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Synthesis of New Ipns and Reactive Coupling of Polymers in the Interface

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SYNTHESIS OF NEW IPNs AND REACTIVE COUPLING OF POLYMERS IN THE INTERFACE

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ABSTRACT

At present, the opportunities for the development of polymer blends made up of two polymers are largely defined. The aim for new blends is to combine the properties of the single components into one material. A precondition for obtaining the desired properties is the construction of heterophase blends, i.e., the partial thermodynamic miscibility range of the components. To avoid a decrease of mechanical properties of the blend due to interfacial failure, block or graft copolymers are used as compatibilizers. One polymer is usually dispersed in the other one by forming particles in the μm-scale. The impact strength of brittle materials (high modulus) can be increased by blending with an elastic polymer (low modulus) and adding a compatibilizer. With many blends, mutually penetrating domain structures larger than 1 μm can be obtained in the phase inversion region. At the same time, synergistic effects in the properties are achieved. A further increase of properties in systems of two high modulus (and crystalline as well) polymers leads to polymer alloys with fibrous or lamellar structures in the submicron scale. In general, there are two ways: 1) Building up a polymer starting from a monomer which is dissolved in another polymer. To prevent phase separation during polymerization, either the other polymer has to be crosslinked (leading to a so-called semi-IPN structure) or the polymerization has to take place below the melting temperature of the other polymer. Simultaneous graft reactions result in in-situ interlayers which stabilize compatibility. The influence of the degree of grafting on phase morphology and some properties are demonstrated for the polymerization of MMA in partially crosslinked EVA. 2) Structures in the submi-

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cron scale can only be produced by separation of mixtures with partial compatibility of the blend components by lowering the temperature (above the LCST region). For alloys of TPU with polyesters (EVA and PET), it is shown that the solubility of PET in TPU is so good that stable interlayers are formed. Crystalline structures of the polyester result in fascinating reinforcements of TPU. The extent to which blending of thermodynamically incompatible polymers and the application of suitable reactive interfacial agents lead to analogous morphologies cannot be answered at the moment.

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INTRODUCTION

One of the aims of the development of new polymer materials is the combination of the properties of different polymers into one material. The desired properties of such a polymer alloy are obtained through predetermined structure and morphology design. Molecular structures result from the reaction conditions of the polymer synthesis. On the other hand, morphologies depend on the structures and the interactions between the polymers. They can be influenced by compatibilizers and are a function of the mixing and cooling parameters. The properties of a polymer in a polymer alloy are primarily determined by its morphology. It is necessary to have knowledge of the formation of the morphology and of the connections between morphology and polymer properties. If one of the polymers or both polymers are partially crystalline, the extent of crystallization is decisive for the quality of the alloy. The dimensions or cellular distribution of one polymer component into the second one, in most cases the excess component, is important to the properties of the alloy. Thus, distribution limits below and above the corresponding alloys in the nm to the μm zone depend on the alloy type and the properties (toughness, stiffness, heat distortion temperature).

Some examples are the impact strength modifications of amorphous or partially crystalline polymers with elastic polymer partners or the part of the compatibilizers in boundary layers of two high modulus blend partners. The production of alloys with particle sizes in the nm range leads to the expectation of new properties which cannot be realized by mechanical mixtures. Such alloys are only realizable by adding effective compatibilizers with a high mixing expenditure (time, energy → costs).

A way of obtaining a highly dispersed mixture of two polymers is by synthesizing an interpenetrating network (IPN). The methods of synthesizing IPNs are the propagation of two polymers side by side in a monomer mixture by a different propagation mixture or the propagation of only one of the polymers in a homogeneous monomer solution of the second polymer. If one of the polymerizations is a radical one, coupling between the polymers by grafting reactions is possible. The grafting products increase the compatibility of the two polymers. The crosslinking reaction process of one or of both polymers after or during polymer buildup stabilizes the interpenetrated polymers and leads to a so-called IPN.

Another possibility is reactive blending of two polymers. In this case low molecular compounds which react with both polymers are added to the mixture of the two polymers. Thus, coupling of the two polymers in the boundary layers of a melting mixture is realizable. In the simplest case radical-forming compounds are added which make polymer radicals of both polymers so that they can be coupled by radical recombination. Multifunctional, low molecular weight compounds are more effective in most cases.

We begin with a discussion of the IPNs. The possibilities and the limits are shown by an example. We will later demonstrate the possibilities of creating of reactive polymer alloys.

