a function of amount of the various compatibilizers. Hardly any difference in the values between TOR and S-EB-S is noticed for all concentrations of the compatibilizers. The elongation at break decreases with increasing amount of PP-EPDM graft copolymer, which also shows the lowest values amongst all.

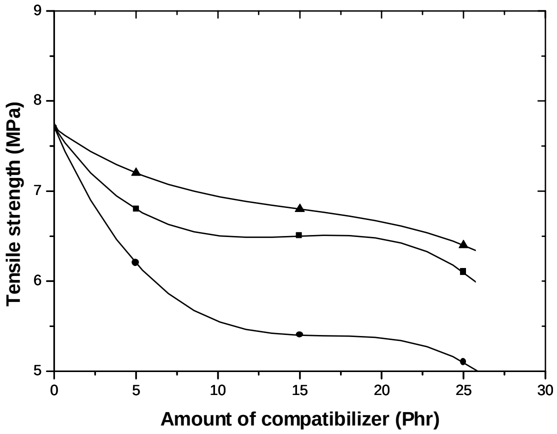


Figure 6.11: Tensile strength of PP/EPDM TPVs as a function of amounts of various compatibilizers; symbols as in Fig. 6.2.

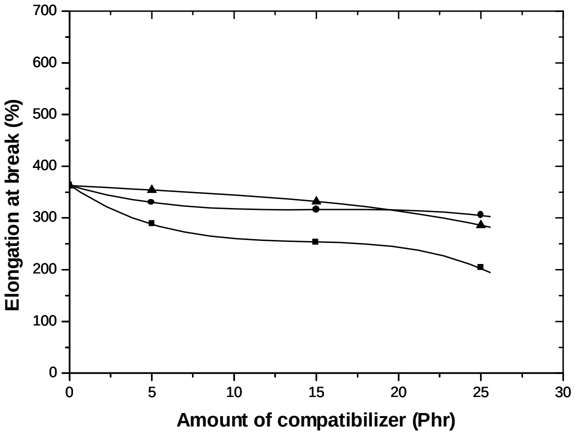


Figure 6.12: Elongation at break of PP/EPDM TPVs as a function of amounts of various compatibilizers; symbols as in Fig. 6.2.

Young’s modulus as a function of amount of the compatibilizer is shown in Figure 6.13. In case of S-EB-S and TOR, the Young’s modulus decreases with increasing concentration of the compatibilizers. In contrast, for PP-EPDM graft copolymer the modulus keeps on increasing with the amount.

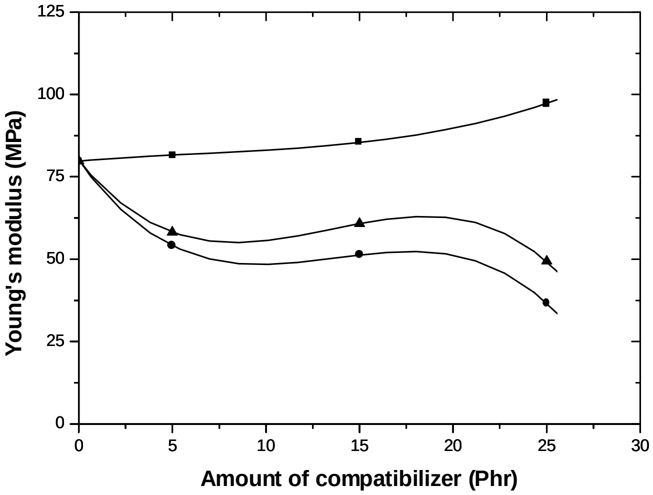


Figure 6.13: Young's modulus of PP/EPDM TPVs as a function of amounts of various compatibilizers; symbols as in Fig. 6.2.

The above-mentioned results reveal that, although PP-EPDM graft copolymer acts as a good compatibilizer in case of TEOs, it cannot play the same role in PP/EPDM TPVs. The most plausible reason is that DCP also reacts with the PP-phase present in that graft copolymer itself, causing degradation which finally leads to deterioration of the physical properties like tensile strength. However, the addition of PP-EPDM graft copolymer improves the Young's modulus of the TPVs to some extent, because of the incorporation of overall more PP in the blend, which comes from the graft-copolymer itself. S-EB-S fails again to act as an effective compatibilizer in case of TPVs, like in TEOs. The slight improvement of physical properties, e.g. tensile strength and Young's modulus, of TOR-containing TPVs as compared to the corresponding TEOs, is most probably due to dynamic crosslinking of TOR itself through DCP.

The above results clearly show, that experiences gained with compatibilizers in unvulcanized TEOs can not simply be translated to TPVs. The vulcanization step, particularly the possible side-reactions when peroxides are used, may cause a complete reversal of effects. Because of the poor results obtained with these pre-made compatibilizers in TPVs, this approach was not further pursued with morphological and rheological characterizations.

6.3.5 Evidence for in-situ compatibilization with TPVs

6.3.5.1 Solid state ^{13}C NMR spectra

Solid state ^{13}C NMR spectra of PP, EPDM rubber and a PP-extracted TPV sample, which may contain the in-situ formed PP-EPDM grafts, are shown in Figures 6.14 – 6.16, respectively.

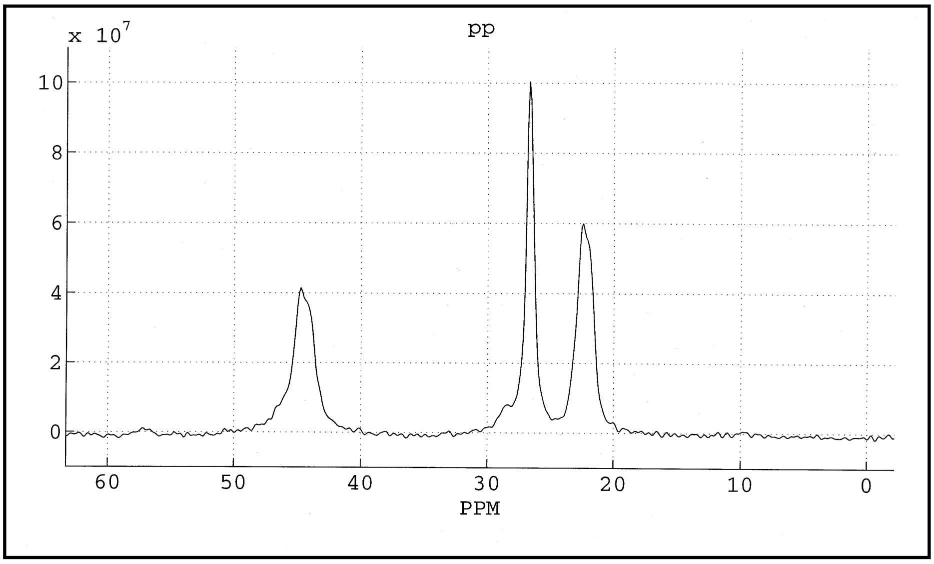


Figure 6.14 : Solid state ^{13}C NMR spectrum of PP at 70℃.

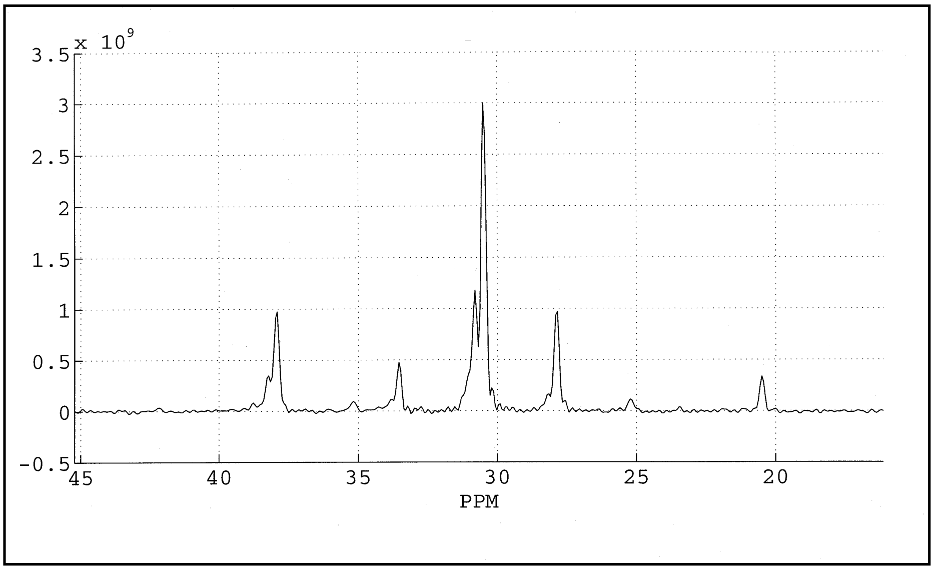


Figure 6.15 : Solid state ^{13}C NMR spectrum of EPDM at 70℃.

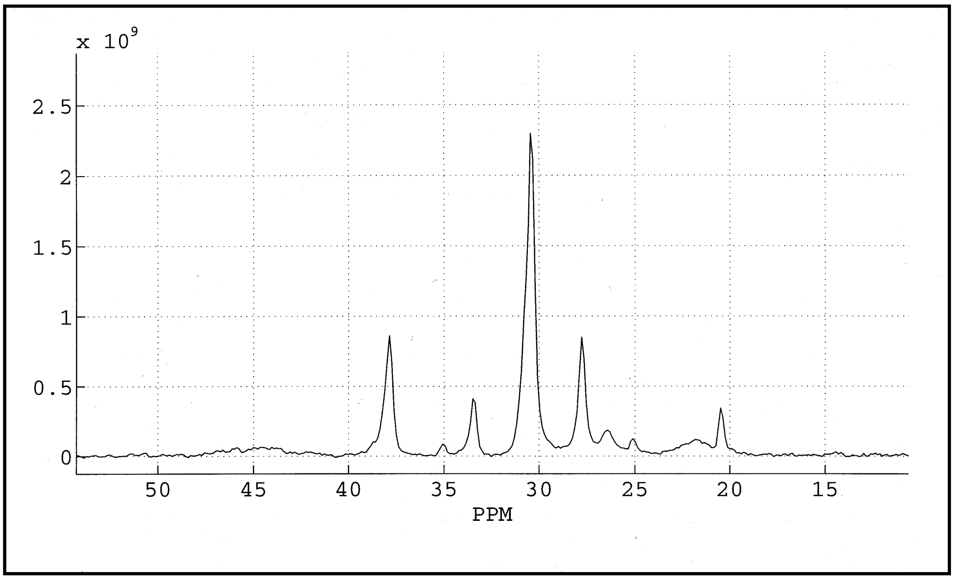


Figure 6.16 : Solid state ^{13}C NMR spectrum of PP extracted TPV at 70°C.

Table 6.4 shows the observed ^{13}C chemical shifts of the main peaks and the corresponding assignments for PP.

Table 6.4 Main peaks of PP.

Chemical shift (ppm)	Carbon type
43.8	$-CH_2-$
25.9	$-CH-$
21.6	$-CH_3$

Chemical shifts and the corresponding assignments of various groups for EPDM rubber containing 50 wt % of paraffinic oil are shown in Table 6.5.

Table 6.5 Main peaks of EPDM+oil.

Chemical shift (ppm)	Carbon type
20.5	$-CH_3$
27.9	$-CH_2-$
31.0	$-CH_2-$
33.5	$-CH_2-$ or $-CH-$
38.0	$-CH_2-$

The ^{13}C spectra of the sample: PP extracted TPV, shows almost all the main peaks as seen in Table 6.5 for EPDM rubber. In addition, it exhibits two other chemical shifts at 22.0 and 26.5 ppm, which indicates the presence of $–CH_3$ and –CH– from isotactic PP. Thus, there is an indication that during the dynamic vulcanization process, PP-EPDM graft-links are generated, which still remains in the system even after the extraction of the PP-phase from the TPV, assuming that the extraction was complete.

