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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 17 November 1999

To cite this Article Fritz, H. G.(1999) 'INNOVATIVE POLYPROPYLENE BLENDS BY REACTIVE COMPOUNDING', Journal of Macromolecular Science, Part A, 36: 11, 1683 – 1698

To link to this Article: DOI: 10.1081/MA-100101620

URL: <http://dx.doi.org/10.1081/MA-100101620>

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INNOVATIVE POLYPROPYLENE BLENDS BY REACTIVE COMPOUNDING

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ABSTRACT

Within this paper, the generation of tailor-made thermoplastic two-phase polymers by means of reactive compounding is described. New strategies for the preparation of heterophasic polypropylenes and thermoplastic vulcanizates (TPV) are presented. Process design, blend components, formulation parameters, and resulting mechanical, thermal and rheological blend properties will be discussed in detail.

INTRODUCTION

The desire for tailor-made material concepts with selected combinations of properties can be fulfilled nowadays efficiently by means of specific polymerization processes and reactor arrangements starting from well-known monomers. The large-scale generation of bimodal polyolefines practiced by traditional plastics manufacturers by means of the suspension or gas-phase technology represents a vivid example.

At this point, also the newly developed cycloolefines (COC) have to be mentioned, amorphous copolymers generated from linear and cyclic olefines (Figure 1). The property profiles (viscosity, stiffness, impact strength, and heat distortion temperature) of such COC-types can be varied in a wide range (f.e. 75°

Property	Unit	Method	Value	Remarks
Density	kg/m ³	ISO 1183	1.02	-
Melt volume index MVI _{260°/2,16}	ml/10 min	ISO 1133	4-56	x:y-Ratio
Tensile strength	N/mm ²	ISO 527	64-66	-
Elongation at break	%	ISO 527	3-10	-
Elasticity modulus	N/mm ²	ISO 527	2600-3200	-
Impact strength (Charpy)	kJ/m ²	ISO 179	13-20	-
Heat distortion temp. (HDT/B)	°C	ISO 75	75-170	Dependent on Y-percentage
Coeff. of therm. expansion	K ⁻¹	DIN 53752	0,6·10 ⁻⁴	

Figure 1. Characteristic material properties of newly developed cycloolefines (COC).

$\leq \text{HDT/B} \leq 170^\circ\text{C}$) by a fine-tuning of the polymerization process (balancing of X/Y-ratio).

By the use of high performance metallocene catalysts, polymer parameters like chain topology, molecular weight, and molecular weight distribution can nowadays be controlled precisely. Typical representatives of those materials can be seen in the widely used ethylene/octene- and ethylene/hexene copolymers, characterized by rapidly growing production rates.

During the introductory phase of novel ambitious products, only small amounts of polymers are needed which can never be generated economically by the above mentioned technologies. Such tailor-made polymeric materials, however can be produced alternatively by means of intelligent compounding strategies as well as by reactive modification procedures of conventional polymers like functionalization, blending or alloying. By the use of co-rotating, close-intermeshing twin-screw extruders, acting simultaneously as mixing unit and chemical reactor, it is evidently possible to generate small-scale batches (0.5-10 kt/a) with subtly differentiated polymer properties still under economic conditions. A comparable situation is given in the area of small batch generation of single-phase polymers by means of reactive extrusion, where monomeric or dimer-

ic structures are linked up to linear macromolecules by a polymerization-, polycondensation- or a polyaddition reaction [1].

Within this paper, two different types of polypropylene blends will be discussed, both of them characterized by a continuous PP-matrix and directed primarily to automotive applications. In the following, formulation and compounding concepts as well as resulting property profiles of heterophasic polypropylenes and thermoplastic vulcanizates (TPV) will be described in detail.

Heterophasic Polypropylene Blends

Occasionally, aspired property profiles can no longer be realized by a sophisticated reactor technology. In such particular cases, nowadays physical blends or reactor blends made from PP and EPM or EPDM are widely used. For such areas of application an increased stiffness, an improved low temperature impact strength and a reduced coefficient of thermal expansion, compared with standard products, would be highly appreciated. These criteria will be fulfilled by innovative heterophasic polypropylene blends including a semi-interpenetrating network structure, generated in a reactive compounding step [2]. The newly developed compounding strategy can be described as follows (Figure 2).