THEORETICAL BACKGROUND

The miscibility of two components is described thermodynamically by the mixing free energy ΔG^{M}:

$$\Delta G^{\mathrm{M}} = \Delta H^{\mathrm{M}} - T\Delta S^{\mathrm{M}} \tag{1}$$

where ΔH^{M} is the enthalpy of mixing and ΔS^{M} is the entropy of mixing.

Two components are miscible if the mixing free energy of the system meets the following conditions:

$$\Delta G^{\mathrm{M}} < 0 \tag{2}$$

$$\left(\frac{\delta^2 \Delta G^{\mathrm{M}}}{\delta \phi^2}\right)_{\mathrm{p,T}} > 0 \tag{3}$$

where ϕ is the molar fraction of one component.

The condition $(\Delta G^{\mathrm{M}})^2 > 0$ mathematically means that ΔG^{M} (ϕ) is a convex function of the composition of the mixture (ϕ).

It is important for the mixing of two polymers that ΔH^{M} is negative and that ΔS^{M} decreases with increasing molecular mass under the influence of temperature. In most cases there are no physical values to calculate the free enthalpy of mixing. For that, measurements of the interaction parameter are necessary, and they were not available for the polymers we used.

On the other hand, the interfacial tension can be calculated by means of the surface tension (Eqs. 4–6). Equation (6) shows that it is necessary to know the interaction parameter for calculating the interfacial tension. For this reason, direct measurements of the surface tension to obtain the interfacial tension are performed on a large scale.

Surface tension γ:

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} \tag{4}$$

where γ^{d} = disperse part and γ^{p} = polar part.

Interfacial tension γ_{12} without reaction of the polymers:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}}{\gamma_1^{\mathrm{d}} + \gamma_2^{\mathrm{d}}} - \frac{4\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}}{\gamma_1^{\mathrm{p}} + \gamma_2^{\mathrm{p}}} \tag{5}$$

Interfacial tension γ_{12} with reaction of the polymers:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Omega(\gamma_1\gamma_2) \tag{6}$$

where Ω is the interaction parameter.

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The layer thickness L in polymer alloys can be obtained from small-angle x-ray scattering (SAXS) with an electron microscope. It can be used in Eq. (7) for surface tension.

Interfacial tension δ_{12} and boundary layer thickness L:

$$\gamma_{12} = 5.5 \times 10^3 L^{-0.86} \quad (7)$$

where γ_{12} is in N/m and L is in nm.

Since in our experiments neither the interaction parameter nor the surface tension are known for semi-IPNs with Cr-EVA + PMMA, we used the difference of the solution parameters for assessment of the compatibility of the monomer and polymer parameters. In this way a coarse estimate is possible. However, measurement of the surface tension and/or of the interaction parameter is necessary to obtain a valid estimate.

INTERPENETRATING POLYMER NETWORKS (IPNs)

IPN Formation and Separation

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New results on interpenetrating polymer networks have been published in the last 20 years. Developments have especially been made by Sperling [1], Frisch [2], Klempner [3], and Lipatov [4]. They found new polymer combinations by polymerizing two different monomers side by side by a different polymerization mechanism or by dissolving one polymer in another polymer so that there is interpenetration of one polymer in another. The "polymer blend" synthesized in this way is not stable thermodynamically. Thermodynamic instability means that a demixing process occurs in the melt. To increase the stability it is necessary to crosslink one or both polymers. IPNs are simulated mixtures of polymers which come from a simultaneous or consecutive buildup of two polymers from their monomer mixtures by different polymer reaction mechanisms. That is, one polymer is created from a homogeneous monomer–polymer mixture, and crosslinking prevents development. In semi-IPNs, only one of the polymer components is crosslinked.

Scheme 1 shows the possibilities of IPN formations.

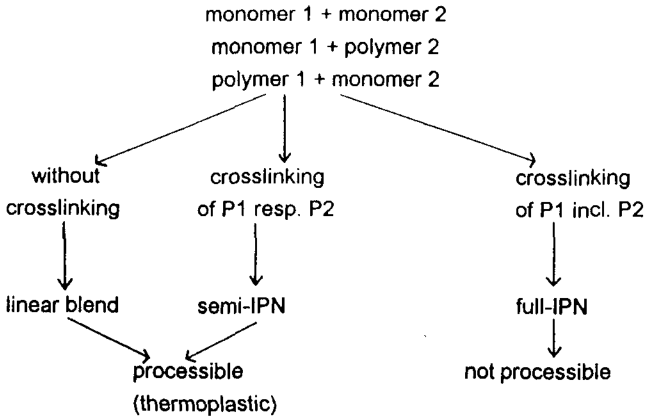
Most investigations are performed in systems of TPU with PS and TPU with acrylates; for instance, Allen [5], Jia [6], Djomo [7], Morin [8], Lee [9], and Kim [10].