6.3.5.2 Relaxation time in the rotating co-ordinate system, $T_{1\rho}$ (^{13}C)

The signal intensity obtained form the highest intense peak of the spectra as a function of spin-lock duration in order to calculate $T_{1\rho}$ values from the curve fitting for PP, EPDM rubber and PP extracted TPV are depicted in Figures 6.17 – 6.19 respectively. The figures for other peaks of the spectra are not very clear because of their poor signal/noise ratio. All the figures show that, after the excitation of all transitions, the relaxation processes in the rotating frame can basically be fitted with an equation, which is bi-exponential in nature. Table 6.6 shows the short and long relaxation times of different polymers. Consequently, PP shows two different rates of decay giving rise to two different $T_{1\rho}$-values. This may be taken as an indication that the PP contains two different domains: amorphous and crystalline. The amorphous phase, having high mobility, shows a long $T_{1\rho}$-value indicative of a slower relaxation process. On the other hand, the crystalline phase, having more rigidity, relaxes at a faster rate leading to a relatively shorter $T_{1\rho}$-value. EPDM rubber also can be fitted with a bi-exponential decay function, indicating the presence of oil showing long $T_{1\rho}$-value. EPDM is mostly amorphous in nature thereby showing short $T_{1\rho}$-value. However, the relaxation times are longer as compared to that of PP. PP extracted TPV, which does not contain oil anymore since xylene also extracts the oil, shows a different trend compared to normal EPDM, since it shows two different types of relaxations. This indicates that, probably due to the formation of crosslinks in the EPDM-phase and in-situ PP-EPDM graft-links along with degraded PP-oligomer branches, which impart more rigidity to the system, the relaxation occurs at a somewhat faster rate than EPDM.

Table 6.6 Short and long relaxation times of different polymers.

Polymer type	$T_{1\rho}$ short (ms)	$T_{1\rho}$ long (ms)
PP	0.0001	0.0100
EPDM	0.0296	0.3971
PP extracted TPV	0.0153	0.0906

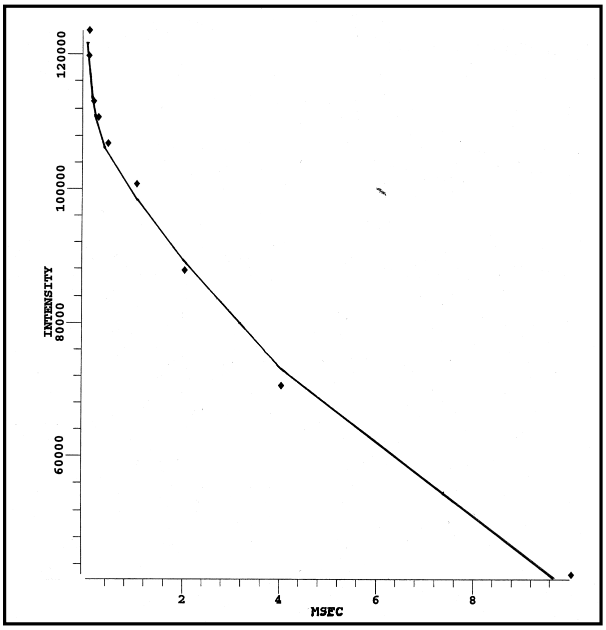


Figure 6.17: Relaxation decay of magnetization of PP at 70℃, peak at 25.9 ppm.

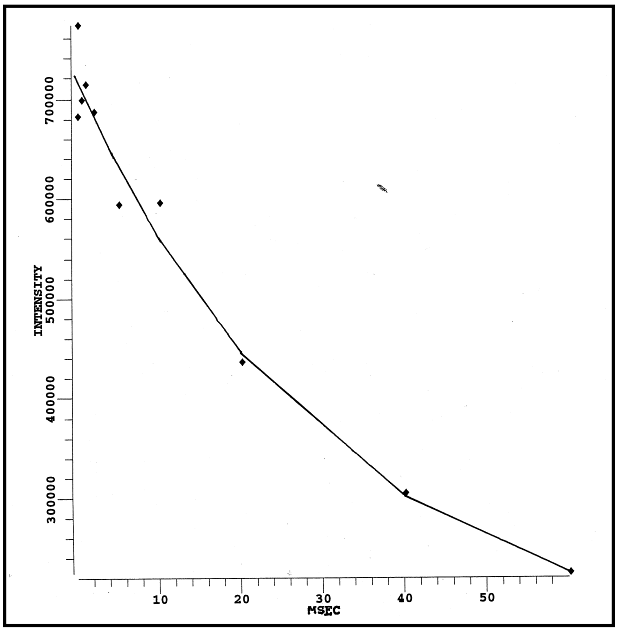


Figure 6.18: Relaxation decay of magnetization of EPDM at 70℃, peak at 30.5 ppm.

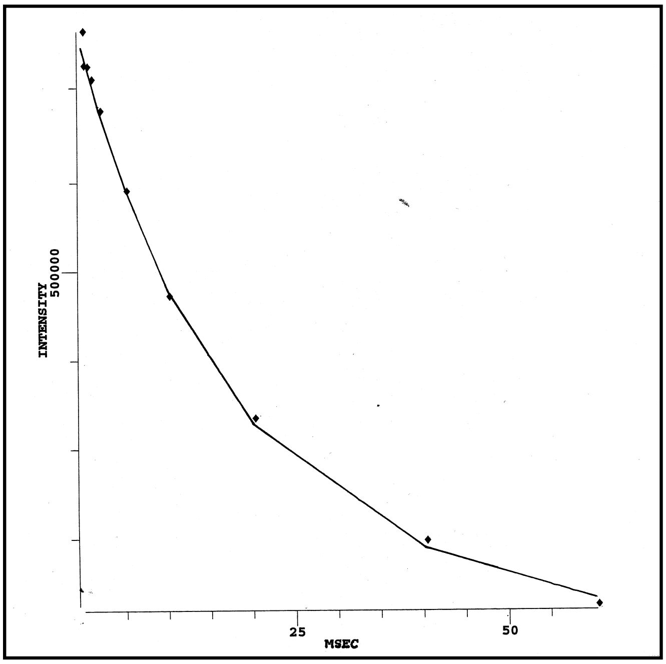


Figure 6.18: Relaxation decay of magnetization of PP extracted TPV at 70°C, peak at 30.4 ppm.

6.4 Conclusions

During dynamic vulcanization of PP/EPDM blends with DCP/TAC, there is a possibility of generation of in-situ graft-links at the interface between both phases. Three potential compatibilizers for PP/EPDM blends were first investigated as references in order to obtain a quantified insight into the effects to be expected from in-situ graft-links: PP-grafted EPDM, S-EB-S and TOR. Only the first one showed some compatibilizing action in straight, unvulcanized blends, as evidenced by a slight increase in tensile strength of the blend and somewhat smaller EPDM particle size within the PP-matrix. Also dynamic mechanical testing, in particular the glass transition temperatures of the PP and EPDM components showed some signs of compatibilization. The PP-grafted EPDM resembles most closely to the structures of PP and EPDM. On the other hand, when mixed into a dynamically vulcanized PP/EPDM-blend, all compatibilizers resulted in an overall deterioration of mechanical properties. The vulcanization step, particularly with peroxides, causes a complete reversal of the effects observed with straight blends.

From the spectra as obtained with high temperature solid state NMR, there is an indication that PP-EPDM graft links are generated during the dynamic vulcanization process, that still remain after the extraction of the free PP-phase from the TPV-film. However, the restriction must be made, that some PP for another possible reason may have remained in the TPV after the extraction was considered complete. NMR-relaxation experiments gave further evidence for the in-situ formed graft-links. In all cases only qualitative indications could be achieved, due to the extremely low amounts of graft-links formed.

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Chapter 7

Influence of various stabilizers on aging of dicumyl peroxide-cured PP/EPDM TPVs

Oxidation is generally considered the main degradation mechanism of saturated polymers. In presence of oxygen, the carbon radicals of the polymer chains can first be converted to peroxy radicals, which further react with labile hydrogens of the polymer to form unstable hydroperoxides, commencing auto-catalytic reactions. Stabilizers are used to prevent the degradation of polymers and thereby, to effectively extend the useful lifetime of polymers. However, the use of stabilizers in combination with a peroxide cure system needs special care, because the main function of these materials is to deactivate the radicals formed after the decomposition of a peroxide, resulting in a reduced crosslinking efficiency of the peroxide and inactivation of the stabilizers being used. In this chapter, the changes of the physical properties after aging, of dicumyl peroxide/triallyl cyanurate-cured TPVs at a fixed PP/EPDM ratio as well as at varied blend ratios in presence of various structurally different stabilizers are studied. TMQ performs the best amongst all the stabilizers being investigated for the study. However, the latter discolors the TPV-end products. Combinations of Irganox 1076+Irgafos 168 and Chimassorb 944 LD+Irgastab FS 042 turn out to be the best stabilizer packages, since they fulfil all the basic criteria required for a good stabilizer: little interaction with the peroxide cure, good stabilization against aging and no discoloration of the TPV.

7.1 Introduction

Environmental factors such as oxygen, ozone, light, heat, humidity, solvents, and other chemicals can severely reduce the longevity of polymers.

Part of this chapter has been accepted in Polymer Degradation and Stability.

Oxidation is generally considered as the main degradation mechanism of saturated polymers like polyolefins and elastomers. In presence of oxygen, the carbon radicals of the polymer chains, as formed by heat or shear etc., are first converted to peroxy radicals, which can further react with labile hydrogens of the polymer, to form unstable hydroperoxides, commencing auto-catalytic reactions.[1,2] The oxidation of polymers is most commonly depicted in terms of the kinetic scheme developed by Bolland and co-workers[3], as shown in Figure 7.1.

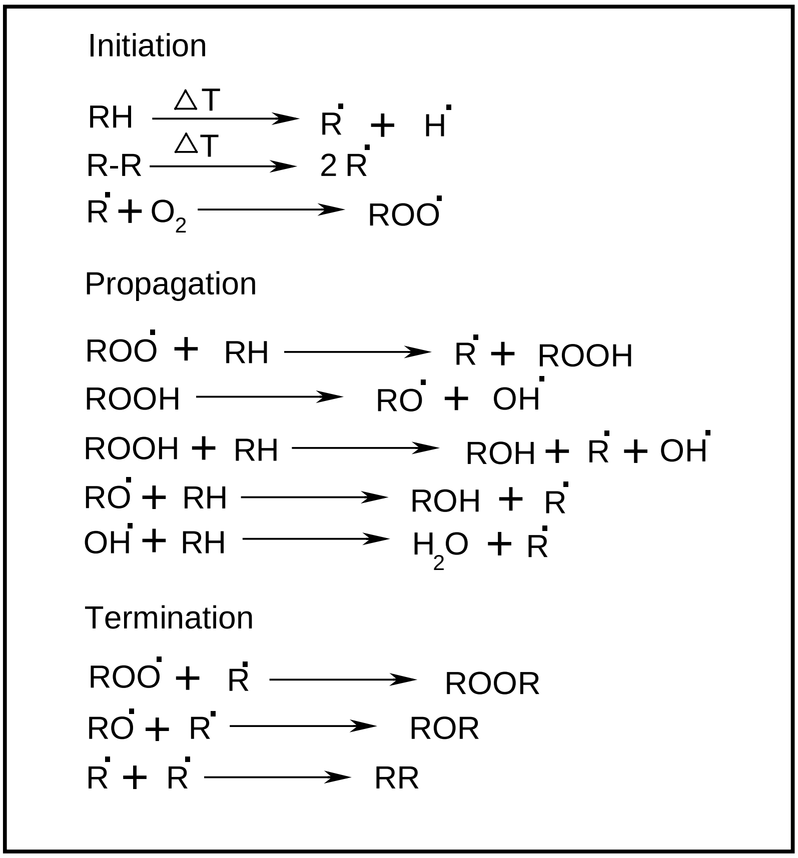


Figure 7.1: Bolland oxidation mechanism (RH = rubber hydrocarbon).[3]

The ultimate effects of the above-mentioned process are a damaging combination of main chain-scission and crosslinking.[4,5] Stabilizers, for instance, antioxidants or antiozonants, are used to prevent the degradation of polymers due to the detrimental effects of oxygen and thereby, to effectively extend the useful lifetime of polymers. In general, the stabilizers do not completely eliminate the oxidation mechanism, but they retard the auto-oxidation reaction as mentioned above by interfering with the mechanism of radical propagation.[2]

There are several types of antioxidants, which are categorized according to the way they interrupt the oxidative process. The most commonly employed antioxidants are hindered phenols and amines, which neutralize alkoxy and peroxy-radicals prior to their harmful actions, by donating hydrogen atoms. These are known as primary antioxidants. They are also called ‘chain stoppers’, because they stop the free-radical chain reaction of oxidation. Extensive studies on stabilization with phenols have been carried out in the last few decades.[1,6] Their mechanism of action is shown in Figure 7.2.