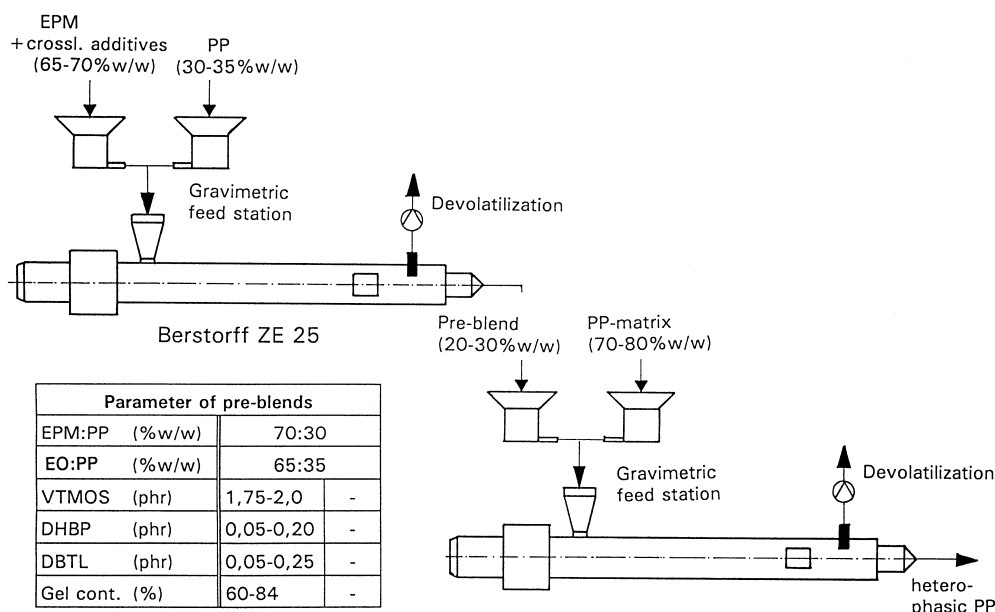


Figure 2. Cascade arrangement of twin-screw extruders for the generation of heterophasic PP-blends.

An EPM-rubber (Vistalon 606), coated with organosilane (VTMOS), peroxide catalyst (DBTL) is mixed with an adequate PP-homo- or -copolymer in such a volume concentration ratio, that within a reactive compounding process, realized in a twin-screw extruder, a pre-blend is generated, characterized by a co-continuous phase structure. The synthetic rubber is incorporated in the network in a fibril-like mode and in a crosslinked state with gel contents in the range of $55\% < C_{gel} \leq 85\%$. Instead of EPM also EO-copolymers can be used as synthetic rubber phases. Exemplary selected formulation parameters of the pre-blend are shown in Figure 2.

Such pre-blends are rediluted in a single-stage process within a second twin-screw kneader. The realized mixing ratios of the pre-blend/PP matrix-system cover a range between 20:80 and 30:70. Under the action of high stresses and deformation rates the co-continuous phase structure of the pre-blend is dispersed. The crosslinked sponge-like filaments rubber are homogeneously distributed in the PP-matrix. Within such two-phase polymers they act as a reinforcing filler and toughening agent. The fibril-like rubber formation reduces the coefficient of thermal expansion and increases blend stiffness respectively modulus of elasticity. An orientation of the rubber filaments in downstream molding processes can generate a low-level anisotropy of material properties. By the incorporation of small amounts of mineral fillers the material-related target parameters can be further improved.

In Table 1 formulation parameters and mechanical properties of selected heterophasic polypropylenes are listed and correlated with data of a currently available product. Increase in σ_{max} - (+45%), E-modulus- (+26%) and impact strength-values (+41%) are remarkable improvements while the decrease of the coefficient of thermal expansion (-24%) should be still intensified.

New Developments in the Field of Thermoplastic Elastomers (TPE)

With two-digit annual growth rates thermoplastic elastomers belong to the most rapidly developing polymeric systems. In this area, one has to differentiate between such systems which include the disperse phase in an uncrosslinked state and those including a synthetic rubber phase in a microdisperse distribution and in a highly crosslinked state (Thermoplastic Vulcanizates (TPV)). Therefore, with the latter ones no morphological changes will occur during subsequent molding steps [3].

TABLE 1. Mechanical Properties of Heterophasic Polypropylene Blends

Blend-type	Pre-blend		Heteroph. PP-blend		Heterophasic PP-blend				
	rubber (phr)	PP-comp. (phr)	pre-blend (phr)	PP-matrix (phr)	σ_{\max}^* (MPa)	ε_{\max}^* (%)	E-modulus* (MPa)	Impact strength ^{*,**} (kJ/m ²)	Coeff. thermal expansion ^{***} α (K ⁻¹) [*]
II	EPM 70	PP-Homo 30	25	PP-Homo 75	23,0	190	1350	8,4	-
II	EPM 70	PP-Copo 30	25 _{n = 230 min⁻¹}	PP-Homo 75	23,8	380	1200	10,2	96·10 ⁻⁶
II	EPM 70	PP-Copo 30	25 _{n = 180 min⁻¹}	PP-Homo 75	22,9	400	1170	12,2	103·10 ⁻⁶
II	EO 65	PP-Copo 35	25	PP-Homo 75	24,0	65	1200	6,4	-
Ref.	Without pre-blend		Reactor-modified reference product		15,0 - 17,6	300 - 400	950	8,6	127·10 ⁻⁶

^{*}) 40 days after blend generation ^{**}) Test temperature: -20°C ^{***}) direction of moulding

Thermoplastic Vulcanizates (TPV) Based on PP/EO-Copolymer Formulations

Recently, new types of TPVs were developed at IKT [4, 5], characterized by the following steps of innovation:

- EPM-co- and EPDM-terpolymers are replaced by saturated metal locenecatalyzed ethylene/octene-copolymers (EO-copolymers);
- For rubber phase crosslinking organosilanes are used instead of peroxide, sulphur or phenolic resins;
- The generation of such two-phase polymers is realized in an optimized single-stage process using a co-rotating, close-intermeshing twin-screw extruder.