When both polymer phases are crosslinked, processing of the so-called full-IPNs is not possible. Most applications are found in the fields of solvent-free coatings, varnishes, high impact materials, or reinforced elastomers. There have also been many experiments for processing semi-IPN materials. These materials can be processed by injection-molding (RIM) and extrusion.

Experimental Work

The experimental work was carried out by Schulze [11] with a solution of ethylene–vinyl acetate copolymers (EVA) as a linear copolymer, and in a differently crosslinked stage after electron beam radiation in methyl methacrylate (MMA) and then polymerizing the MMA to PMMA by a radical mechanism. The polymerization of MMA in uncrosslinked EVA was done by Laurienzo [12] and is described in a patent [13].

structure



SCHEME 1. IPN formation.

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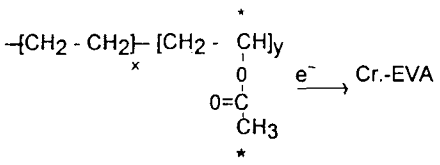
In one example, bisbutandimethacrylate (BDMMA) was added to the MMA to crosslink the PPMA during the polymerizing process.

EVA (28 mass% VA) was used as 130 × 130 × 2 mm specimens. In a mixture with 0–65% MMA, a swollen gel results. With higher MMA concentrations, a solvent results. The polymerization of the MMA is done in heatable, metallic equipment which is adapted for the swollen material. The polymerizations were done at 60, 120, and 130°C. AIBN was the initiator.

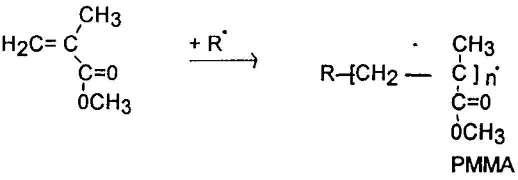
Crosslinking of EVA was done before mixing with MMA in an electron-beam radiation plant with the following characteristics: accelerator voltage, 1.1 MeV; current (internal intensity), 4.0 A; and at different residence times in the accelerator. The samples were radiated with 50, 100, 200, and 300 kGy.

The following reactions occur: EVA copolymer crosslinking:



$$-[CH_2-CH_2]_x-[CH_2-\overset{*}{C}H]_y(-O-C(=O)-\overset{*}{C}H_3) \xrightarrow{e^-} \text{Cr.-EVA}$$

MMA polymerization:



$$H_2C{=}C(CH_3)-C(=O)-OCH_3 \xrightarrow{+R^\bullet} R-[CH_2-\overset{\cdot}{C}(CH_3)(C(=O)OCH_3)]_n^\bullet \quad \text{PMMA}$$

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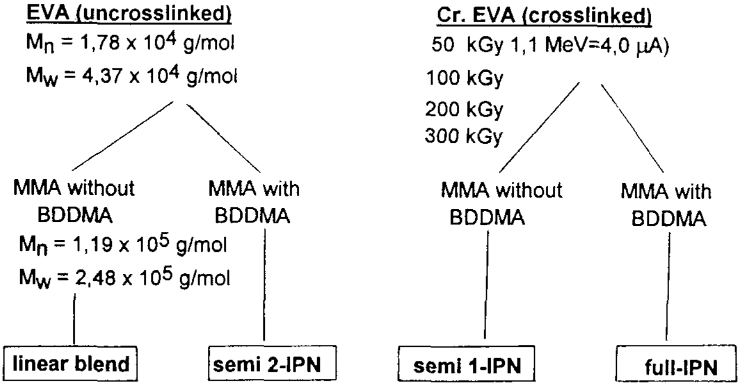
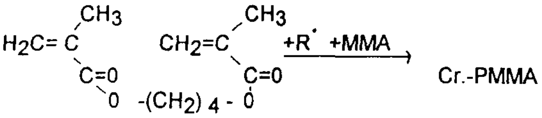


SCHEME 2. In-situ polymerization of MMA in EVA (0.2% AIBN).

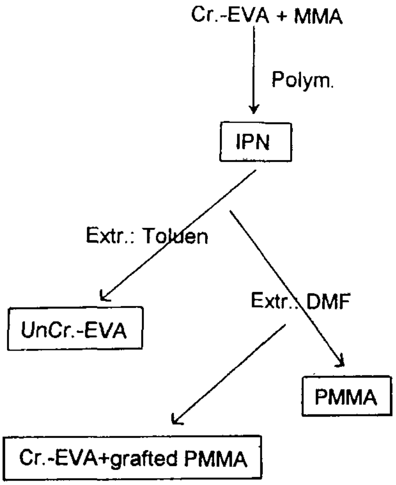
BDDMA crosslinking reaction:



$$H_2C{=}C(CH_3){-}C({=}O){-}O{-}(CH_2)_4{-}O{-}C({=}O){-}C(CH_3){=}CH_2 \xrightarrow{+R^{\bullet}\ +MMA} \text{Cr.-PMMA}$$

The production of IPNs by the in-situ polymerization of MMA in EVA (initiated with 0.2% AIBN) is shown in Scheme 2.