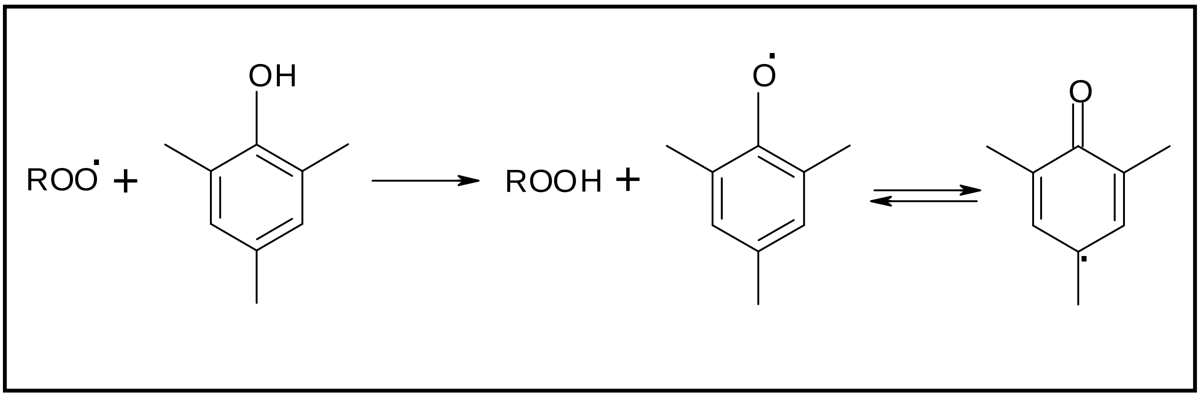


Figure 7.2: Mechanism of action of a primary phenolic antioxidant.

Conversely, thio-compounds or phosphites, known as secondary types of antioxidants or preventive antioxidants[1], decompose hydroperoxides and thereby stop the propagation of radicals. They convert hydroperoxides to more stable products. Their mechanism of action is shown in Figure 7.3.

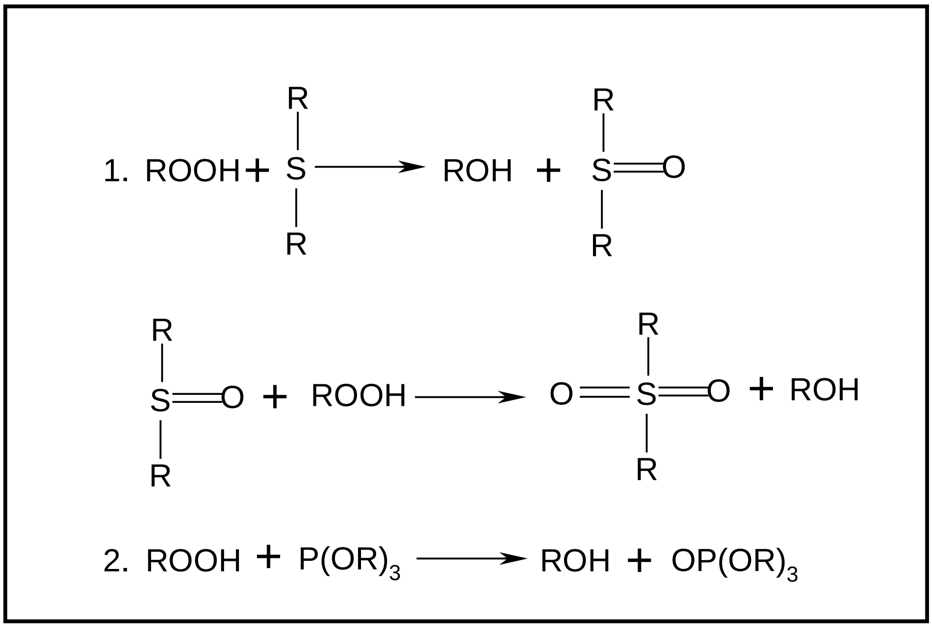


Figure 7.3: Mechanism of action of secondary antioxidants.

Phosphites show strong synergistic effects in combination with phenolic antioxidants.[1,6]

The use of the antioxidants in combination with a peroxide cure system needs special care, because these materials compete with the polymer for the radicals formed after the decomposition of the peroxide.[7] Reactions between antioxidants and peroxy and/or polymer-radicals take place, resulting in a reduced crosslinking efficiency of the peroxide and inactivation of the antioxidants being used.[5,7-11] It has been reported that the most effective antioxidants are also the most effective inhibitors of peroxide crosslinking.[11] This is because of the fact that the antioxidants contain easily abstractable hydrogen atoms and can neutralize oxy or polymer-radicals by donating a hydrogen atom. Consequently, the radical is transferred to the antioxidant molecule and the crosslinking process is hampered. In addition to diminishing efficiency of the peroxide cure, radical transfer depletes the antioxidant as well.[5] Both phenolic and amine antioxidants have a strong inhibitory influence on the peroxide vulcanization process.[11-13] It was also reported that unhindered phenolics depress the final state of cure more than hindered phenolic antioxidants.[13]

Antioxidants are also often classified into two categories: processing stabilizers and thermal/heat stabilizers. Some polymers, e.g. EPDM, exhibiting a fair heat-resistance and excellent ozone and weather-resistance, can still be stabilized by a relatively small addition of antioxidants.

Several studies have been carried out by many authors on the antioxidant selection for peroxide-cured elastomer applications.[7,14-19] The influence of physical parameters such as volatility, diffusion, solubility and molecular mass has been examined in detail. Recently, some new approaches to the melt stabilization of polyolefins were launched by Voigt et al.[20] In addition to the traditional phenol/phosphite binary blends, new synergistic ternary systems, combining a carbon centered lactone radical scavenger like arylbenzofuranone with phenol and phosphite proved their efficiency as stabilizers in polymer grades. These combinations offered extraordinary efficacy for the processing stability of the polymers. The long term aging behavior of high performance, 150°C capable polyacrylate/polyamide based TPVs was studied by Cail et al.[21] However, hardly any research work has been reported so far on the applications of stabilizers in peroxide-cured PP/EPDM TPVs.

The selection of a suitable stabilizer for peroxide-cured PP/EPDM TPVs mainly depends on the following three important criteria:

(a) the interaction and consumption of peroxide-radicals by the stabilizer during the production stage;
(b) the effectiveness of the antioxidant in stabilizing the polymer(s) against oxidation during the process of aging and
(c) the color of the stabilizer(s) and consequently the same of the TPV-end products, made out of these stabilizers.

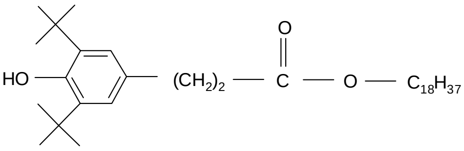
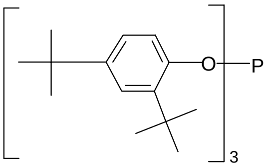
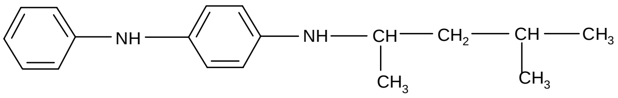
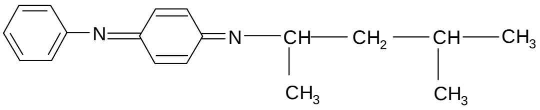
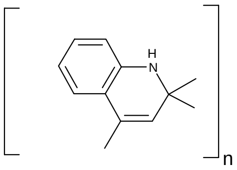
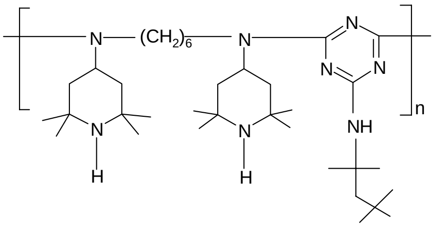
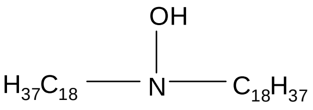
A stabilizer package, consisting of Irganox 1076 and Irgafos 168 was used in all the recipes as described in previous chapters. The main objective of the present chapter is therefore to show the influences of various stabilizers, relative to the Irganox 1076+Irgafos 168 combination in dicumyl peroxide-cured TPVs, in order to find the most suitable system.

7.2 Experimental

7.2.1 Materials

EPDM and PP used in this chapter were the same as mentioned before in Chapter 3. Dicumyl peroxide (DCP) was employed as the crosslinking agent. Triallyl cyanurate (TAC), 50 % was used as co-agent. Different types of stabilizers were used for the present investigation. The chemical/commercial names and structures of the various stabilizers used are given in Table 7.1. Irganox 1076, Irgafos 168, Chimassorb 944 LD and Irgastab FS 042 were obtained from Ciba Specialty Chemicals Inc., Switzerland; Santoflex 6PPD, Q-Flex QDI and Flectol TMQ were obtained from Flexsys B.V., The Netherlands. The stabilizers, as chosen for this study are hindered phenol, or phosphite, or hindered amine or p-phenylenediamine type.

Table 7.1 Chemical/commercial names and structures of the various stabilizers used.

Chemical/commercial name	Chemical structure
octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate (Irganox® 1076)	
tris(2,4-di-tert-butylphenyl) phosphite (Irgafos® 168)	
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (Santoflex® 6PPD)	
N-{4-[(1,3-dimethylbutyl) imino]-2,5-cyclohexadien-1-ylidine} benzenamine (Q-Flex® QDI)	
2,2,4-trimethyl-1,2-dihydroquinoline, polymerized (Flectol® TMQ)	
poly{[6-[(1,1,3,3-tetramethylbutylamino -1,3,5-triazine-4-piperidinyl) -imino] -1,6-hexanediyl[(2,2,6,6-tetramethyl -4-piperidinyl)imino]} (hindered amine light stabilizer) (HALS) (Chimassorb® 944 LD)	
bis(hydrogenated tallow alkyl)amines, oxidized (Irgastab® FS 042)	 $H_{37}C_{18}-N(OH)-C_{18}H_{37}$

7.2.2 Preparation of PP/EPDM TPVs

The TPV compositions employed for the study are given in Tables 7.2 and 7.3. The experimental variables are the types and concentrations of stabilizers: Table 7.2, and PP/EPDM blend ratios: Table 7.3. The method of preparation of all TPVs used in this chapter was the same as mentioned before in Chapter 3.