Blend Components

The conventional EPM- and EPDM synthetic rubber phases were substituted, as already mentioned, by newly developed ethylene/octene copolymers. Metallocene catalysts used for its polymerization generate an outstanding chain topology resulting in advanced material properties (Figure 3). The octene-

Ethylene/Octene-Copolymers			
$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_m \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H} \quad \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$			
Property	Unit	Value	Remarks
Density	g/cm ³	0,86-0,87	Laboratory product: 0,795
Octene-Content	%	20 - 35	-
m : n	-	4:1 - 2:1	-
Molecular weight distribution	-	1,9 - 2,1	i.a. $\bar{M}_w/\bar{M}_n \approx 2.0$
Long chain branching (LCB)	z/1000C _{Eth}	0.3 - 0.5	-
Melt flow index	g/10 min	0.5 - 5.0	MFI _{190°/2.16}
Crystalline melting point	°C	45 - 63	-
Hardness (Shore A)	SHE	69 - 72	-
Tensile Strength	MPa	12 - 15	-
100%-Module	MPa	2.5 - 3.0	-
Elongation at break	%	700 - 1000	-
Glass transition temperature	°C	< - 76	-

Figure 3. Material parameters of metallocene-catalyzed ethylene/octene-copolymers.

comonomer is incorporated in the EO-macromolecules in a very regular distribution in the form of shortside chains. With increasing octene content (20-35%) the side chain distances will decrease. If they become smaller than 80 Å lamellar, crystallites can no longer be folded; fringed micelles with a domain size of $80 \leq d_D \leq 130$ Å will be generated, causing no light scattering. An increase of the octene content will lower the density ($\rho_{20^\circ} = 0.870 \rightarrow (\rho_{20^\circ} = 0.855 \text{ g/cm}^3)$) and the degree of crystallinity, leading to a growth of flexibility, elasticity, and transparency. Low values of crystallinity also heighten the ability to absorb paraffinic oil used as an extender for the reduction of blend hardness. Metallocene-catalyzed EO-copolymers are characterized by a narrow molecular weight distribution of $\overline{M}_w/\overline{M}_n \approx 2$. Because of the lack of a low molecular tail in MWD high gel contents and crosslinking densities can be expected from the crosslinking procedure on the basis of organosilanes. An improved thermal/oxidative stability, an excellent miscibility with PP-copolymers, as well as an improved mixing efficiency at short mixing periods are highly advantageous EO-copolymer attributes with regard to the generation of TPVs.

In the experimental studies, four different types of EO-copolymers, produced by DuPont/Dow Elastomers, were used, identified in this paper by the grades ENGA-GE EG 8200, 8100, 8150, and 8180, which differ in molecular weight and rheological behavior (Figure 4). Additional advantages of these copolymers can be seen in the homogenous network structure generated by the organosilane crosslinking step and in the pellet structure as supplied.

Composition and structure of the polypropylene matrices influence to a high degree the property profiles of the generated TPVs. With regard to compatibility of the blend components, PP-block copolymers should be used as matrix materials. If oil-swelling is a decisive quality criterion for the TPVs under discussion, PP-copolymers with a high degree of crystallinity α_K should be selected ($\alpha_K > 38\%$). An approved formulation window is defined by PP:EO-ratios in the range of 60:40 and 30:70. These volume concentration ratios $\lambda_3 = \phi_{DP}/\phi_{CP}$ have to be adapted to the viscosity ratios $\lambda_1 = \eta_{DP}(\dot{\gamma})/\eta_{CP}(\dot{\gamma})$ to avoid the generation of undesired co-continuous phase structures.

Oil addition is realized to reduce TPV-hardness. If such extenders are already present during the peroxide initiated grafting step of the organosilanes, the added oil components can act as radical interceptors due to the presence of double bonds, tertiary C-atoms and heterocyclic aromatic structures. The consequence would be a reduction of grafting rates and a decrease of crosslinking densities debasing the TPV property profiles. To eliminate such interactions refined