In order to examine the grafting reaction of the EVA polymer which may possibly arise as a side reaction in PMMA polymerization, the IPN obtained was extracted with a 1:1 mixture of toluene and DMF. Scheme 3 shows that with toluene



SCHEME 3. IPN separation.

uncrosslinked EVA and then the linear (i.e., nongrafted and uncrosslinked) PMMA was extracted with DMF.

The EVA copolymers and PMMA in the melt were mixed in a Werner & Pfleiderer extruder. The phase distribution of this physical mixture was examined.

To estimate the compatibility of the MMA with EVA and PMMA with EVA mixtures, the difference of the solubility parameters $\delta P1$ and $\delta P2$ was used. Schröder et al. [14] found a difference of 3.5 $(\mathrm{J/cm^3})^{1/2}$ for a homogeneous, thermodynamically soluble system, whereas Elias [15] found a range of values: 1.6–6.9 $(\mathrm{J/cm^3})^{1/2}$.

Based on the following values

$\delta\mathrm{MMA} = 18.0\text{–}18.2\ (\mathrm{J/cm^3})^{1/2}$ [16]

$\delta\mathrm{PMMA} = 18.7\text{–}19.5\ (\mathrm{J/cm^3})^{1/2}$ [16]

$\delta\mathrm{PVA} = 19.2\ (\mathrm{J/cm^3})^{1/2}$ [15]

$\delta\mathrm{PE} = 16.4\ (\mathrm{J/cm^3})^{1/2}$ [15]

we calculated EVA (28% VA):

$$\begin{aligned}\delta\mathrm{EVA} &= m_{\mathrm{VA}}\delta_{\mathrm{PVA}} + m_{\mathrm{E}}\delta_{\mathrm{PE}}\\ &\ 17.2\ (\mathrm{J/cm^3})\end{aligned}$$

We obtained a difference of EVA copolymer and the monomer MMA of 0.9 ± 0.1 $(\mathrm{J/cm^3})^{1/2}$ and a difference of PMMA and EVA of 1.9 ± 0.4 $(\mathrm{J/cm})^{1/2}$.

From these results we conclude that the mixture of MMA and EVA is soluble and the mixture of PMMA and EVA is insoluble. This is consistent with our experimental results.

Results

Figure 1 shows the crosslinking of the EVA copolymer as the average netpoint distance of the irradiation dose. It appears that the average netpoint distance is 55 g/mol at 50 kGy and drops to 5 g/mol at 300 kGy. If the particle size of the PMMA dispersed in the EVA is compared to the netpoint distance, a correlation between them is the result (shown in Fig. 2).

It is amazing that the particle diameter at 50 kGy has already dropped to 100 nanometers. Then it nearly decreases linearly for a little while to approximately 50 nm. The results shown in Figs. 1 and 2 are of a EVA/PMMA proportion of approximately 40:60. The particle size of PMMA is an indicator of the distribution of PMMA in the EVA copolymer at different compositions. Diverse irradiation doses as indicators of the degree of networking of the EVA and the addition of BDMMA as a PMMA crosslinker are summarized in Table 1.

The particle size was determined by TEM measurements and, preliminarily, by SAXS examinations. The correlation was satisfactory. At a 50 kGy irradiation dose for crosslinking EVA, i.e., at an average netpoint distance of 50 g/mol, the particle size drops far below 100 nm. It can clearly be seen that at a EVA:PMMA ratio of 54:46, the particle size is no longer measurable, which means that the phases have coalesced. Table 1 also shows that further crosslinking of PMMA does not lead to an additional reduction of particle size. On the contrary, the particle size

