Dynamically Vulcanized PP/EPDM Blends by Multifunctional Peroxides: Characterization with Various Analytical Techniques

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ABSTRACT: The characterization of peroxide-cured PP/EPDM TPVs using various spectroscopic techniques is difficult. These techniques are most suited for analysis of solutions, while the PP-phase does not dissolve in common organic solvents at room temperature. To obtain more insight into the chemistry and reactivity involved between the multifunctional peroxides and EPDM rubber, several characterization techniques were employed. In the present investigation, FTIR, GC-(FID + MS), HP-SEC, and element analysis were used to characterize 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 most likely grafted onto the EPDM-rubber, thereby reducing their volatility and avoiding the common unpleasant smell. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1393–1403, 2005

Key words: dynamic curing; FTIR; GC-(FID + MS); HP-SEC; multifunctional peroxides; PP-EPDM blends

INTRODUCTION

The emergence of thermoplastic elastomers (TPEs) in the 1950s[1] provided a new dimension 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 condition as a thermoplastic polymer at elevated temperature. The sort of TPEs based on polyolefin rubber/thermoplastic polymer 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); in the other class, the rubber phase is dynamically vulcanized, giving rise to a thermoplastic vulcanizate (TPV) or dynamic vulcanizate. Morphologically, TPVs are characterized by the presence of finely dispersed crosslinked rubber particles distributed in a continuous thermoplastic matrix. If the elastomer particles of such a blend are small enough and if they are sufficiently vulcanized, then the physical and chemical properties of the blend are generally improved.[2,3]

The dynamic vulcanization process was first claimed by Gessler[4] in 1962 and then further developed by Fisher,[5] Coran and colleagues,[6,7] and Sabet Abdou-Sabet and Fath.[8] TPVs based on polypropylene (PP) and EPDM-rubber blends are the most important representatives of this class of materials. Several crosslinking agents are employed to crosslink the EPDM phase in PP/EPDM blends. Each and every crosslinking system has its own merits and demerits. Crosslinking systems often used for that purpose are activated phenol-formaldehyde resins, commonly known as resols. However, there are two major problems associated with TPVs based on these resol resins[9]: (a) hygroscopicity, even at ambient temperature; the absorbed moisture must be removed through lengthy, high-temperature drying procedures before processing, to eliminate product defects; and (b) appearance of a very dark brownish color, which is difficult to mask and sometimes necessitates the use of two different pigment systems to achieve a given color. These disadvantages of the resols impose a demand for alternative crosslinking agents.

Crosslinking rubber with peroxides has been well known for more than 50 years. The general advantages of peroxides as crosslinking agents are: (1) their ability to crosslink unsaturated as well as saturated elastomers; (2) good high temperature resistance; (3)

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good elastic behavior (compression set), particularly at elevated temperature; (4) no moisture uptake; and (5) no staining or discoloration of the finished products.[10] A coagent is often used to improve crosslinking efficiency of the peroxide by a tighter network formation.[11] Our earlier work[12] has demonstrated that the application of a proper peroxide in combination with a suitable classical coagent provides a good overall balance of physical properties in 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. Also, blooming phenomena can take place due to the formation of dihydroxy isopropyl benzene from the decomposition of di(*tert*-butylperoxyisopropyl)benzene, due to its limited solubility in rubber.[13] Multifunctional peroxides have recently been developed to overcome the drawbacks of the commonly used peroxides, particularly unpleasantly smelling by-products. They consist of a peroxide and coagent-functionality combined in a single molecule. The multifunctional peroxides provide performance-properties of TPVs, which are comparable with commonly employed coagent assisted peroxides.[14,15] 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.

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.[16–21] 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 common organic solvents at room temperature. Therefore, 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 chain-scission reactions. In the present investigation, FTIR, GC-(FID + MS), HP-SEC, and element analysis have been employed to characterize the multifunctional peroxides TBIB and DTBT, before and after dynamic curing of the EPDM phase.

EXPERIMENTAL

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) @ 125°C of 52. The two types of multifunctional peroxides were synthesized at Akzo Nobel

TABLE I
Chemical Names and Structures of 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%)	

TABLE II
Pure EPDM Vulcanizate Compositions (PHR)

Component	A0	A1	A2	A3
EPDM#	200	200	200	200
Peroxide:				
TBIB	—	5.1 (15)*	—	—
DTBT	—	—	4.5 (15)	22.5 (75)
Co-agent:				
α-MeS	—	1.8 (15)	—	—

Includes 50 wt % paraffinic oil.
* Numbers between parentheses represent milli-equivalents of peroxides and co-agents per 100 parts of pure EPDM rubber.

Polymer Chemicals, The Netherlands. They combine peroxide and coagent functionality in a single molecule. The chemical names and structures of these multifunctional peroxides investigated are given in Table I. α-methyl styrene (α-MeS), 99%, was used as coagent to TBIB, to adjust the total coagent functionality to be comparable with the peroxide and coagent functionality of DTBT.