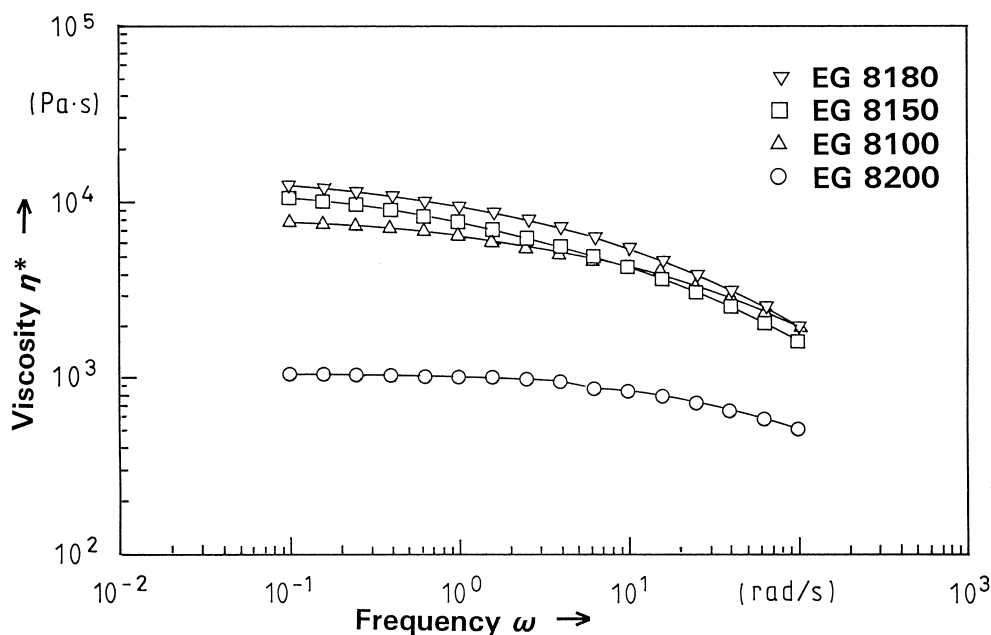


Figure 4. Viscosity functions of EO-copolymers used within this study.

paraffinic oil should be selected, characterized by reduced volatility and migration rates to make sure that the extender will stay within the TPV.

Crosslinking of EO-Copolymers by Means of Organosilanes

The conventional crosslinking of the synthetic rubber component by means of peroxides, sulphur or phenolic resins is replaced by organosilane grafting and crosslinking reactions (Figure 5): Peroxide radicals resulting from a thermal multi-stage peroxide degradation initiate hydrogen abstraction from EO-macromolecules. By breaking up the vinyl double bonds of the organosilane, the vinyltrimethoxy-silane (VTMOS) molecules are grafted onto the chain radicals causing a remarkable increase of viscosity especially in the low shear rate range, which has to be taken into account for morphology formation. Under the influence of water molecules and dibutyltin dilaurate (DBTL) acting as a catalyst, hydrolysis and condensation reactions downstream occur, leading to a formation of stable Si-O-Si-bridges and a polyfunctional network structure within the synthetic elastomer.

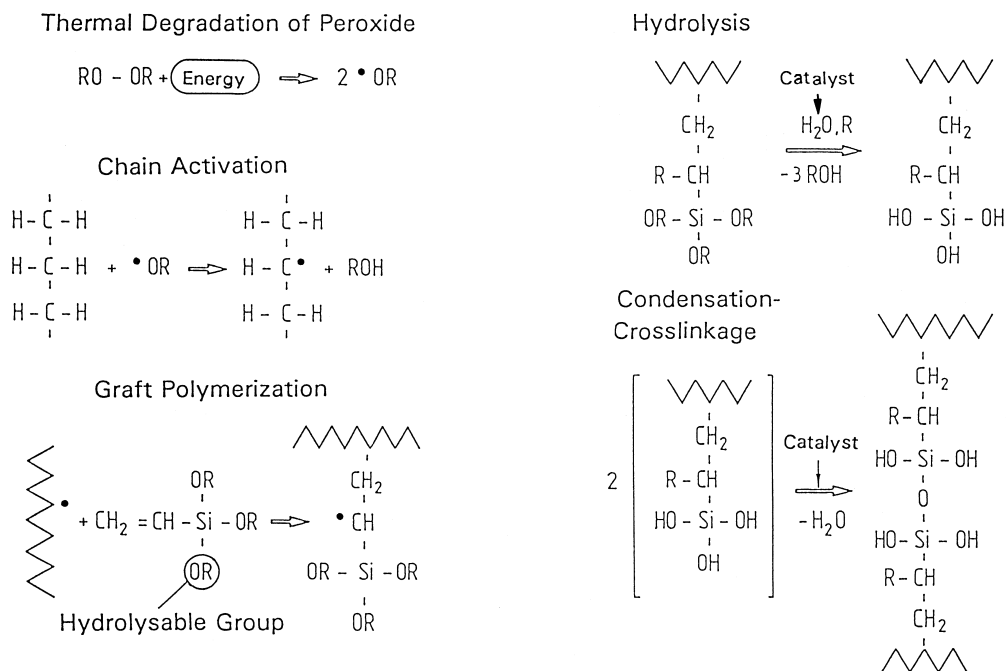


Figure 5. Crosslinking of EO-copolymers by means of organosilanes.