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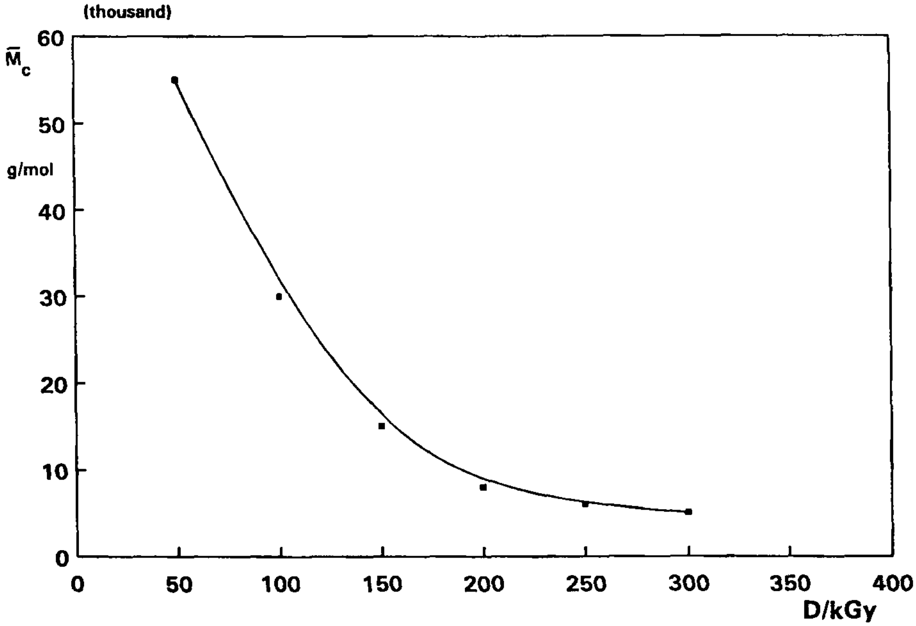

FIG. 1. PMMA particle size ($\overline{M}_c$ [g/mol]) in semi-1-IPNs depending on the irradiation dose D [kGy].

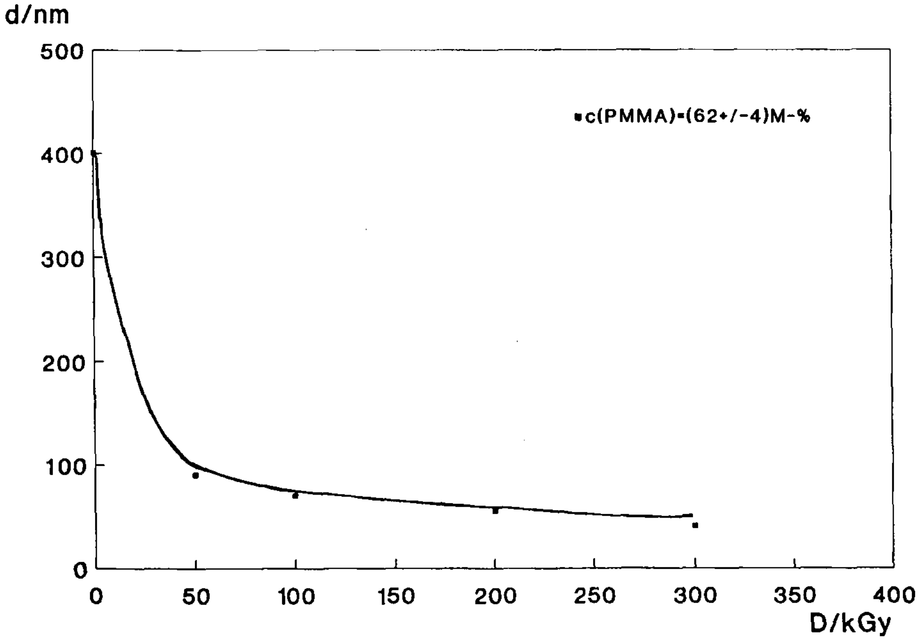

FIG. 2. PMMA particle size d [nm] in semi-1-IPNs with partially crosslinked copolymers after irradiation with a different irradiation dose d [kGy].

TABLE 1. DMMA Particle Size in EVA/PMMA IPNs

EVA/PMMA	EVA network degree (irradiation dose), kGy	PMMA network degree (BDMMA content), mol%	d_{PMMA} (TEM results and SAXS results), nm
10/90	0	0	854
30/70	0	0	724
40/60	0	0	518
50/50	0	0	431
36/64	50	0	74
41/59	100	0	66
42/58	200	0	60
41/59	300	0	38
54/46	300	0	Not measurable
40/60	100	0.5	87
48/52	100	10.0	83
44/56	200	1.0	76
49/51	300	1.0	63

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increases at 200–300 kGy and 1% BDMMA compared with uncrosslinked PMMA. An explanation for this result is not possible without further examinations. The reason may be found in the polymerization mechanism. Until now there has been no basic research concerning the mechanism of radical polymers in high viscous, crosslinked systems. It is not yet known what influence the diffusion of the monomer has on the active center, i.e., what primary particle size is built up during polymerization and what it depends on.