Preparation of the samples

Samples of EPDM (no peroxide), TBIB + α-MeS + EPDM, and DTBT + EPDM were prepared according to recipes A0–A3, as shown in Table II, by mixing at 30–40°C on a two-roll mill and at 180–190°C in a Brabender Plasticorder by dynamic curing. The latter was possible because of the fact that the EPDM itself contains a lot of oil for the material to remain sufficiently "plastic." 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.

Characterization of the multifunctional peroxides in the EPDM phase

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

A. Fourier transform infrared (FT-IR) is one of the most sensitive spectroscopic methods to identify molecules containing functional groups such as C=C, C=O, and so forth. With the horizontal ATR Golden Gate, diamond probe accessory, FT-IR 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 h at room temperature. Analyses of the clear DCM solutions were carried out using n-undecane as the internal standard. These solutions were subjected to
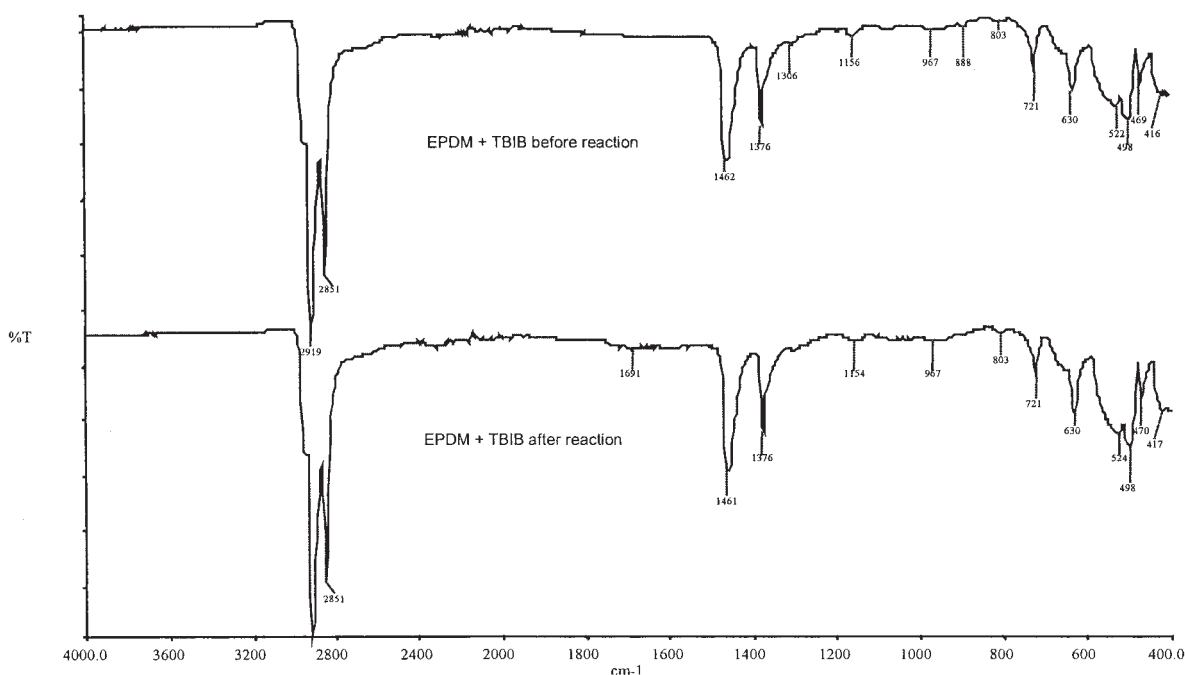

Figure 1 FT-IR ATR-spectra of TBIB + α-MeS + EPDM before and after dynamic curing reaction.

Figure 2 FT-IR ATR-spectra of TBIB + α-MeS + EPDM before and after dynamic curing reaction: expansion of the carbonyl region.