Table 7.2 TPV compositions (phr) at varied stabilizer concentrations and fixed PP/EPDM blend ratio.

Component	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16
EPDM*	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
PP	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
DCP	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1
TAC	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
I 1076	–	0.5	–	–	–	–	1.0	–	–	–	–	1.5	–	–	–	–
I 168	–	0.5	–	–	–	–	1.0	–	–	–	–	1.5	–	–	–	–
6PPD	–	–	1.0	–	–	–	–	2.0	–	–	–	–	3.0	–	–	–
QDI	–	–	–	1.0	–	–	–	–	2.0	–	–	–	–	3.0	–	–
TMQ	–	–	–	–	1.0	–	–	–	–	2.0	–	–	–	–	3.0	–
944 LD	–	–	–	–	–	0.5	–	–	–	–	1.0	–	–	–	–	1.5
FS 042	–	–	–	–	–	0.5	–	–	–	–	1.0	–	–	–	–	1.5

*Includes 50 wt % paraffinic oil

Table 7.3 TPV compositions (phr) at varied PP/EPDM blend ratios and fixed stabilizer concentrations.

Component	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15
EPDM*	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
PP	75	75	75	75	75	100	100	100	100	100	125	125	125	125	125
DCP	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1
TAC	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
I 1076	0.5	–	–	–	–	0.5	–	–	–	–	0.5	–	–	–	–
I 168	0.5	–	–	–	–	0.5	–	–	–	–	0.5	–	–	–	–
6PPD	–	1.0	–	–	–	–	1.0	–	–	–	–	1.0	–	–	–
QDI	–	–	1.0	–	–	–	–	1.0	–	–	–	–	1.0	–	–
TMQ	–	–	–	1.0	–	–	–	–	1.0	–	–	–	–	1.0	–
944 LD	–	–	–	–	0.5	–	–	–	–	0.5	–	–	–	–	0.5
FS 042	–	–	–	–	0.5	–	–	–	–	0.5	–	–	–	–	0.5

*Includes 50 wt % paraffinic oil

7.2.3 Testing procedures

Physical properties

All the tensile and hardness tests were performed according to the procedures, as described in Chapter 3.

Aging tests

Accelerated aging tests were carried out according to ISO 188 on dumb-bell shaped specimens after putting them at 150°C for 14 days in an air-aging oven without forced aeration. The percentage change in the value of the property measured, was calculated from the following formula:

$$\frac{x_a - x_0}{x_0}.100\,\% \qquad 7.1$$

where, x_0 is the value of the property before aging and x_a is the value of the property after aging.

Curing properties of EPDM gum-compounds containing the various stabilizers

A rubber process analyzer, RPA-2000 (Alpha Technologies) was used to measure the cure-characteristics of EPDM gum-compounds, containing the different types of stabilizers, at 180°C according to ISO 6502. The recipes employed for that purpose are given in Tables 7.4 and 7.5. The concentration of DCP was 6.1 phr, whereas that of TAC was 5.0 phr in order to correspond with the quantities employed in Tables 7.2 and 7.3. Table 7.4 corresponds to stabilizer amounts of 1.0 phr and a reference compound C1 without any stabilizer. In Table 7.5 stabilizer quantities of 3.0 phr are employed.

Table 7.4 **Pure EPDM gum-vulcanizate compositions (phr), at 1.0 phr stabilizer concentration and corresponding RPA-2000 rheometer data.**

Component	C1	C2	C3	C4	C5	C6
EPDM	200	200	200	200	200	200
DCP	6.1	6.1	6.1	6.1	6.1	6.1
TAC	5.0	5.0	5.0	5.0	5.0	5.0
I 1076	–	0.5	–	–	–	–
I 168	–	0.5	–	–	–	–
6PPD	–	–	1.0	–	–	–
QDI	–	–	–	1.0	–	–
TMQ	–	–	–	–	1.0	–
944 LD	–	–	–	–	–	0.5
FS 042	–	–	–	–	–	0.5
RPA data						
Minimum torque (dN.m)	0.29	0.22	0.26	0.20	0.23	0.26
Maximum torque (dN.m)	1.60	1.47	1.22	1.22	1.52	1.52
Maximum – Minimum torque (dN.m)	1.31	1.25	0.96	1.02	1.29	1.26
t_{S2} (min)	0.33	0.39	0.40	0.51	0.37	0.38
$t_{0,90}$ (min)	3.69	4.12	4.31	4.53	3.59	3.89

Table 7.5 **Pure EPDM gum-vulcanizate compositions (phr), at 3.0 phr stabilizer concentration and corresponding RPA-2000 rheometer data.**

Component	D1	D2	D3	D4	D5
EPDM	200	200	200	200	200
DCP	6.1	6.1	6.1	6.1	6.1
TAC	5.0	5.0	5.0	5.0	5.0
I 1076	1.5	–	–	–	–
I 168	1.5	–	–	–	–
6PPD	–	3.0	–	–	–
QDI	–	–	3.0	–	–
TMQ	–	–	–	3.0	–
944 LD	–	–	–	–	1.5
FS 042	–	–	–	–	1.5
RPA data					
Minimum torque (dN.m)	0.34	0.31	0.35	0.36	0.34
Maximum torque (dN.m)	1.50	0.69	1.01	1.57	1.47
Maximum – Minimum torque (dN.m)	1.16	0.38	0.66	1.21	1.13
t_{S2} (min)	0.37	0.30	0.46	0.36	0.47
$t_{0,90}$ (min)	3.51	5.52	4.64	4.64	3.93

7.3 Results and discussion

The general decomposition scheme of DCP is shown in Figure 7.4.

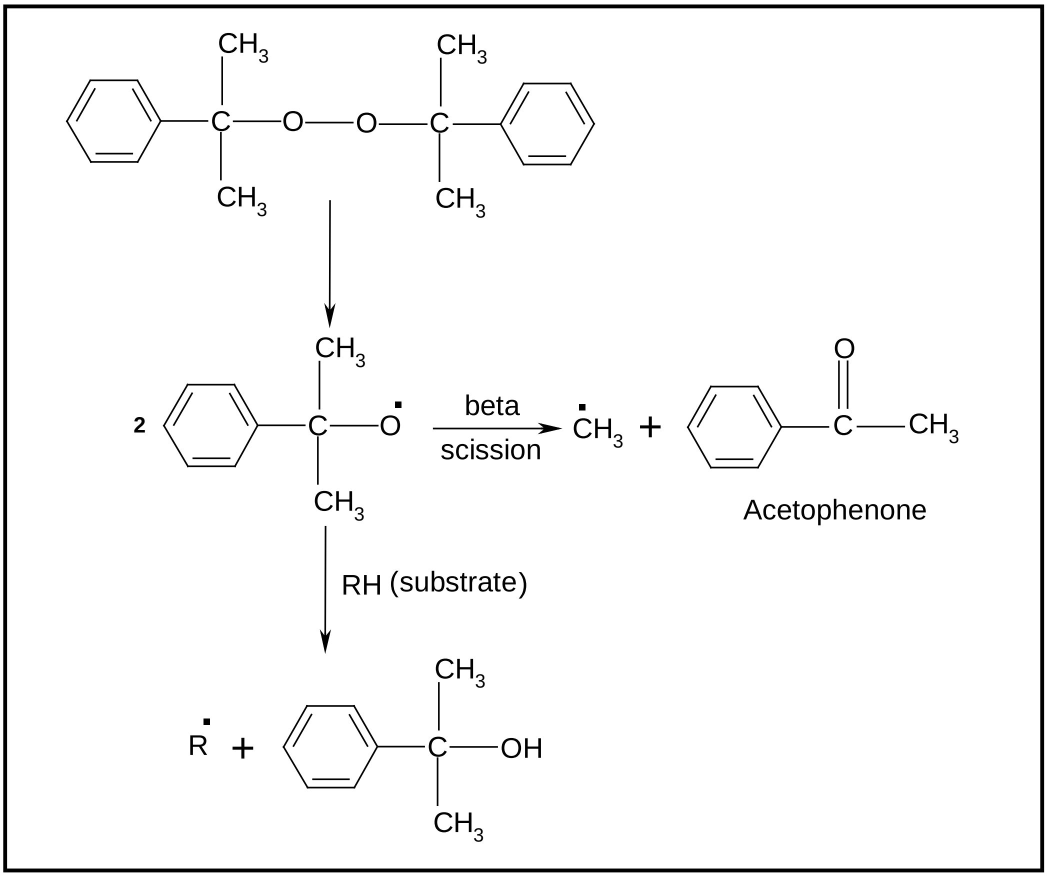


Figure 7.4: Decomposition scheme of DCP.

Basically, methyl and cumyloxy-radicals are formed as the main decomposition products from DCP. Both these radicals are very reactive towards abstracting hydrogen atoms from the polymer chains. The stabilizers used in this study possibly interact with those radicals. The latter lowers the yield of the expected peroxide curing of rubber.

In line with the main aim of this investigation to find out the most suitable stabilizer for DCP-cured TPVs, three main features are emphasized in the screening of the stabilizers in the following: their interaction with the peroxide curing, as seen in the properties obtained; their stabilizing action by the level of retention of properties after aging and their tendency to discolor the TPVs.

7.3.1 Influence of stabilizers on cure properties before aging

Influence of different types of stabilizers at varied concentrations and at fixed PP/EPDM blend ratio: the physical properties: tensile strength, elongation at break and hardness, before and after aging, for the recipes A1 – A16 are shown in Table 7.6. Especially at the higher concentration of 3.0 phr of stabilizers, 6PPD and QDI give poor physical properties before aging: recipes A13 and A14, indicating more interactions followed by consumption of peroxi-radicals by the stabilizers.

Influence of different types of stabilizers at varied PP/EPDM blend ratios: the physical properties, before and after aging, for the recipes B1 – B15 are shown in Table 7.7. In most cases, TMQ, I 1076+I 168 and 944 LD+FS 042 perform better than the other stabilizer packages before aging, irrespective of the content of PP in the PP/EPDM TPVs.

Table 7.6 Physical properties of TPVs, before and after aging, for the recipes A1 – A16.

Recipe No.	Tensile strength (MPa)			Elongation at break (%)			Hardness (Shore A)		
	Before Aging	After Aging	% Change	Before Aging	After Aging	% Change	Before Aging	After Aging	Change (Degree)
A1	4.2	0	-100	352	0	-100	65	80	+15
A2	4.4	3.5	-20	404	17	-96	65	79	+14
A3	3.7	1.2	-68	406	36	-91	64	57	+7
A4	3.2	1.2	-63	309	35	-89	63	74	+11
A5	3.5	2.0	-43	299	199	-33	67	59	-8
A6	3.5	1.3	-63	307	103	-66	65	55	-10
A7	3.6	3.2	-11	385	16	-96	63	69	+6
A8	2.4	3.8	+58	409	525	+28	61	63	+2
A9	3.2	4.0	+25	397	463	+17	62	64	+2
A10	3.8	4.5	+18	406	433	+7	69	71	+2
A11	4.2	1.9	-55	339	119	-65	65	62	-3
A12	4.6	0	-100	448	0	-100	65	70	+5
A13	2.2	4.5	+105	400	551	+38	60	63	+3
A14	2.9	4.4	+52	399	468	+17	62	64	+2
A15	3.2	4.1	+28	306	357	+17	69	70	+1
A16	3.5	2.1	-40	289	175	-39	65	62	-3

Table 7.7 Physical properties of TPVs, before and after aging, for the recipes B1 – B15.