However, it appears that the creation of small particles through IPNs is possible by systems which can neither be reached by a mixture of the two polymers in the melt nor by the use of compatibilizers. If PMMA and EVA copolymers with high shear rates are mixed in a Werner & Pfleiderer extruder, a particle distribution of 1.5–2 μm results. With a 50 mol% mixture, a particle size of 2 μm is reached. Phase inversion of the system is found at 80–85 mol%.

If we look at the dynamic mechanical analysis [tan δ(Δ) versus temperature], Fig. 3 shows a decrease of the maxima and a simultaneous increase of the temperature of the PMMA peak at semi-IPNs by a EVA crosslinking type with 50 kGy. The increase of the PMMA peak indicates a hindered mobility of the PMMA molecule. The new maximum arising at 80°C indicates interaction between the polymers. At 300 kGy this second peak arises with a flattened zone between T_g peaks of the two initial phases.

A decrease of the T_g peak with the formation of the IPN structure is also clearly recognizable with DSC measurements. Figure 4 shows the T_g maximum measured with DSC for melt mixtures (SM); for linear IPNs (L), i.e., uncrosslinked EVA as an IPN; for semi-1 (S1) IPNs, i.e., crosslinking of the EVA at 50–300 kGy; and for semi-2 (S2) IPNs, i.e., an exclusive crosslinking of the PMMA with 2.5 mol% PMMA.

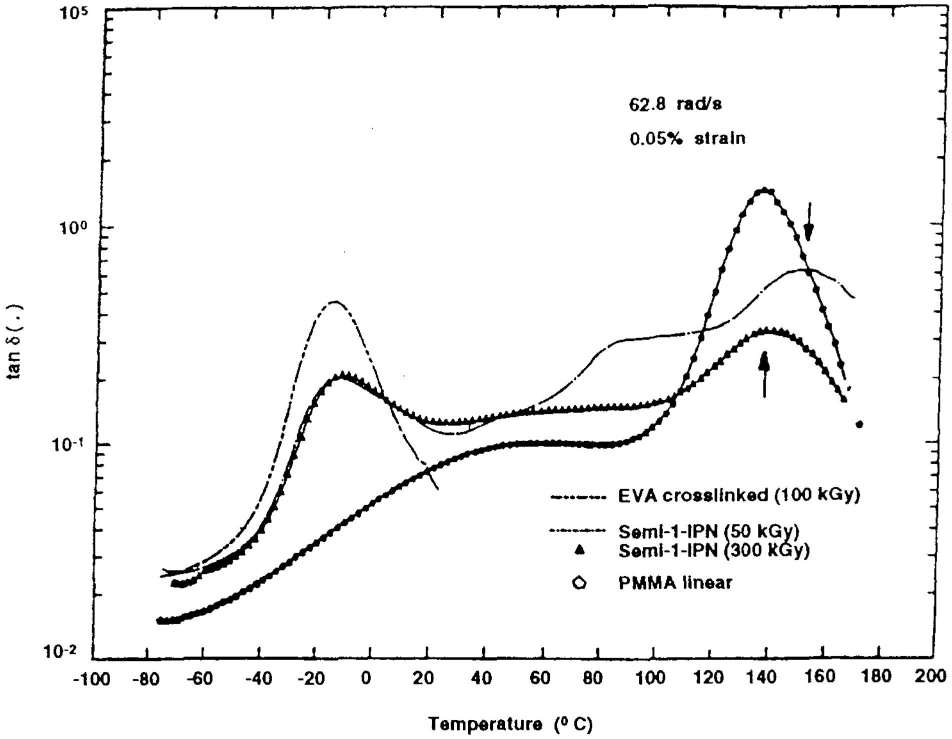

FIG. 3. Tan Δ versus temperature of partially crosslinked EVAs (100 kGy), linear PMMA, as well as semi-1-IPNs at 50 and 300 kGy.

With an increasing EVA proportion in the melt mixture (SM), no significant increase occurs. With all semi-IPNs (S1, S2), a significant increase of T_g results, which decreases with increasing EVA network density. The large T_g increase of the semi-2 (S2) IPNs and the T_g increase at higher EVA proportions, which also increases in linear blends (L) (which show no important increase at lower EVA proportions), is very interesting.

The results of DSC vs DMA measurements can only be understood when interaction between the two polymers is assumed. Schulze [11] demonstrated in his work that with this T_g variation, a grafting reaction of PMMA to the polymer chain of the EVA results. He showed that grafting yields in the 94–99% range exists, i.e., that the main part of the PMMA is bound to the EVA chain. This fact also explains that the reason the T_g peak of PMMA increases is because the mobility of the chain is hindered. A further argument for this interpretation is that the T_g increase in semi-2-IPNs occurs at low EVA proportions. Because of this crosslinking, the mobility of the PMMA molecules is limited.