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, HP-SEC 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 h at room temperature. A large part of the samples (EPDM-peroxide blends after dynamic curing) did not dissolve in the solvent. The clear THF solution was analyzed. A Waters 2414 refractive index (RI) detector and HP Series 1050 ultra
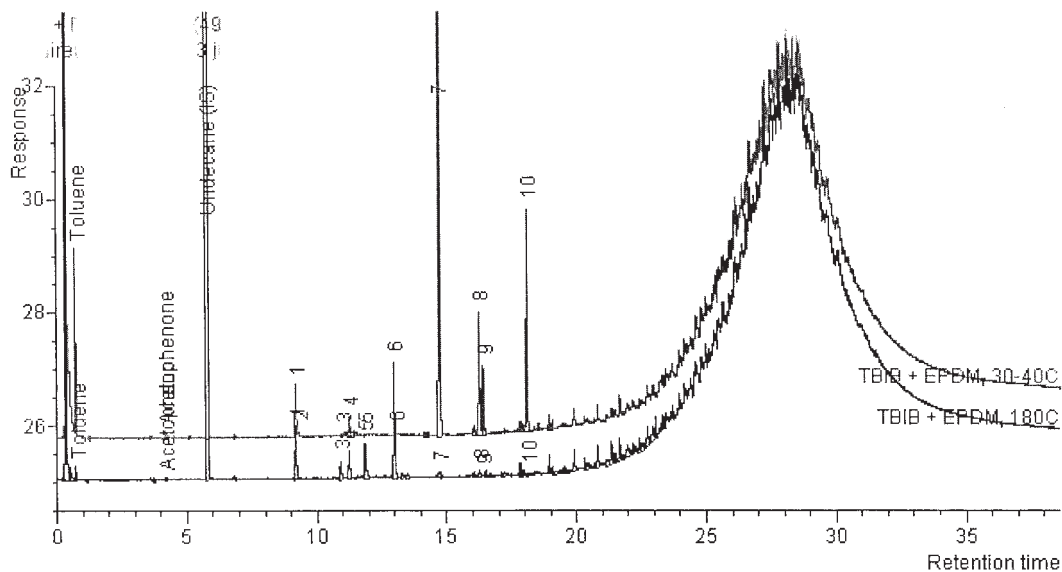
Figure 3 GC chromatograms of TBIB + α-MeS + EPDM before and after dynamic curing reaction.
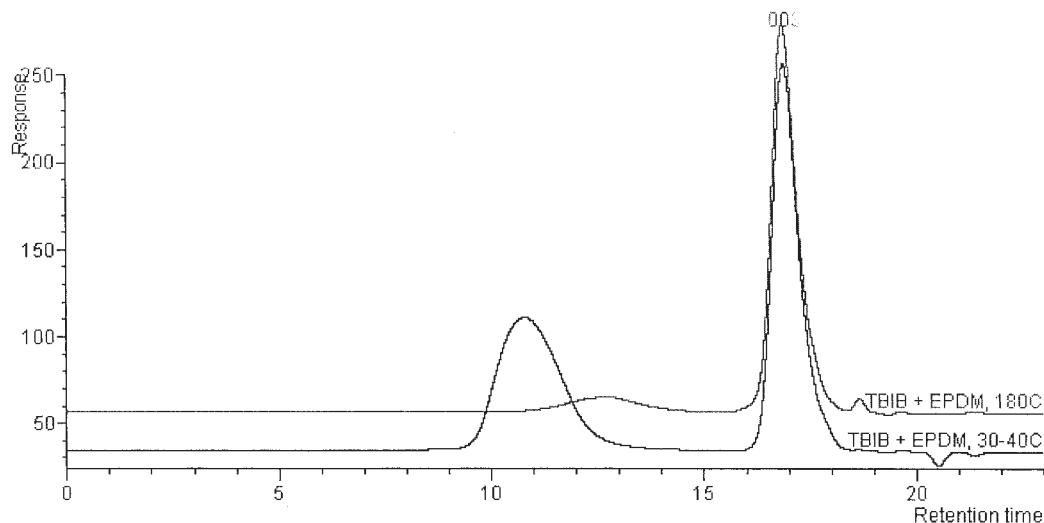
Figure 4 HP-SEC chromatograms of TBIB + α-MeS + EPDM before and after the curing reaction using RI detector.

violet (UV) detectors were used for detection purposes.

D. Element analysis was performed in an Element Analyzer 3201–1 A001, Hekatech. Approximately 1–2 mg of sample was taken in a tin cup at an oven temperature of 1000°C. However, due to an exothermic reaction in the tin cup, the temperature went up to 1800°C.

RESULTS AND DISCUSSION

Figure 1 shows the FT-IR ATR-spectra of TBIB + α-MeS + EPDM before and after the curing. Figure 2 shows the same after expansion of the carbonyl (C$=$O) region. A closer look at Figures 1 and 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 im-

plies that at high temperature, TBIB decomposes into an acetophenone moiety to some extent.

Figure 3 shows the GC chromatograms of TBIB + α-MeS + EPDM before and after the 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 cannot 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.

To check this hypothesis, HP-SEC was carried out. HP-SEC chromatograms, using a refractive index (RI) detector, are shown in Figure 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 at a retention time of approximately 9–13 min, the position of high molecular weight components, in
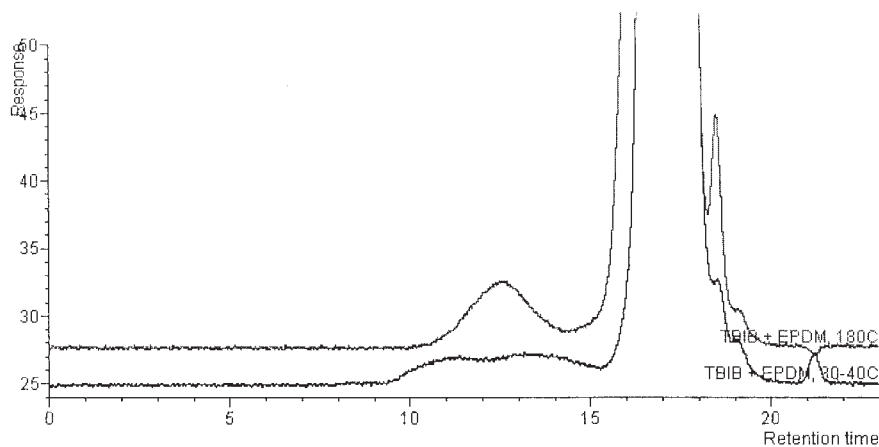