Dependent on the type and percentage of organosilane (VTMOS, VTEOS) and peroxide (\rightarrow active oxygen content) and influenced by molecular weight and molecule structure of the synthetic rubber, high gel contents, and outstanding crosslinking densities derived from swelling ratio measurements can be realized by the inclusion of an optimized process control concept. VTMOS-concentrations of 2.5 to 3.5 phr and VTMOS/DHBP-ratios between 20:1 and 50:1 guarantee gel contents up to 98% and high crosslinking densities between $35 \cdot 10^{-5}$ and $40 \cdot 10^{-5}$ moles/ml. The latter one also reduces the oil swelling (IRM 903; 70°C-22 hours) of such two-phase polymers. VTMOS/DHBP ratios lower than 15 can cause an undesired peroxide-initiated pre-crosslinking of the rubber phase. Problems during morphology formation would arise.

The Generation of PP/EO-Thermoplastic Vulcanizates

For the generation of the PP/EO-blends, a co-rotating close-intermeshing twin-screw kneader, type ZSK 40 from Werner & Pfleiderer, with a L/D-ratio of 56 was used. The following complex operations go off in the different kneader sections (Figure 6):

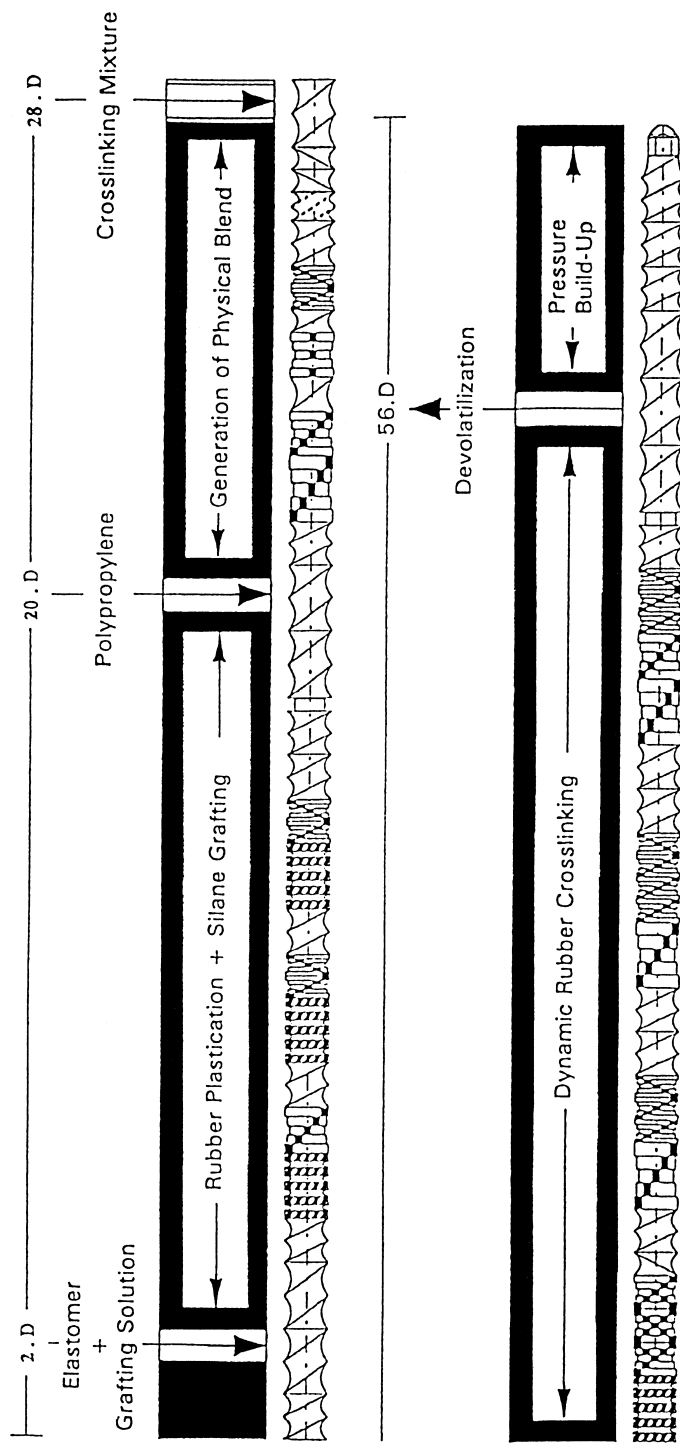


Figure 6. TPV-generation in a single-stage process (ZSK 40 with $L/D = 56$).