Davies [17] worked out the equation $G^{1/5} = f_1G_1^{1/5} + f_2G_2^{1/5}$ (G = shear modulus, f = proportion of volume) for the shear modulus that describes a continuous double-phase morphology. By means of this equation, s- and f-IPNs can be described. Figure 5 shows that calculations of the storage modulus for the synthesis of PMMA/EVA s- and f-IPNs can be satisfactorily described by the Davies equation, i.e., IPNs are realized.

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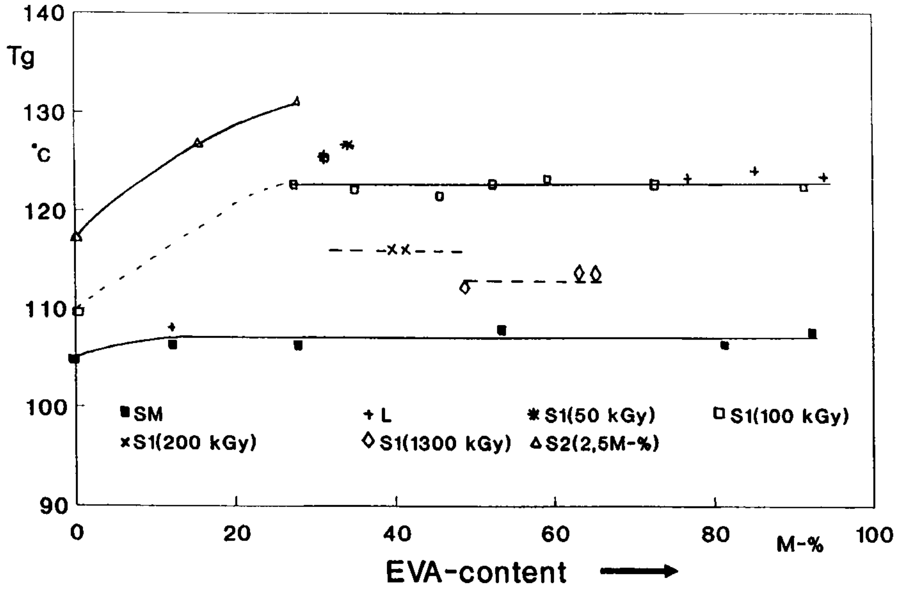

FIG. 4. Dependence on T_g (DSC measurements) versus EVA content in EVA-PMMA blends, blends in the melt (SM), of linear blends (L), semi-1-IPNs (S1) at different grades of network, and semi-2-IPNs (S2).

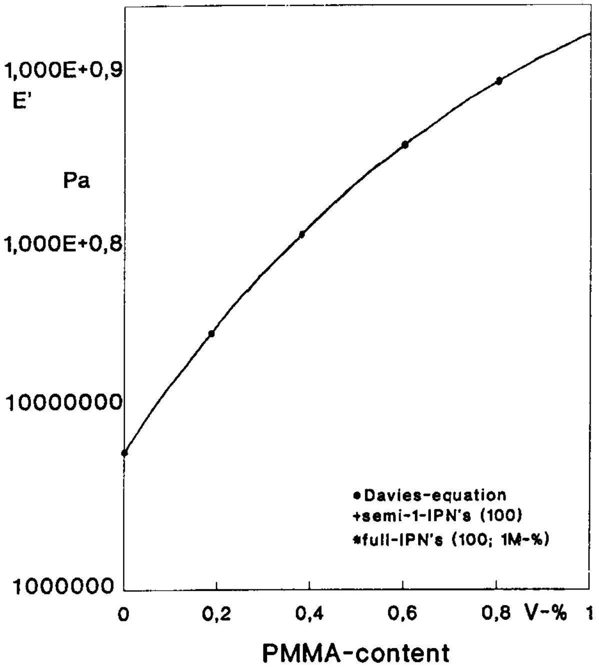

FIG. 5. DMA storage modulus according to the Davies equation as well as for semi-1-IPNs at 100 kGy and for full IPNs (100 kGy; 1% BDMMA).