Figure 5 HP-SEC chromatograms of TBIB + α-MeS + EPDM before and after the curing reaction using UV detector.
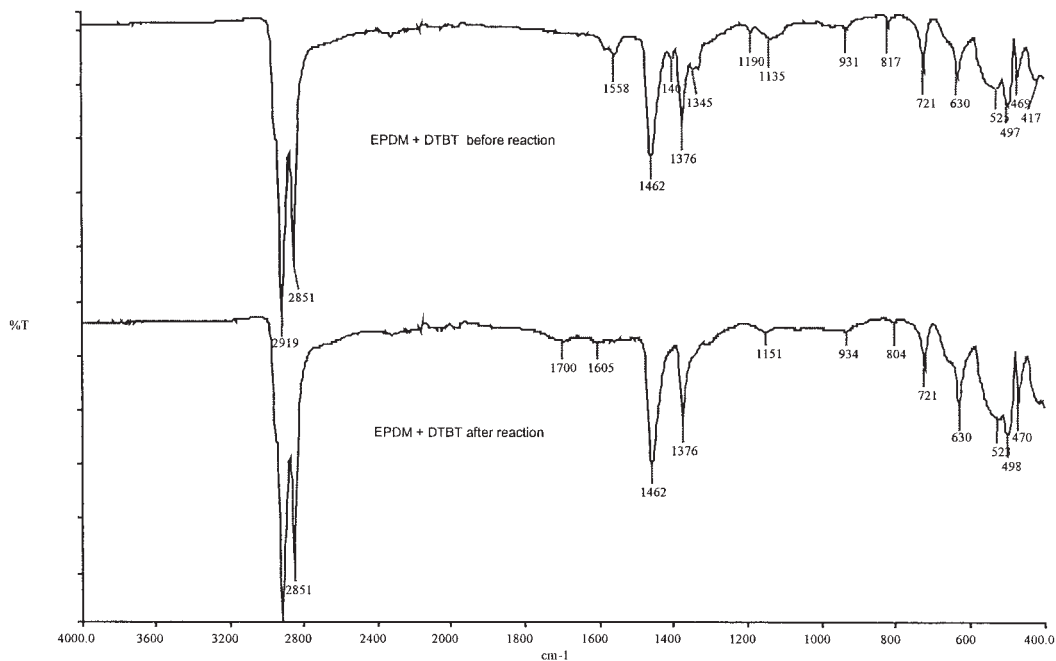
Figure 6 FT-IR spectra of DTBT + EPDM before and after the dynamic curing reaction.

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; there is an absence of a broad peak of EPDM in the chromatogram, and peroxide crosslinked EPDM does not dissolve in THF.

Only a very small amount of low molecular weight EPDM oligomer can still be noticed in the chromatogram.

HP-SEC analysis using a UV detector at a wavelength of 275 nm was done to see whether peroxide is actually grafted to the EPDM, as shown in Figure 5.
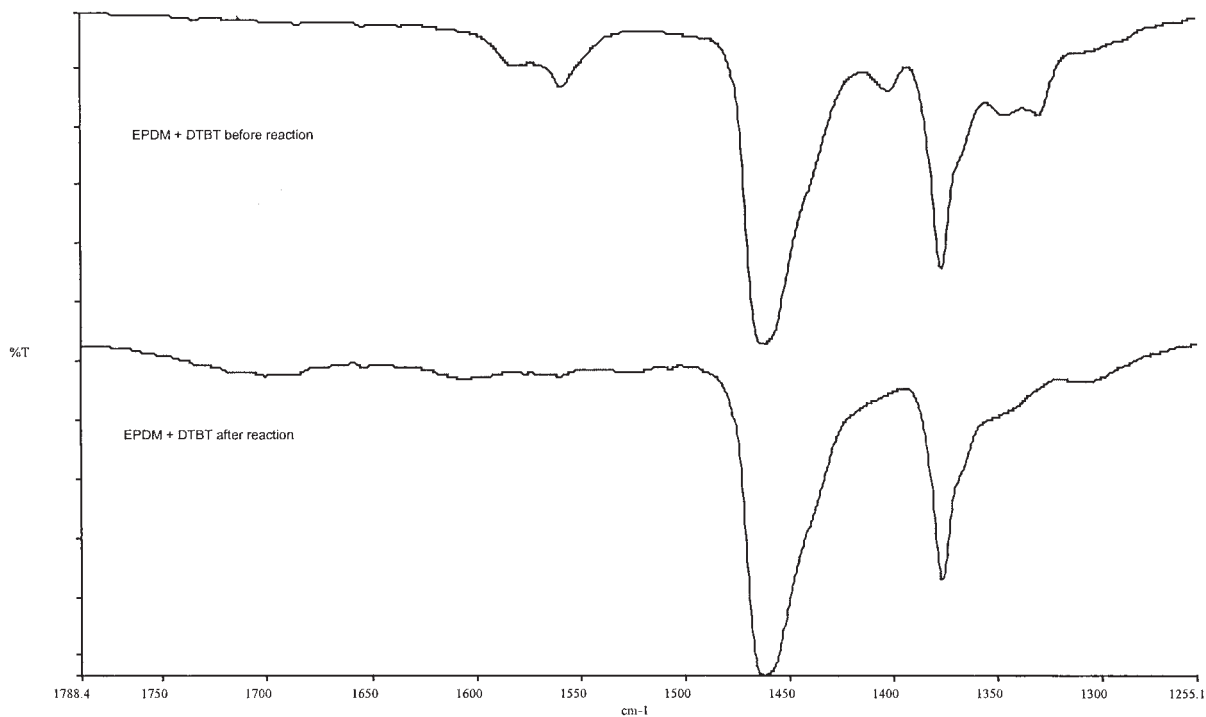