- The EO-copolymer is coated within an external preparation unit with the organosilane/peroxide mixture, which is spontaneously absorbed, leading to an optimal pre-distribution of the grafting chemicals.
- In the entrance section of the ZSK 40 the EO-copolymer is melted, peroxide degradation, chain activation and grafting reaction occur. With regard to reaction time, peroxide decomposition seems to be the most time consuming reactive process.
- The PP-copolymer coated with a heat stabilizer, acting also as a radical interceptor, and a metal-ion deactivator is fed into the twin-screw kneader by means of a side-stream feeder. After the PP-melting process a physical blend of the TPV-components is generated. The morphology formation of the two-phase polymer begins.
- In the following section a crosslinking mixture consisting of water, ethandiol and dibutyltin dilaurate is injected into the blended melt by means of a diaphragm pump. The crosslinking reaction has to take place under the effect of high stress components and deformation rates to continue rubber dispersion. If a set of criteria, derived from a microrheological analysis, is fulfilled, a two-phase polymer is generated including the PP as a continuous matrix and the highly crosslinked EO-copolymer as a micro-disperse phase of discrete rubber particles with particle diameters in the range of $0.1 \mu\text{m} \leq d_p \leq 2 \mu\text{m}$. The formation of a co-continuous phase structure must be avoided, for such blends are no longer remeltable.

Property Profiles of PP/EO-Thermoplastic Vulcanizates

Mechanical Properties

TPV- properties are determined by the type and content of the matrix resin (PP), the elastomeric phase (EO-copolymer) and the extender (paraffinic oil), as well as by the size, size distribution and the crosslinking density of the elastomeric particles. For many TPV-applications the TPV-hardness represents an important material criterion.

By a systematic variation of the above mentioned parameters a broad spectrum of TPV-types was generated, covering Shore-A-values between 55 and 90 SHE. The formulation-dependent ultimate tensile strength values ϵ_B are closely related to TPV-hardness. With increasing hardness the ultimate tensile strength progressively increases. As can be seen from Figure 7 the ultimate tensile

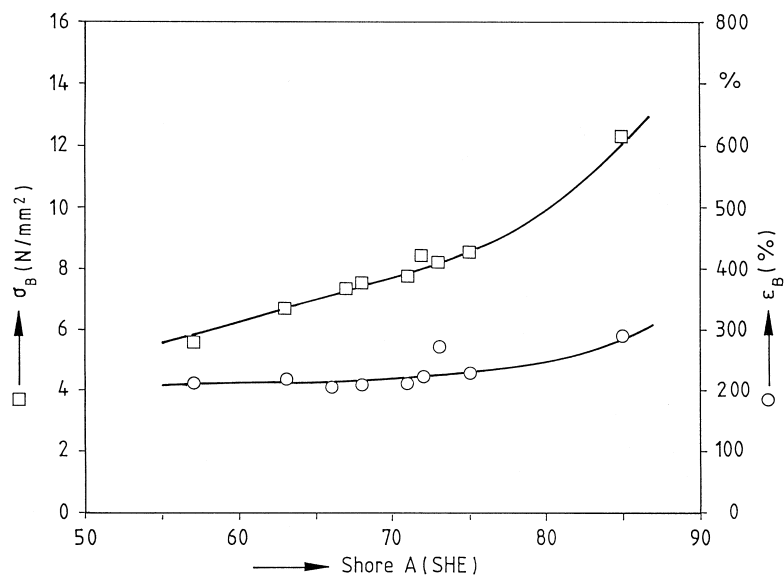


Figure 7. Ultimate tensile strength (σ_B) and elongation-at-break (ϵ_B) values of TPV depending on Shore-A-hardness.

strength values of the newly developed TPV-types are higher than those of currently available products based on PP/EPDM formulations. The corresponding values of the elongation-at-break, ϵ_B are in the range of 200 to 500%, thus also remarkably high. The PP/EO-blends with a Shore-A hardness between 60 and 90 SHE do not show a yield point on the stress-strain curve measured at room temperature. With increasing hardness (Shore D \geq 40) a shoulder appears.

Using a pre-set test temperature of 70°C and a loading time of 22 hours compression set values CS between 22 and 50% were measured for the samples described above (Figure 8). Compression set data increase with increasing TPV-hardness. A drop of gel content and crosslink density immediately causes a deterioration of the elastic material properties and an increase of the compression set. For the same TPV-types tension set values (TS) were determined at room temperature ($23 \pm 2^\circ\text{C}$). Dependent on TPV-hardness, the tension set varies between 12 and 30% (Figure 8).