Recipe No.	Tensile strength (MPa)			Elongation at break (%)			Hardness (Shore A)		
	Before Aging	After Aging	% Change	Before Aging	After Aging	% Change	Before Aging	After Aging	Change (Degree)
B1	3.7	2.5	-32	445	30	-93	75	80	+5
B2	5.2	1.4	-73	415	67	-84	77	74	-3
B3	3.6	2.0	-44	466	24	-95	74	77	+3
B4	4.7	2.0	-57	412	34	-92	79	77	-2
B5	3.6	2.1	-42	238	51	-79	76	72	-4
B6	4.3	0	-100	354	0	-100	84	89	+5
B7	4.2	0	-100	158	0	-100	86	88	+2
B8	5.7	0	-100	323	0	-100	86	90	+4
B9	5.7	4.2	-26	374	134	-64	88	87	-1
B10	5.6	2.8	-50	298	38	-87	87	83	-4
B11	5.9	0	-100	348	0	-100	90	94	+4
B12	6.1	0	-96	139	0	-100	91	92	+1
B13	5.8	0	-100	175	0	-100	89	93	+4
B14	5.1	6.4	+25	300	289	-4	91	88	-3
B15	5.2	0	-100	326	0	-100	99	90	-9

In order to explain the results of physical properties before aging, the curing characteristics of various stabilizer-containing pure EPDM-rubbers were evaluated at 180°C. The RPA data at two different concentrations (1 and 3 phr) of stabilizers are given in Tables 7.4 and 7.5. Figure 7.5 shows the rheograms of the various stabilizer-containing EPDM gumstock vulcanizates at 1 phr concentration of the stabilizers; Figure 7.6 shows the same at 3 phr of stabilizers. From the delta torque values (maximum – minimum torque) it can be noticed, that all the stabilizers basically interact and consume peroxide-radicals and thereby diminish the delta torque values to some extent, as compared to that of the control: no stabilizer added. 6PPD and QDI interact and consume the peroxide-radicals to considerable extents, thereby drastically decreasing the delta torque values. In the case of 3 phr concentration of the stabilizer, it is noticed that 6PPD consumes the peroxide-radicals even more than QDI. This is because of the fact that QDI is the oxidized form of 6PPD, having a lower amount of easily abstractable hydrogen atoms. On the other hand, TMQ interacts and consumes the least amount of peroxide-radicals, still showing reasonable values of the delta torque, very close to that of the control. I 1076+I 168 and 944 LD+FS 042 combinations perform moderately regarding the delta torque values, as shown in Figures 7.5 and 7.6. These figures can therefore be related to the values of physical properties as obtained before aging, as shown in Table 7.6.

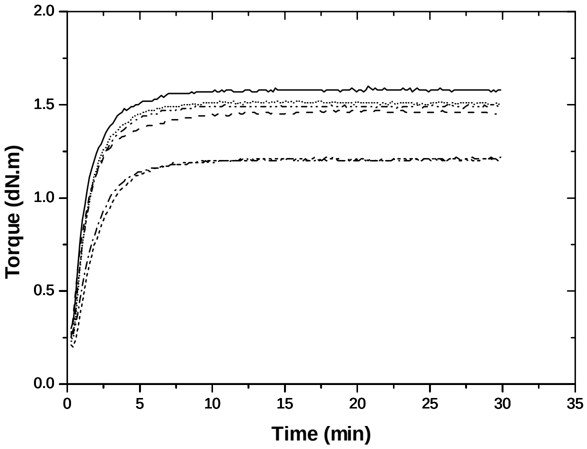


Figure 7.5: Rheograms of various stabilizers-containing EPDM gumstocks at 1 phr concentration at 180°C: (——): Control; (— —): I 1076+I 168; (-·-·-): 6PPD;(- - -): QDI; (··········): TMQ; (—···): LD 944+FS 042.

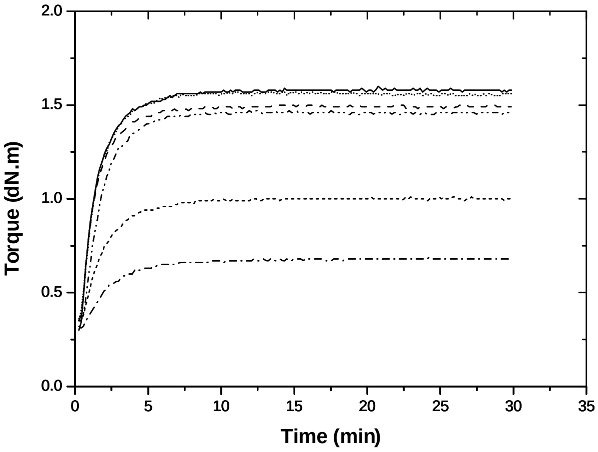


Figure 7.6: Rheograms of various stabilizers-containing EPDM gumstocks at 3 phr concentration at 180°C; symbols as in Fig. 7.5.

Generally, the scorch time (t_{S2}), as obtained from RPA is also a very important parameter for the study of the stabilizers. Figure 7.7 shows the relative ranking of the values of the scorch time of the EPDM gumstocks containing the various stabilizers at 1 phr concentration; the same at 3 phr concentration is depicted in Figure 7.8. It is noticed that the addition of all the stabilizers causes an increase in the t_{S2} values, prolonging the scorch time of the vulcanization process. It is also seen that QDI gives higher scorch times, indicating the strongest interactions with the peroxide-radicals before the onset of peroxide-vulcanization.

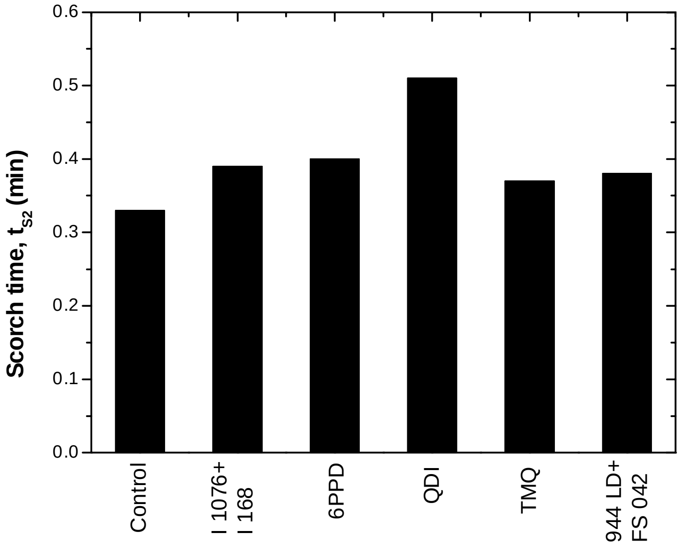


Figure 7.7: Scorch times of EPDM gumstocks with various stabilizers at 1 phr concentration at 180°C.

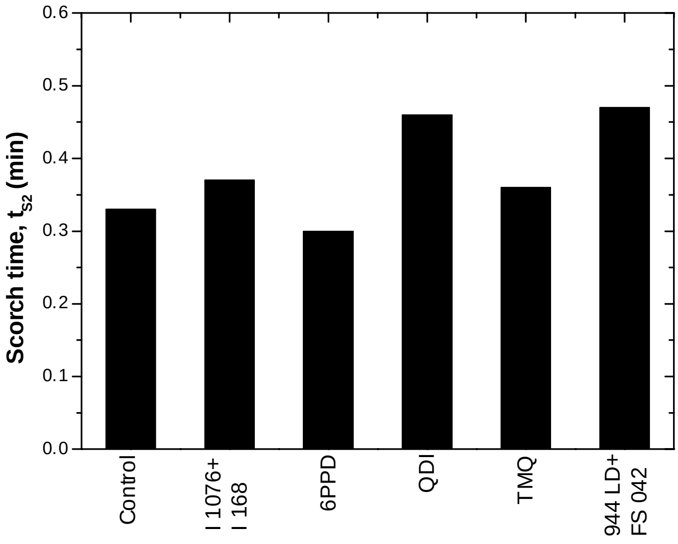


Figure 7.8: Scorch times of EPDM gumstocks with various stabilizers at 3 phr concentration at 180°C.

Furthermore, it is also observed from Table 7.4 that the greater the retardation of cure, scorch time, the larger is the dampening of the final cure state: delta torque value. This means that during the peroxide vulcanization process, QDI interacts more with the peroxide-radicals, thereby lowering the torque value, as observed in Figures 7.5 and 7.6.

From the results before aging, it turns out that 6PPD and QDI are no suitable stabilizers for DCP-cured PP/EPDM TPVs, because they show a strong deactivation of the peroxides relative to the other packages investigated. The latter only shows a minor interaction relative to the control without stabilizer added.

7.3.2 Influence of stabilizers on aging

Influence of different types of stabilizers at varied concentrations and at fixed PP/EPDM blend ratio: without the addition of a stabilizer the aging performance of the PP/EPDM TPVs is poor: recipe A1; when a stabilizer is incorporated in the recipe, aging behavior becomes better depending on the nature of the stabilizer and its concentration: recipes A2 – A16. The higher the concentrations of the stabilizers, in most cases, the smaller are the changes in the values of tensile strength, elongation at break and hardness of the PP/EPDM TPVs, before and after aging. From the values of the percent change of the properties it is noticed, that I 1076+I 168 (recipes A2, A7 and A12) and TMQ (recipes A5, A10 and A15) perform the best amongst the stabilizers used for this study. On the other hand, 6PPD performs the worst: recipes A3, A8 and A13. The good performance of TMQ concurs with many researches, that have already advocated the use of TMQ as having the least effect on peroxide cure and providing the best protection against oxidation.[8,12, 22, 23]

Influence of different types of stabilizers at varied PP/EPDM blend ratios: for most properties, TMQ and 944 LD+FS 042 perform the best amongst all the stabilizers used, irrespective of the content of PP in the PP/EPDM TPVs. The combination of I 1076 and I 168 performs nearly as good.

7.3.3 Discoloration

The TPVs prepared with TMQ, QDI and 6PPD as stabilizers are brownish in color; therefore, those stabilizers can only be used for the production of dark-colored TPVs. On the other hand, the TPVs using I 1076+I 168 and 944 LD+FS 042 combinations as stabilizers do provide a neutral influence on the color.

Therefore, in line of the basic objective to find out the most suitable stabilizer for peroxide-cured TPVs, it is found that I 1076+I 168 and 944 LD+FS 042 fulfil best all the important criteria required. Thus, the use of I 1076+I 168 as the stabilizer package in all the recipes as described in all the chapters is justified.

7.4 Conclusions

Before aging, the physical properties of dicumyl peroxide/triallyl cyanurate-cured TPVs significantly depend on the chemical nature and concentration of the stabilizers, as a result of interaction and consumption of peroxy-radicals by the stabilizer molecules. RPA-data on EPDM gumstock vulcanizates using various structurally different stabilizers support those results. By observing the percentage of retention of tensile strength and elongation at break and from hardness changes before and after aging, in most cases it was found that TMQ performs the best amongst all the stabilizers being investigated, irrespective of the concentrations of stabilizers and PP-content in the PP/EPDM blends. The combinations of I 1076+I 168 and 944 LD+FS 042 perform nearly as good. On the other hand, 6PPD and QDI were found to be the worst. However, the TPVs prepared with TMQ, QDI and 6PPD are often brownish in color, whereas I 1076+I 168 and 944 LD+FS 042 do not discolor the products. Therefore, use of the combination of I 1076+I 168 is justified as the most suitable stabilizer package for dicumyl peroxide-cured PP/EPDM TPVs, since it complies best with all the basic criteria required.