Figure 7 FT-IR spectra of DTBT + EPDM before and after dynamic curing: expansion of the region 1790–1250 cm^{-1}.
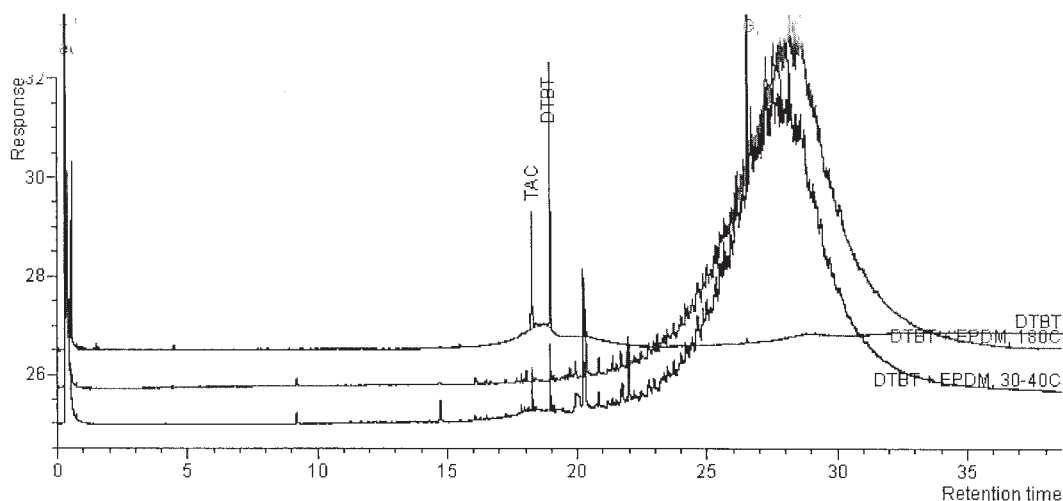
Figure 8 GC chromatograms of DTBT + EPDM before and after dynamic curing along with reference DTBT (Sil 5 CB column with fd: 0.4 μm).

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 cannot be analyzed. Only low molecular weight oligomers of EPDM can dissolve in THF. 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.

The same sets of experiments were also carried out using DTBT. The FT-IR spectra of DTBT + EPDM before and after curing are shown in Figure 6, and Figure 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 cannot be concluded whether the reaction products of the peroxide are grafted onto the EPDM polymer yet.

Figure 8 shows the GC chromatograms of DTBT + EPDM, before and after curing, along with the reference (pure DTBT). It can be seen that DTBT shows very little response in GC-FID and probably decomposes to a large extent during analysis. Analyses of
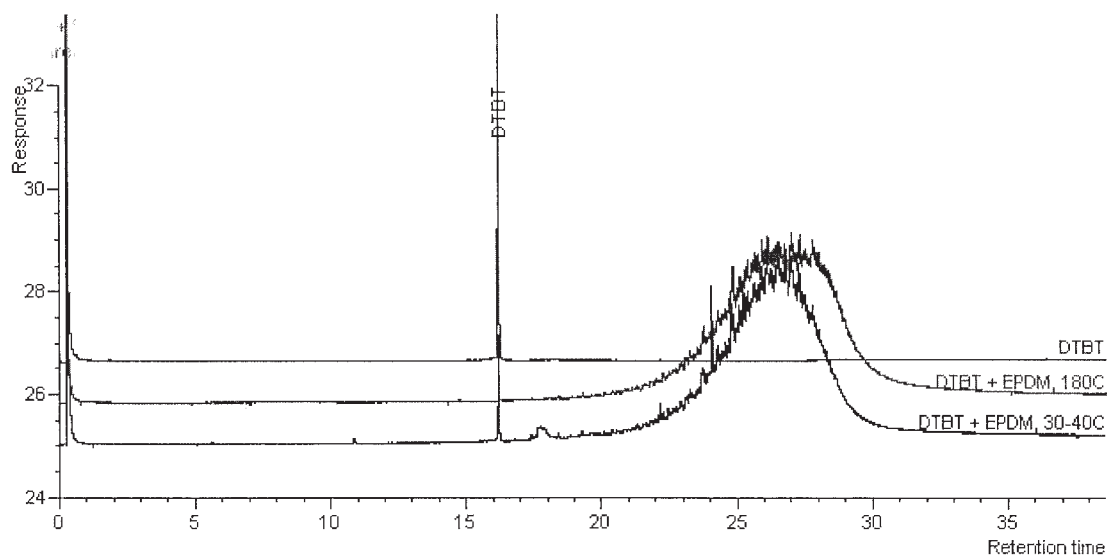