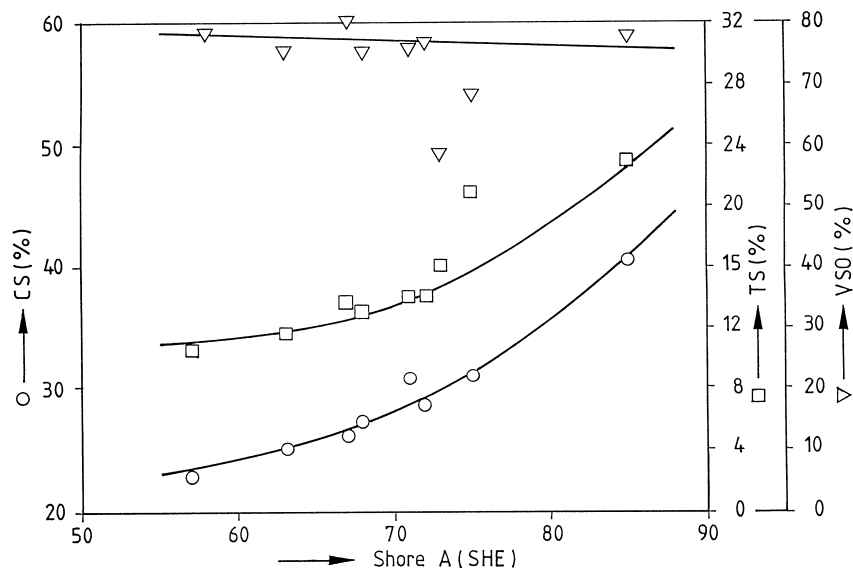


Figure 8. Compression and tension set as well as volume oil swelling values of PP/EO-TPVs depending on Shore-A-hardness.

Thermal Properties

For optimized TPV-samples, the complex shear modulus G_s^* was detected as a function of temperature by storage (G'_s) and loss modulus (G''_s) measurements, using a mechanical spectrometer, type RMS 800 from Rheometrics Inc. [Figure 9] shows the function $G'_s(T)$ of four TPV-grades characterized by different PP-matrices and Shore-A values. The vertical lines indicate the beginning of material softening. Depending on formulation parameters (type of polypropylene, volume concentration ratio, degree of dispersion) the softening temperature is shifted from 140°C down to 120°C.

Rheological Properties

Rheological properties of a physical PP/EO-blend, including the rubber in an uncrosslinked state, and of a TPV two-phase polymer, based on the same formulation parameters, differ fundamentally. While the physical blend shows non-linear viscoelastic flow properties, the cross-over point, where G' is equal G'' , disappears when the rubber particles are crosslinked. Independent of fre-

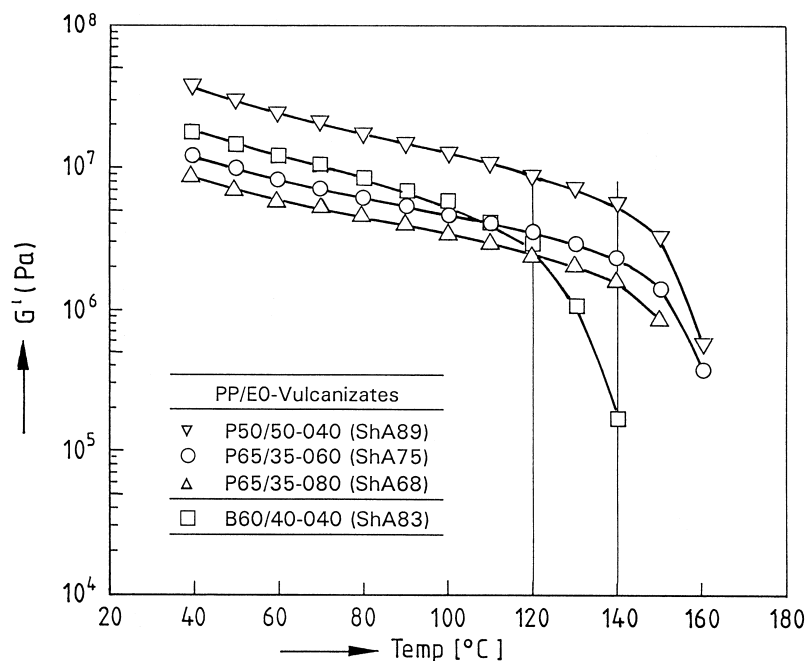


Figure 9. Temperature dependence of storage modulus $G_s'(T)$ of four TPV-grades characterized by different PP-matrices.

quency ω , the storage modulus G' is always bigger than G'' (Figure 10). The phase displacement $\tan \delta(\omega)(G''(\omega)/G'(\omega))$ is highly reduced indicating a significant increase in elastic TPV properties (Figure 11). While the complex viscosity $\eta^*(\omega)$ of the physical blends ends up in a plateau (= Newtonian viscosity), the same rheological parameter increases progressively, indicating a yield point, when the TPV-structure is fixed by a crosslinking step.

Advantages of the Newly Developed Thermoplastic Vulcanizates (TPV)

The resulting innovative TPV-grades are characterized by attractive property profiles due to blend composition and crosslinking concept. The main advantages of the newly developed thermoplastic vulcanizates are: processability without material pre-drying, excellent surface quality, the absence of smell (as a result of the innovative rubber phase and the modified crosslinking concept), uncomplicated colouring, and reduced cost of ingredients. High ultimate strength (σ_B) and elongation (ϵ_B) values, as well as a broad spectrum of different Shore A