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List of symbols

α	coefficient of linear thermal expansion	$[K^{-1}]$
δ	solubility parameter	$[J/cm^3]^{1/2}$
ε_c	crosslinking efficiency	[-]
η	melt viscosity of the component	[Pa.s]
ρ	density of the solvent or polymer	$[g/cm^3]$
τ_s	spin-lock duration	[ms]
ν	crosslink density	[mole/ml]
ν+PP	overall crosslink density	[mole/ml]
φ	volume fraction of the component	[-]
χ	polymer-swelling agent interaction parameter	[-]
Δe_j	energy of vaporization contribution of group j	[J/mole]
ΔE_V	total energy of vaporization of the solvent	[J/mole]
ΔG_m	Gibbs free energy change of mixing	[J/mole]
ΔH_m	enthalpy change of mixing	[J/mole]
ΔS_m	entropy change of mixing	[J/mole.K]
k_d	rate constant for peroxide decomposition	$[s^{-1}]$
n_j	number of groups of type j in the molecule or polymer	[-]
$t_{1/2}$	half-life time	[min]
$t_{0,90}$	optimum cure time	[min]
t_{S2}	scorch time	[min]
A	Arrhenius frequency factor	$[s^{-1}]$
A_r	ratio of the volume of absorbed cyclohexane to that of EPDM after swelling	[-]
E'	storage modulus	[MPa]
E_a	activation energy for peroxide decomposition	[J/mole]
F_j	molar attraction constant for group j	[-]
H_v	molar heat of vaporization	[J/mole]
M	molecular weight	[-]
M_∞	magnetization when the spin system and the lattice reach a quasi-equilibrium during the spin-lock	[-]
M_0	initial magnetization	[-]
M_{300}	stress at 300 % strain	[MPa]
ML(1+4)	Mooney viscosity	[-]

R	gas constant	[J/mole.K]
T	temperature	[K]
$T_{1\rho}$	relaxation time in rotating frame	[ms]
$T_{1\rho}^{l}$	long relaxation time in rotating frame	[ms]
$T_{1\rho}^{s}$	short relaxation time in rotating frame	[ms]
T_g	glass transition temperature	[K]
T_m	melting temperature	[K]
V	molar volume	[cm^3/mole]
V_r	volume fraction of EPDM-rubber in the swollen network	[-]
V_s	molar volume of cyclohexane	[cm^3/mole]

List of abbreviations

α-MeS	alpha-methyl styrene
944 LD	poly{[6-[(1,1,3,3-tetramethylbutylamino-1,3,5-triazine-4-piperidinyl)-imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]}
6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
ABS	acrylonitrile-butadiene-styrene thermoplastic polymer
ACM	acrylate rubber
AES	Advanced Elastomer Systems
AFM	atomic force microscopy
ASTM	American society for testing and materials
ATR-IR	attenuated transmission reflection infra-red spectroscopy
BR	polybutadiene rubber
CED	cohesive energy density
CFSTR	continuous flow stirred tank reactor
CM	chlorinated polyethylene rubber
CP-MAS	cross polarization-magic angle spinning
CR	polychloroprene rubber
CSA	chemical shift anisotropy
DCM	dichloromethane
DCP	dicumyl peroxide
DD	dipolar decoupling
DRS	dielectric relaxation spectroscopy
DSC-TAM	differential scanning calorimetry-thermal activity monitoring
DSM	Dutch State Mines
DTBP	di-tert-butyl peroxide
DTBPH	2,5-dimethyl-2,5-di(tert-butylperoxy)hexane
DTBPHY	2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3
DTBPIB	di(tert-butylperoxyisopropyl)benzene
DTBT	2,4-diallyloxy-6-tert-butylperoxy-1,3,5-triazine
DV	dynamic vulcanizate
DVB	divinyl benzene
EASC	ethylaluminum sesquichloride
ENB	2-ethylidene-norbornene
ENBH	2-ethylidene-norbornane
EPDM	ethylene propylene diene rubber
EPM	ethylene propylene rubber
EPR	electron paramagnetic resonance
ESR	electron spin resonance
EVA	ethylene vinyl acetate rubber

FS 042	bis(hydrogenated tallow alkyl)amines
FTIR	Fourier transform infra-red spectroscopy
GC-FID-MS	gas chromatography-flame ionization detection-mass spectroscopy
GC-MS	gas chromatography-mass spectroscopy
GPC	gel permeation chromatography
HALS	hindered amine light stabilizer
HPLC	high performance liquid chromatography
HP-SEC	high pressure-size exclusion chromatography
I 1076	octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate
I 168	tris(2,4-di-tert-butylphenyl) phosphite
IIR	butyl rubber
iPP	isotactic polypropylene
ISO	international organization for standardization
L/D	length to diameter ratio
MBTS	dibenzothiazole disulfide
MFI	melt flow index
MNB	methylene-norbornene
NBR	acrylonitrile-butadiene rubber
NMR	nuclear magnetic resonance
NR	natural rubber
PA	polyamide thermoplastic polymer
PBT	polybutylene terephthalate thermoplastic polymer
PC	polycarbonate thermoplastic polymer
PE	polyethylene
phr	parts per hundred rubber
PMMA	polymethyl methacrylate thermoplastic polymer
PP	polypropylene
ppm	parts per million
PS	polystyrene
QDI	N-{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine} benzenamine
RI	refractive index
RPA	rubber process analyzer
rpm	revolutions per minute
SADT	self accelerating decomposition temperature
SAN	styrene-acrylonitrile thermoplastic polymer
SAXS	small angle X-ray scattering
SBR	styrene-butadiene-rubber
S-B-S	styrene-butadiene-styrene block copolymer
S-EB-S	styrene-ethylene butylene-styrene block copolymer
SEM	scanning electron microscopy
SiO_2	silica
STEM	scanning transmission electron microscopy
TAC	triallyl cyanurate

TAIC	triallyl isocyanurate
TAP	triallyl phosphate
TBCP	tert-butyl cumyl peroxide
TBIB	1-(2-tert-butylperoxyisopropyl)-3-isopropenyl benzene
TEM	transmission electron microscopy
TEO	thermoplastic elastomeric olefin
THF	tetrahydrofuran
TMQ	polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
TMTD	tetramethyl thiuram disulfide
TPA	thermoplastic polyamide
TPE	thermoplastic elastomer
TPU	thermoplastic polyurethane
TPV	thermoplastic vulcanizate
TTTP	3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane
UV	ultra-violet
VNB	vinylidene-norbornene
$VOCl_3$	vanadium oxitrichloride
WAXS	wide angle X-ray scattering
ZnO	zinc oxide

Summary

A thermoplastic elastomer (TPE) is a rubbery material with properties and functional performance similar to those of a conventional vulcanized rubber; still it can be processed in a molten state as a thermoplastic polymer. The unique characteristics of TPEs make them very useful and attractive alternatives for conventional elastomers in a variety of markets, such as automotives, buildings and constructions, wires and cables etc. Thermoplastic vulcanizates (TPVs) or dynamic vulcanizates are a special class of TPEs, produced by simultaneous mixing and crosslinking of a rubber with a thermoplastic. TPVs are prepared by melt-mixing techniques, either by batch processes (typically in internal batch mixers) or by continuous processes (typically in co-rotating twin-screw extruders). TPVs comprise the fastest growing thermoplastic elastomer market. They are generally characterized by finely dispersed micron-size crosslinked rubber-particles, distributed in the thermoplastic matrix. If the rubber-particles of such a blend are small enough and if they are sufficiently vulcanized, then the final rubber-like properties of the blend are generally very good.

TPVs based on polypropylene/ethylene propylene diene rubber (PP/EPDM) blends are the most important from a commercial point of view. Several crosslinking agents are employed to crosslink the EPDM-phase in the PP/EPDM blends. The crosslinking systems most commonly used for the production of PP/EPDM TPVs are activated phenol-formaldehyde resins, usually known as resol-resins. There are two major problems associated with this crosslinking system: (a) hygroscopicity of the TPVs produced with this resin; the tendency to absorb moisture even at ambient temperature and (b) appearance of a dark brown color. These disadvantages of the resol-resins create a demand for other alternatives. Crosslinking of TPVs with peroxides is a potential option.

However, when peroxide is added to a PP/EPDM blend, two competing processes take place simultaneously: EPDM crosslinking and PP degradation by β-scission. Therefore, there is a need for a proper peroxide in combination with a suitable co-agent to diminish the extent of PP degradation and improve the degree of EPDM crosslinking. The objective of the research described in this thesis was to investigate the effects of different types of peroxides on the properties of PP/EPDM TPVs at fixed as well as at varied PP/EPDM blend ratios in order to widen the possible use of peroxides for the production of TPVs. The potential of recently developed multifunctional peroxides as alternatives for conventional peroxide/co-agent combinations was also explored. Solid state NMR experiments were performed to search for the formation of in-situ graft-links of PP with EPDM during the process of dynamic vulcanization. Effects of pre-made compatibilizers to influence the morphology and final properties were also investigated. The behavior of various kinds of thermal and processing stabilizers in peroxide-cured TPVs were studied by aging experiments.

A general introduction is given in Chapter 1. The classification of polymer blends in general and that of TPEs in particular, the development of TPVs and the use of various types of crosslinking systems, with special emphasis on peroxides and co-agents as crosslinking agents for PP/EPDM blends, are reviewed in Chapter 2. The morphology and rheology of TPVs and their typical end-use applications are also touched upon.

The effects of different types of peroxides as crosslinking agents in combination with triallyl cyanurate (TAC) as a co-agent on the properties of PP/EPDM TPVs at a fixed as well as at varied blend ratios are described in Chapter 3. The physical properties of TPVs change significantly with the chemical nature of the peroxides, the extent of crosslinking of EPDM-phase and the extent of degradation of the PP-phase. Three main parameters are identified governing the final mechanical properties of the TPVs: the solubility parameter of a peroxide relative to the polymers, PP and EPDM; the decomposition mechanism of the peroxide and the kinetic aspects of the peroxide fragmentation. The tensile strength and compression set of the TPVs with the various peroxides can be correlated with the solubility parameters of the various components: the closer the solubility parameter of the peroxide to that of the EPDM, the higher is the tensile strength and the better is the compression set property. The Young's modulus of peroxide-cured TPVs only shows a slight correlation with the delta torque values of RPA measurements on 'equivalent' pure EPDM vulcanizates. The latter correspond to the crosslinking efficiencies of the peroxides. Dicumyl peroxide (DCP) in combination with TAC gives the best overall balance of all properties, since it complies the best of all with the parameters described above.

Commonly used peroxides like DCP generally produce volatile decomposition products, which provide an unpleasant smell or can show a blooming effect. In Chapter 4, recently developed multifunctional peroxides are described, which reduce the above-mentioned problems. They consist of a peroxide and co-agent functionality combined in a single molecule. The multifunctional peroxides provide performance properties of TPVs, which are comparable with commonly employed co-agent assisted peroxides. Particularly, 2,4-diallyloxy-6-tert-butylperoxy-1,3,5-triazine (DTBT) turns out to be a good alternative for the DCP/TAC combination. DTBT has a solubility parameter on the high side of the spectrum, which directs this peroxide/co-agent combination preferably to the EPDM-phase during mixing. The co-agent functionality of this compound helps to improve the crosslinking effect, so as to be comparable with DCP. DTBT further shows a decomposition temperature related to a $t_{½}$ = 1 hr, close to DCP, which results in a similar vulcanization rate. Moreover, the multifunctional peroxides investigated do provide by-products after their decomposition, but without unpleasant smell, unlike DCP.

The characterization of peroxide-cured PP/EPDM TPVs using common spectroscopic techniques is difficult, because these techniques are most suited for analysis of solutions. The vulcanized EPDM-fraction cannot be dissolved in any solvent and the PP-phase does not dissolve in common organic solvents at room temperature. In order to obtain more insight into the chemistry and reactivity involved between the multifunctional peroxides and EPDM rubber, several characterization techniques were employed in Chapter 5. FTIR, GC-(FID+MS) and HP-SEC were used to characterize the multifunctional peroxides, before and after the dynamic curing of the EPDM-phase. The experiments described in this chapter give strong indications, that the decomposition products, as obtained from the multifunctional peroxides, are grafted to the EPDM-phase. The latter reduces the volatility of the peroxides and consequently providing no significant smelly by-products. It is also demonstrated that the co-agent functionalities present in those peroxides play a role in the grafting reactions.