Figure 9 GC chromatograms of DTBT + EPDM before and after dynamic curing along with reference DTBT (Sil 5 CB column with fd: 0.1 μm).
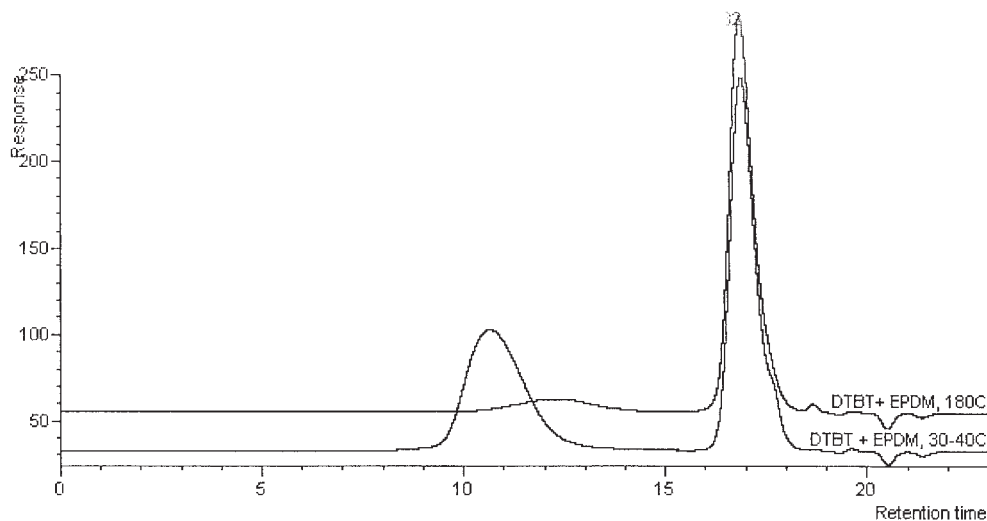
Figure 10 HP-SEC chromatograms of DTBT + EPDM before and after curing (RI detector).

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 9. Using this thin film column, DTBT appears as one peak, but the response is still very low (ref. 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.

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 an RI detector before and after curing are shown in Figure 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 a UV detector was attempted to see whether peroxide is actually grafted to EPDM. HP-SEC chromatograms using the UV detector are shown in Figure 11. The same phenomenon as already found before is again observed here. Most likely, the decomposition products of the DTBT are also grafted to the EPDM.

More experiments were performed on DTBT to get further insight into the chemistry involved. The samples containing 15 milli-equivalents of DTBT + EPDM and 75 milli-equivalents of DTBT + EPDM after the chemical treatment at 180°C were extracted with THF for 24 h, followed by filtration. The residues thus obtained were then dried. The expanded FT-IR spectra of DTBT (15 milli-equivalents) + EPDM and DTBT (75 milli-equivalents) + EPDM are shown in Figure 12.
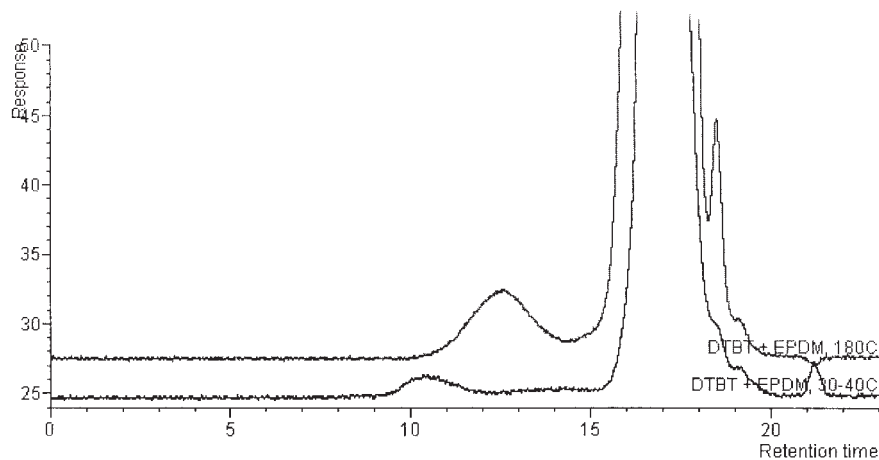