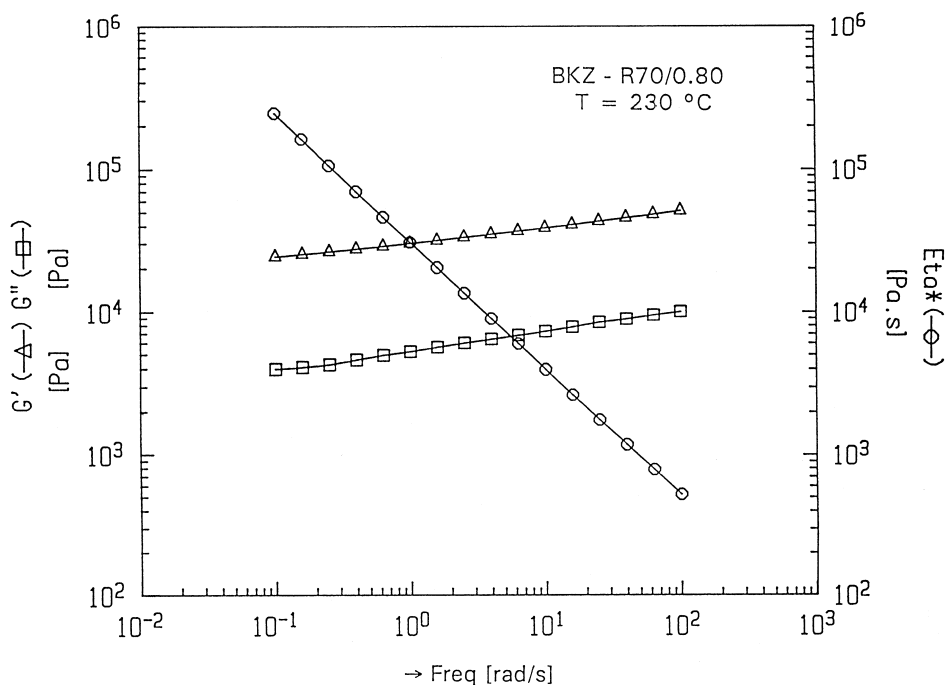


Figure 10. Storage and loss modulus as well as complex viscosity of a soft TPV type (Shore A = 63) depending on frequency.

grades open up interesting fields of application. However, the main focus is on automotive industry, not least due to low fogging rates.

CONCLUSION

The generation of new or modified polymeric materials becomes more and more an interesting sphere of activity for polymer compounding and polymer processing companies equally. As a result, also niche-products have a chance to be established in the market, although they are not in the focus of the traditional polymer producers due to a reduced requirement. Due to a not extremely expensive plant design and lay-out, a broad spectrum of development projects are installed in this area, which will enrich continuously the existing range of polymer materials. In some cases tailor-made property profiles which are not reproducible even with a sophisticated reactor technology can be generated by reactive compounding.

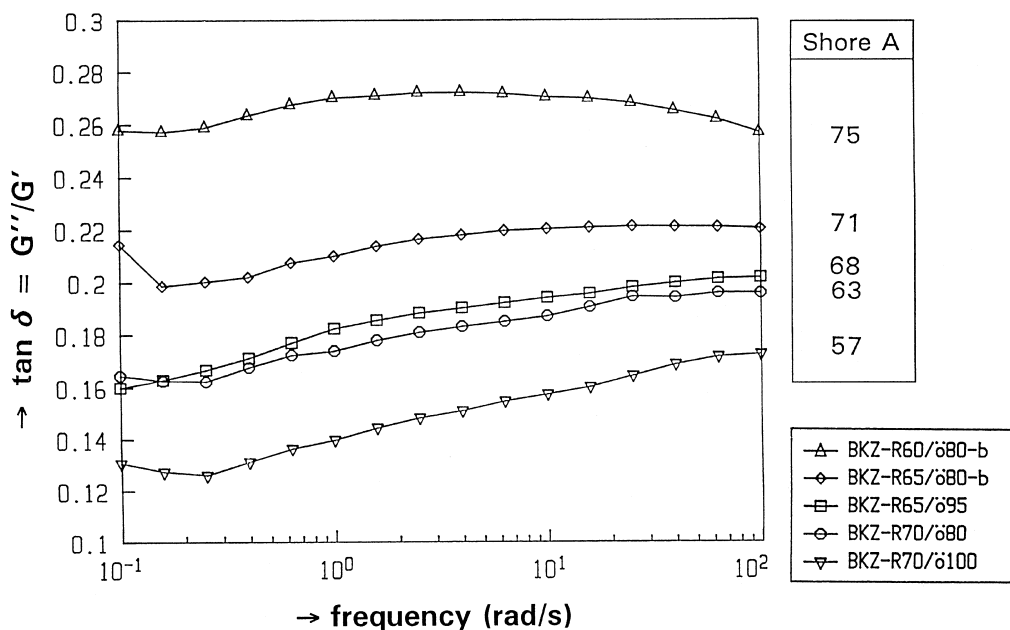


Figure 11. Phase displacement $\tan \delta = G''/G'$ of TPVs with different Shore A hardness depending on frequency.

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