There is a possibility of formation of in-situ graft-link structures of PP with EPDM at the interface during the process of dynamic vulcanization in co-agent assisted peroxide-cured PP/EPDM blends. These in-situ formed graft-links can act as a compatibilizer in such a system, which in turn can improve mechanical properties. It is very difficult to prove the generation of those graft-links by conventional characterization techniques like FTIR, DSC or DMTA. An attempt was made in Chapter 6 to search for the existence of such graft-link structures by the high temperature solid state CP-MAS NMR technique, in terms of spectra and relaxation time, $T_{1\rho}(^{13}C)$. In addition, the effects of purposely adding various pre-made compatibilizers, e.g., PP-EPDM graft copolymer, trans polyoctenamer (TOR) and S-EB-S, on the morphology and final properties of TEOs and TPVs are also described in this chapter. PP-EPDM graft copolymer was found the best amongst three different kinds of pre-made compatibilizers investigated for unvulcanized PP/EPDM TEOs. The latter resembles most close to the structural similarities with those of PP and EPDM. However, once applied in dynamically vulcanized PP/EPDM TPVs all these pre-made compatibilizers failed.

Oxidation is generally considered the main degradation mechanism of saturated polymers. Stabilizers are used to prevent degradation and thereby, to effectively extend the useful lifetime of polymers. However, the use of stabilizers in combination with a peroxide cure system needs special care, because the main function of these materials is to deactivate the radicals formed after decomposition of the peroxide. This results in a reduced crosslinking efficiency of the peroxide and inactivation of the stabilizers being used. A stabilizer package, consisting of octadecyl-3,5-di-tert-butyl-4-hydroxy hydrocinnamate (Irganox 1076) and tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168) was used in all the recipes as described in all chapters of this thesis. The main objective of Chapter 7 was therefore to show the influences of various stabilizer packages on DCP/TAC-cured TPVs, in order to find the most suitable system. Before aging, the physical properties of the TPVs significantly depend on the chemical nature and concentration of the stabilizers, as a result of interaction and consumption of peroxi-radicals by the stabilizer molecules. RPA-data on EPDM gumstock vulcanizates using various structurally different stabilizers support those results. By observing the percentage of retention of tensile strength and elongation at break and from hardness changes, before and after aging, in most cases it was found that polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) performs the best amongst all the stabilizers investigated, irrespective of the concentrations of stabilizers and PP-content in the PP/EPDM blends. The combination of Irganox 1076 and Irgafos 168 performs nearly as effective. On the other hand, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) was found to be the worst. However, the TPVs prepared with TMQ, N-{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine} benzeneamine (QDI) and 6PPD are often brownish in color. Irganox 1076 + Irgafos 168 and poly{[6-[(1,1,3,3-tetramethylbutylamino}-1,3,5-triazine-4-piperidinyl)-imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]} (Chimassorb 944 LD) + oxidized bis(hydrogenated tallow alkyl)amines (Irgastab FS 042) combinations do not discolor the products and are approximately equally effective stabilizer packages. Therefore, use of the combination of Irganox 1076 + Irgafos 168 is justified as the most suitable stabilizer package for dicumyl peroxide-cured PP/EPDM TPVs. The latter complies the best with all the basic criteria required of a good stabilizer: little interaction with the peroxide cure, good stabilization against aging and no discoloration of the final TPV.

Samenvatting

Een thermoplastisch elastomeer (TPE) is een rubberachtig materiaal met eigenschappen en functionele mogelijkheden, die overeenkomen met die van een conventioneel gevulkaniseerd rubber. Een TPE kan echter, net als een thermoplastisch polymeer, nog wel verwerkt worden in gesmolten toestand. De unieke eigenschappen zorgen ervoor dat TPEs erg nuttige en aantrekkelijke alternatieven zijn voor conventionele elastomeren op verscheidene gebieden, zoals de automobielindustrie, bouwmaterialen, draden en kabels, etc. Thermoplastische vulkanisaten (TPVs) of dynamische vulkanisaten (DVs) vormen een specifieke groep binnen de TPEs. Ze worden geproduceerd door gelijktijdige menging en crosslinking van een rubber met een thermoplast. TPVs worden gemaakt door middel van ‘melt-mixing’ technieken, ofwel door batch processen (typisch in interne mengers) of door continue processen (typisch in co-roterende dubbelschroefsextruders). TPVs omvatten de snelst groeiende thermoplastische elastomerenmarkt. Ze worden in het algemeen gekarakteriseerd door fijn verdeelde, gecrosslinkte rubberdeeltjes in de orde van micrometers, in een thermoplastische matrix. Als de rubberdeeltjes van zo’n mengsel klein genoeg zijn, dan zijn de uiteindelijke rubberachtige eigenschappen van het mengsel in het algemeen erg goed.

Op polypropyleen/etheen-propeen-diëen rubber (PP/EPDM) mengsels gebaseerde TPVs, vormen commerciëel gezien de belangrijkste groep. Verscheidene crosslinking agents zijn ontwikkeld om de EPDM-fase in het PP/EPDM mengsel te crosslinken. De crosslink systemen, die het meest worden gebruikt voor de productie van PP/EPDM mengsel, zijn geactiveerde fenol-formaldehyde harsen, in het algemeen bekend als resol-harsen. Er zijn echter twee grote problemen, die deze crosslink systemen met zich meebrengen: (a) hygroscopiciteit van de TPVs geproduceerd met deze hars; de neiging om vocht te adsorberen, zelfs bij omgevingstemperatuur; en (b) vorming van een donker bruine verkleuring. Deze nadelen van de resol-harsen creëren de vraag naar alternatieven. Crosslinken van TPVs met peroxiden is een potentiële mogelijkheid.

Wanneer peroxide wordt toegevoegd aan een PP/EPDM mengsel vinden er echter twee processen tegelijkertijd plaats: EPDM-crosslinking en PP-degradatie door β-splitsing van de polymeer keten. Het is daarom noodzakelijk een geschikte peroxide in combinatie met een geschikte co-agent te vinden om de PP-degradatie te minimaliseren en de EPDM crosslinking te optimaliseren. Het doel van het onderzoek beschreven in dit proefschrift was te onderzoeken wat de effecten zijn van verschillende types peroxiden op de eigenschappen van PP/EPDM mengsels. Dit is onderzocht bij zowel constante, alswel bij variabele PP/EPDM mengverhoudingen. Het potentieel van recentelijk ontwikkelde multifunctionele peroxiden als alternatieven voor de conventionele peroxide/co-agent combinaties is ook onderzocht. Vaste stof NMR-experimenten zijn uitgevoerd om te zoeken naar de vorming van in-situ graft-links van PP met EPDM gedurende het dynamische vulkanisatieproces. Effecten van vooraf gemaakte compatibilizers op de morfologie en uiteindelijke produkt-eigenschappen is ook onderzocht. Het gedrag van verschillende soorten thermische- en verwerkings-stabilisatoren in met peroxide gevulkaniseerde TPVs is bestudeerd aan de hand van verouderingsexperimenten.

In Hoofdstuk 1 wordt een algemene inleiding gegeven. De klassifikatie van polymeermengsels in het algemeen en die van TPEs in het bijzonder, wordt behandeld in Hoofdstuk 2. Tevens wordt in dit hoofdstuk de ontwikkeling van TPVs en het gebruik van verschillende types crosslink-systemen beschreven, met speciale nadruk op peroxide en co-agents als crosslinking agents voor PP/EPDM mengsels. De morfologie en rheologie van TPVs en hun uiteindelijke toepassingen worden ook aangestipt.

De effecten van verschillende types peroxiden als crosslinking agents in combinatie met triallyl cyanuraat (TAC) als co-agent op de eigenschappen van PP/EPDM TPVs, bij constante alswel bij variable mengverhoudingen, worden beschreven in Hoofdstuk 3. De fysische eigenschappen van TPVs veranderen significant met de chemische aard van de peroxiden, de mate van crosslinking van de EPDM-fase en de mate van degradatie van de PP-fase. De drie belangrijkste parameters, die de mechanische eigenschappen van de TPVs bepalen, zijn geïdentificeerd als: de oplosbaarheidsparameter van het peroxide relatief ten opzichte van die van de polymeren PP en EPDM; het ontledingsmechanisme van de peroxide en de kinetische aspecten van de peroxide fragmentatie. De treksterkte en compressie set van de TPVs met verschillende peroxiden kan gecorreleerd worden met de oplosbaarheidsparameters van de verschillende componenten: hoe dichter de oplosbaarheidsparameter van de peroxide bij die van EPDM ligt, hoe hoger de treksterkte is en hoe beter de compressie set eigenschap. De Young’s modulus van de met peroxide gevulkaniseerde TPVs toont maar een lichte correlatie met de delta-torque waarden ontleend aan RPA-metingen aan “equivalente” pure EPDM vulkanisaten. Dit komt overeen met de crosslink- efficiënties van de peroxiden. Dicumylperoxide (DCP) in combinatie met TAC geeft de beste overall balans van eigenschappen, omdat het het beste voldoet aan de bovengenoemde parameters.

Veel gebruikte peroxiden, zoals DCP, produceren in het algemeen vluchtige ontledings-producten, welke een onaangename geur of een ‘blooming effect’ veroorzaken. In Hoofdstuk 4 worden recent ontwikkelde multifunctionele peroxiden beschreven, die de bovengenoemde problemen kunnen verminderen. Zij bestaan uit een peroxide en een co-agent functionaliteit gecombineerd in één enkel molekuul. De multifunctionele peroxiden bezorgen de TPVs eigenschappen, welke vergelijkbaar zijn met die van TPVs geproduceerd met de veelgebruikte co-agent geassisteerde peroxiden. In het bijzonder, 2,4-diallyloxy-6-tert-butylperoxy-1,3,5-triazine (DTBT) blijkt een goed alternatief te zijn voor de DCP/TAC combinatie. DTBT heeft een oplosbaarheidsparameter aan de hoge kant van het spectrum, wat ervoor zorgt dat deze peroxide/co-agent combinatie de EPDM-fase prefereert tijdens het mengen. De co-agent functionaliteit van deze verbinding helpt het crosslinkingseffect te verbeteren, zodanig dat het vergelijkbaar is met dat van DCP. DTBT heeft verder een ontledingstemperatuur, gerelateerd aan een $t_{½}$ = 1 uur, bijna gelijk aan DCP, wat resulteert in een vergelijkbare vulkanisatiesnelheid. Bovendien resulteren de onderzochte multifunctionele peroxiden in geurloze bijproducten na ontleding, in tegenstelling tot DCP.

De karakterisatie van met peroxide gevulkaniseerde PP/EPDM TPVs door middel van veel gebruikte spectroscopische technieken is moeilijk, omdat deze technieken vooral geschikt zijn voor de analyse van oplossingen. De gevulkaniseerde

EPDM-fase kan – per definitie – niet worden opgelost in enig oplosmiddel en de PP-fase lost bij kamertemperatuur niet op in gebruikelijke organische oplosmiddelen. Om meer inzicht te krijgen in de chemie en reactiviteit tussen de multifunctionele peroxiden en EPDM-rubber zijn er in Hoofdstuk 5 verscheidene karakterisatiemethoden gebruikt. FTIR, GC-(FID+MS) en HP-SEC zijn gebruikt om de multifunctionele peroxiden te karakteriseren, voor en na dynamische vulkanisatie van de EPDM-fase. De experimenten beschreven in dit hoofdstuk geven sterke aanwijzingen dat de ontledings-producten, die ontstaan uit de multifunctionele peroxiden, aan de EPDM-fase geënt worden. Dit vermindert de vluchtigheid van de peroxiden en voorkomt daardoor onaangenaam ruikende bijproducten. Ook wordt aangetoond, dat de in deze peroxide aanwezige co-agent functionaliteiten een rol spelen in de entings reacties.