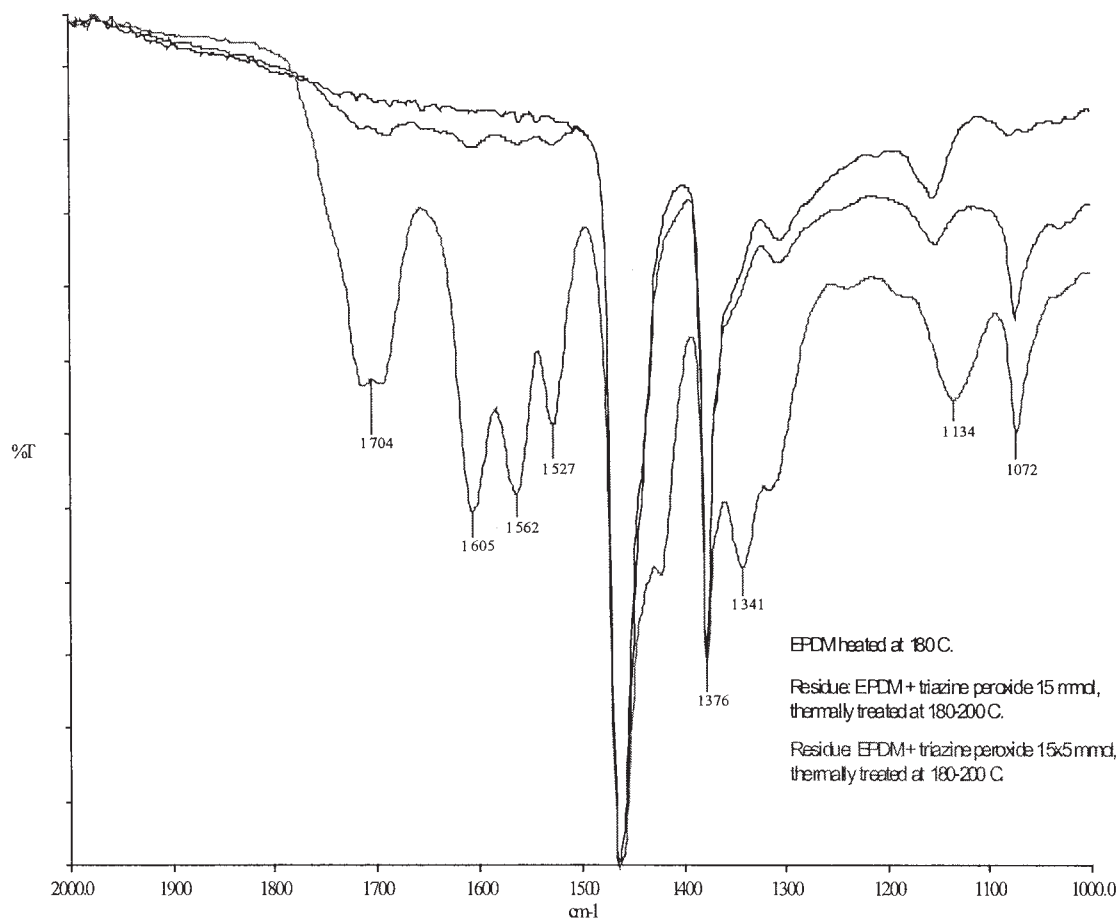**Figure 11** HP-SEC chromatograms of DTBT + EPDM before and after curing (UV detector).

Figure 12 Expanded FT-IR ATR-spectra of DTBT (15 and 75 milli-equivalents) + EPDM after curing reaction.

EPDM (no peroxide) treated at 180°C was taken as a reference. It can be clearly seen that there are some extra bands present (unlike in Fig. 7) in the thermally treated DTBT + EPDM blend-residues at the region of 1705 cm^{-1}, which are certainly due to the presence of carbonyl group(s). The latter is most likely formed due to the aerial oxidation at the EPDM-surface. This band was absent in the thermally treated EPDM sample (no peroxide). This indicates that the oxidation only takes place in the presence of peroxide, which initiates the proton abstraction and thereby the formation of a radical. Other prominent bands are present at 1605,
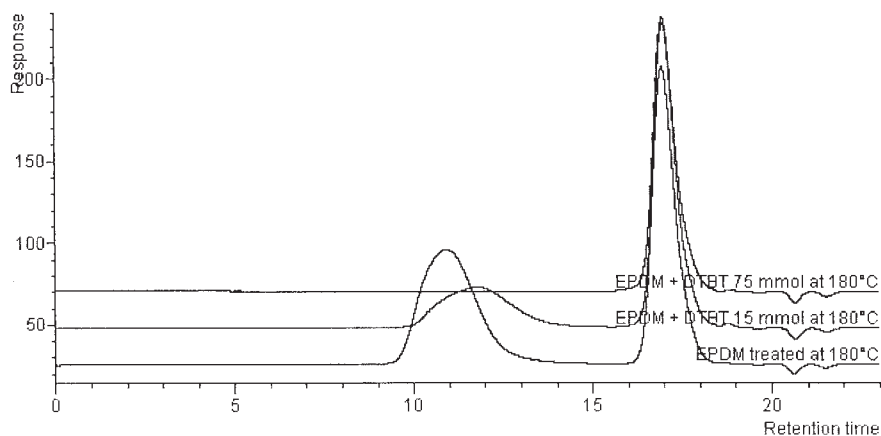

Figure 13 HP-SEC chromatograms of EPDM (no peroxide), DTBT (15 meq) + EPDM, and DTBT (75 meq) + EPDM after heat treatment at 180°C (RI detector).
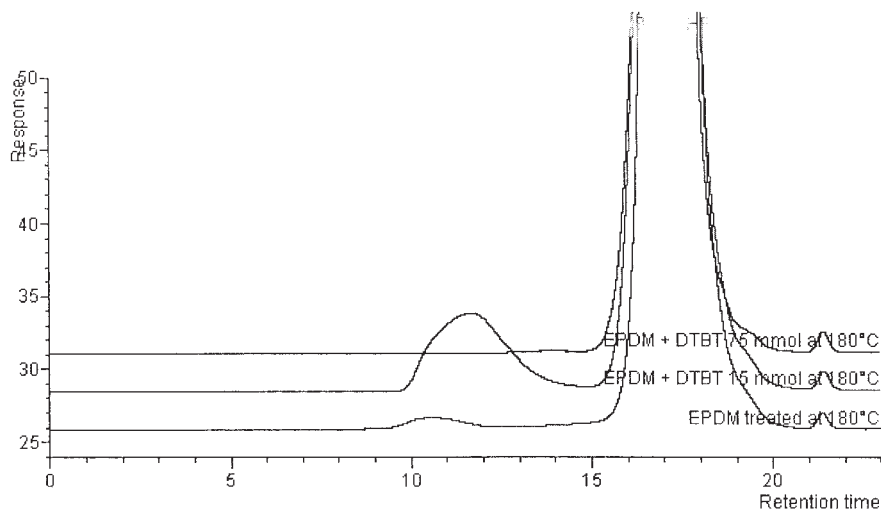
Figure 14 HP-SEC chromatograms of EPDM (no peroxide), DTBT (15 meq) + EPDM, and DTBT (75 meq) + EPDM after heat treatment at 180°C (UV detector).

1562, and 1527 cm^{-1}. When a significantly higher amount of peroxide (75 milli-equivalents) is used, a band is also observed at 1341 cm^{-1}. The starting material, DTBT, the triazine-peroxide, has characteristic bands at 1550 cm^{-1} and at 1405 cm^{-1}. Therefore, it can be stated that the grafted triazine is not exactly present in its original form. It is known in the literature that alkyl or aryl-substituted triazines show two strong bands at the region of 1580–1525 cm^{-1} and also another band at the region of 1350 cm^{-1}.[22] Hence, it may be concluded that the extra bands detected are due to triazine-like components. A band found at 1070 cm^{-1} is of THF solvent.

As already mentioned, the DTBT + EPDM blend after thermal treatment only partly dissolves in THF. HP-SEC chromatograms of EPDM (no peroxide) and DTBT + EPDM using an RI detector after the heat treatment at 180°C are shown in Figure 13. The chromatograms thus obtained are of the THF-soluble part. It is again clear that only comparatively low molecular weight EPDM-oligomers dissolve. However, it cannot be stated whether this part is grafted to peroxide or not. HP-SEC chromatograms using the UV detector are shown in Figure 14. EPDM as such has a very low response. However, an increase in UV-response is observed for the low molecular weight EPDM oligomers containing 15 milli-equivalents of DTBT + EPDM. The EPDM-triazine peroxide blend containing 75 milli-equivalents of DTBT + EPDM (the amount of peroxide used was 5 times more than the usual concentration) after thermal treatment hardly dissolves in THF. This indicates that the residue thus obtained is composed totally of crosslinked EPDM.

To confirm that the DTBT triazine peroxide is grafted to the THF-insoluble crosslinked EPDM, element analysis was carried out (Table III). As expected,

the EPDM sample (no peroxide) after thermal treatment hardly contains any oxygen and nitrogen. However, the residues of DTBT triazine peroxide + EPDM blends contain both nitrogen and oxygen. These residues can only contain nitrogen if the triazine part of the DTBT peroxide is grafted to the EPDM by some means. Theoretically, if the amount of nitrogen only originates from triazine directly grafted to EPDM, the amount of nitrogen obtained should be approximately 1.3 times higher than that of oxygen. However, in both cases, the amount of oxygen is higher than that of nitrogen. This leads to the conclusion that the oxygen is not only coming from the triazine grafted to EPDM, but also from carbonyl groups, most likely present at the EPDM rubber surface due to oxidation.

CONCLUSIONS

The experiments described in this investigation give strong indications that the decomposition products 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 is also demonstrated

TABLE III
Element Analysis

Element	O (% m/m)	N (% m/m)	C (% m/m)
EPDM-after thermal treatment	< 0.1	< 0.1	87.5–87.8
DTBT (15 mmol) + EPDM-residue	0.8–0.9	0.26	85.8–86.4
DTBT (75 mmol) + EPDM-residue	2.9–3.0	2.03	81.9–82.3

that the coagent functionalities present in those per-oxides are playing a role in the grafting reactions.

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