Er bestaat een mogelijkheid, dat er aan het kontakt-vlak tussen PP en EPDM in-situ graft-link structuren gevormd worden, gedurende het proces van dynamische vulkanisatie in co-agent geassisteerde, met peroxide gevulkaniseerde PP/EPDM mengsels. Deze in-situ gevormde graft-links kunnen in zulke systemen optreden als compatibilizers, welke weer de mechanische eigenschappen kunnen verbeteren. Het is wederom erg moeilijk de vorming van deze graft-links te bewijzen met de conventionele karakteriseringsmethoden, zoals FTIR of DSC. In Hoofdstuk 6 is een poging gedaan om het bestaan van zulke graft-link structuren te bewijzen met de hoge temperatuur vaste stof CP-MAS NMR techniek, aan de hand van spectra en relaxatietijd, $T_{1\rho}$ (^{13}C). Bovendien worden in dit hoofdstuk de effecten van verscheidene, met opzet toegevoegde, vooraf gemaakte compatibilizers op de morfologie en uiteindelijke eigenschappen van Thermoplastische Elastomere Polyolefinen (TEOs) en TPVs beschreven: bijvoorbeeld van PP-EPDM graft copolymeren, trans polyoctenameer (TOR) en Styreen-Etheen-Buteen blok-copolymeren (S-EB-S). Het blijkt, dat PP-EPDM graft copolymeer de beste is van de drie onderzochte, vooraf gemaakte compatibilizers voor ongevulkaniseerde PP/EPDM TEOs. Deze vertoont de beste structurele overeenkomst met PP en EPDM. Al de vooraf gemaakte compatibilizers falen echter als ze worden toegepast in dynamisch gevulkaniseerde PP/EPDM TPVs.

Oxidatie wordt in het algemeen beschouwd als het belangrijkste degradatiemechanisme voor onverzadigde polymeren. Stabilisatoren worden gebruikt om degradatie te voorkomen en daarbij, om de effectieve bruikbare levensduur te verlengen. Echter, het gebruik van stabilisatoren in combinatie met een peroxide vulkanisatiesysteem vereist speciale aandacht, omdat de belangrijkste functie van deze materialen het deactiveren van de radicalen na ontleding van de peroxide is. Dit resulteert in een verminderde crosslink efficiëntie van de peroxide en deactivering van de gebruikte stabilisatoren. Een stabilisatiepakket, bestaande uit octadecyl-3,5-di-tert-butyl-4-hydroxy hydrocinnamaat (Irganox 1076) en tris(2,4-di-tert-butylfenyl) fosfiet (Irgafos 168) is gebruikt in alle recepten, zoals beschreven in alle hoofdstukken van dit proefschrift. Het belangrijkste doel van Hoofdstuk 7 was de invloed van verschillende stabilisatorpakketten op met DCP/TAC gevulkaniseerde TPVs aan te tonen, om zodoende het meest geschikte systeem te vinden. Voor veroudering hangen de fysische eigenschappen van de TPV significant af van de chemische aard en concentratie van de stabilisatoren, als gevolg van de interactie en consumptie van peroxy-radicalen door stabilisatormoleculen. Dit wordt onderbouwd met RPA-gegevens van EPDM gumstock vulkanisaten, met structureel verschillende stabilisatoren daaraan toegevoegd. Door vaststelling van het percentage behoud van de treksterkte en rek bij breuk, en van de veranderingen in hardheid, blijkt dat in de meeste gevallen gepolymeriseerd 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) het beste presteert van alle onderzochte stabilisatoren, ongeacht de concentraties van de stabilisatoren en het PP-gehalte in de PP/EPDM mengsels. N-(1,3-dimethylbutyl)-N'-fenyl-p-fenyleendiamine (6PPD) blijkt de slechtste te zijn. Echter, de TPVs bereid met TMQ, N-{[(1,3-dimethylbutyl)imino]-2,5-cyclohexadieen-1-ylideen} benzeenamine (QDI) en 6PPD zijn vaak bruin gekleurd. Irganox 1076 + Irgafos 168 en poly{[6-[(1,1,3,3,-tetreamethylbutylamino]-1,3,5-triazine-4-piperidinyl)-imino-1,6-hexaandiyl[(2,2,6,6-tetramethyl-4-piperidinyl)-imino]} (Chimassorb 944 LD) + geoxideerd bis(gehydrogeneerde talk alkyl) amines (Irgastab FS 042) combinaties verkleuren de producten niet en zijn ongeveer net zulke effectieve stabilisatorpakketten. Daardoor is het gebruik van de combinatie Irganox 1076 + Irgafos 168 gerechtvaardigd als het meest geschikte stabilisatorpakket voor met dicumylperoxide gevulkaniseerde PP/EPDM TPVs. Laatstgenoemde combinatie beantwoordt het beste aan alle basis criteria, die nodig zijn voor een goede stabilisator: weinig interactie met de peroxide vulkanisatie, goede stabilisatie tegen veroudering en geen verkleuring van de uiteindelijke TPV.

CURRICULUM VITAE

Kinsuk Naskar was born in Calcutta, India on 23rd of October 1973. In 1995, he completed his Bachelor of Science (B.Sc.) in Chemistry from the University of Calcutta. He received Bachelor of Technology (B.Tech.) degree in Polymer Science and Technology in 1998, also from the same university. During his bachelor study, he was involved in a short-term project on “the optimization of UV-CON resistance for automotive paints”. In 2000, he completed his Master in Rubber Technology from Indian Institute of Technology, Kharagpur, India. During his Master study, he also worked in a project on “the development of thin-walled halogen-free cable insulation and halogen-free fire-resistant low-smoke cable sheath based on Engage-EVA blends”. In April 2000, he joined the University of Twente, The Netherlands as a Ph.D. employee under the supervision of Prof. Dr. Jacques W. M. Noordermeer in a project from Dutch Polymer Institute (DPI). The title of the project was “thermoplastic elastomers by dynamic crosslinking using radical curing agents”.

Acknowledgements

“There are two ways to live your life. One is as though nothing is a miracle. The other is as though everything is a miracle.”

Albert Einstein

Time flies…. It is hard to realize that four years have elapsed so fast. Now time has come to stroll down the memory lane to ruminate those eventful and significant four years of my life in The Netherlands. I feel like a free bird flying in the sky after finishing my research. Yes, indeed it was quite heavy. It is difficult to express my warm gratitude to all my friends, colleagues and well-wishers I came across during that time period, just by writing few words. However, I am trying my best to do so in the following, which makes me nostalgic and emotional.

First and foremost, it is a great pleasure for me to extend my deep sense of gratitude to Prof. Dr. J. W. M. Noordermeer for giving me the opportunity to carry out the research at the Rubber Technology Group in the University of Twente. Thank you very much for your sincere interest, valuable guidance and endless encouragement throughout the tenure of this project as being my promoter. I acknowledge the freedom and lively atmosphere I enjoyed while working with you. I also thank you for sharing your experience and knowledge of life.

I wish to express my humble regards to my assistant promoter, Dr. R. N. Datta for all your active advice, suggestions and constant support. Thank you very much for your hospitality when I was invited at your place few times.

I wish to acknowledge the Dutch Polymer Institute (DPI) for financially supporting this research project. I am grateful to all my DPI committee members, namely Dr. J. Jelenic (Akzo Nobel), Dr. M. van duin (DSM), Dr. X. Muyldermans (Kraton Polymers), Mr. A. Dozeman (DSM), Mr. B. van Baarle (TNO) and Mr. R. Sturme (Océ) for your useful suggestions and cooperation.

I am thankful to Dr. Mrs. S. Datta (Akzo Nobel), Prof. Dr. A. Kentgens and Mr. A. Klaassen (University of Nijmegen), Mr. W. Debets, Mr. G. van Doremaele, Mr. B. Wang and Mr. N. Friederichs (DSM) for all your help and kind cooperation regarding my research. Mark Smithers is also gratefully acknowledged for the help regarding electron microscopy.

My special thanks are also due to my Polish student, Dorota for your valuable contributions. We made a very good team!!

I am thankful to Gerda, Karin and Geneviève for all kinds of official help and for arranging important stuff. I wish to appreciate the help and cooperation I got from Zlata regarding lab-work.

I am really grateful to all my RBT-colleagues and friends namely Louis, Annemieke, Geert, Montse, Vipin, Dr. N. Naskar (my uncle), Subhas, Pratip, Francesca, Wilco W (amar naam Kinsuk!), Marek, Dries, Nico, Richard, Joost H, Wilma, Auke, Jan, Kuno and Alexej for all your assistances. I will certainly miss the friendly and lively multinational and multicultural environment in our group. I appreciate the great sense of humor of Dutch people. It was indeed great pleasure for me to participate in RBT-group activities like bowling, cricket, laser quest and of course the special dinners and movie-evenings. How can I forget our study trips to Maastricht and Barcelona (unfortunately I could not join the London trip)!! I also enjoyed the lunch at mensa almost everyday with occasional complaints about the foods. The word ‘half-life’ sounds quite intriguing to me; during working hours this means something related to peroxides but after work sometimes it means a big competition amongst all the rough and tough shooters like DON.

Annemieke, thank you for being so kind to arrange our memorable trips to the touristic attractions like Keukenhof, Floriade, Deltawerken etc. Rui and Hongmei, thanks for your hospitality preparing special delicious Chinese dishes.

I want to thank all the members from PBM, STEP and MTP, specially Priscilla, Christine, Bas, Menno, Laura, Boon Hua, Zhiyuan, Fenghua, Ype, Ingrid, Mark t B, Mark A, Piet, Debby, Wilco Z, Martijn v d S, Edwin, Nina, Beata, Douwe-Wiebe, Leon S, Monique, Attila, Ewa and Alex. We had lots of fun together during daily coffee breaks. For our stress relaxations we often shared hilarious jokes and humors, different complaints about different people and non-scientific but interesting discussions. I really enjoyed reading the gossip magazine ‘Duursport’ and relishing lekkere birthday cakes. Apart from these, the events and parties like wadlopen, triathlon, sinterklaas, oliebollen etc. are also unforgettable.

My friends and well-wishers, namely Pratip, Sankha, Saheli, Diptish, Richa, Kaushik, Rituparna M, Nikhil, Rituparna S, Raja, Sharmistha, Rabin, Sumana, Pupun, Pranab, Nelly, Natasha, Swapan, Anjana and Kanya are gratefully acknowledged for sharing wonderful time while chatting, travelling in many touristic places, having nice dinners and enjoying movies together.

Kuno, Francesca, Wilco W and Martijn v d S, thank you very much for your thorough scrutiny of different chapters of my thesis. Kuno, you deserve my special thanks for making the translation of the summary in Dutch (Prof. Noordermeer thought that my Dutch skill had improved tremendously all of a sudden!!). I will remember our discussions about the ‘compatibilizers’.

My sincere gratitude goes to Pratip and Francesca, my ‘paranimfen’ and TPV-gang members. Thank you very much for your warm friendship, kind cooperation and moral support all the time. Thanks to you also for all philosophical and scientific discussions, sharing funny jokes and humors etc. We did so many things together!! I will surely miss you two.

Last but not the least, I would like to thank each and every member of my family, who spurred my effort with their love and affection, inspiration and care even from India.

Kinsuk