From the spectrum of properties of IPNs from copolymers of EVA and PMMA, toughness was chosen as a parameter. It is described by notched bar impact bending strength (see Fig. 6). This figure shows the dependence of notched bar impact bending strength on the proportion of PMMA in EVA copolymers. Mixtures of the components in the melt (SM), in the linear blend (L), and in the full (F) and semi-IPNs (S1, S2) are also presented. The figure evidently shows that for the melting mixture (SM) an increase of the notched bar impact bending strength from 2 to 10 can only be reached in a mixture which contains 60% EVA copolymer. Values for semi-2-IPNs (S2), i.e., mixtures in which only the PMMA is crosslinked, increase very slowly, and they need a high EVA content to reach a high notched bar impact bending strength. On the contrary, the notched bar impact bending strength of the linear blend (L) increases nearly linearly with the proportion of VA, whereas the semi-1 and full-IPNs (S1, F), i.e., all mixtures which contain partial crosslinking of the EVA copolymers, increase with an excess proportion. IPNs where only the EVA copolymers are crosslinked with 100 kGy are outstanding.

These results correlate with the theoretical conception of Wu [18] which describes the toughness in relation to particle distance and particle size. Michler [19] describes the context of other systems in his work.

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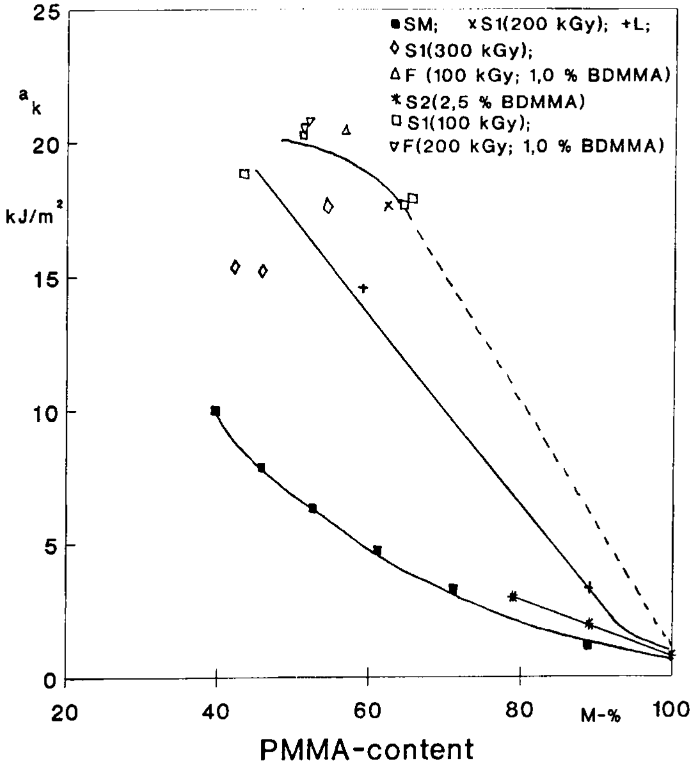

FIG. 6. Notched bar impact bending strength of EVA/PMMA mixtures versus the PMMA content of melting mixtures of linear blends, S-1- and S-2-IPNs, and full IPNs.

Summary

The results presented for the simple system EVA–PMMA copolymers show the limits of IPNs. However, they have potential not yet realized which justify further research.

The limits are given by the miscibility of two monomers versus the solubility of one monomer in polymer. There are also limits in the realization that two build-up reactions can take place independently of each other without a demixing of the phases during the build-up process. This is the reason why the addition and the radical mechanism could be developed successfully side by side for IPNs from monomer mixtures as with TPU/PMMA vs TPU/St. These are homogeneously catalyzed and initiated reactions in which the increasing viscosity quickly hinders the demixing processes. That is especially true of thin layers in which a polymer building-up reaction can occur at low temperatures.

High viscosities also become possible if one of the components is present as a polymer and the monomer of the second polymer is dissolved in it. That is the situation in the Cr.-EVA–PMMA case. The precondition that the polymer must be dissolved in the monomer limits the number of combinations. However, the work of Borsig et al. [20] on the PE/PS system, in which styrene is dissolved in polyethylene and then polymerized according to the radical mechanism, shows that the possibilities have not yet been exhausted. There are a number of questions still to be answered.

Do the polymers propagate by adding the dispersed "fixed" monomers to the matrix or do the monomers diffuse to a propagating chain by building-up dispersed phases?

What is the primary particle size of the built-up polymer phase in the solid carrier phase dependent on? How fast and at what temperatures do the primary particles coagulate during the melt?

Does coagulation depend on the grafting proportion, the crosslinking proportion, and other parameters?

Other questions concern the processing behavior of s-IPNs, how stable the phases are during processing, and many features decisive for practical application.

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REACTIVE POLYMER ALLOYS

Basis

Reactive polymer blending for the production of thermoplastic elastomers has been pursued since the 1980s. Coran and Patel [21] were pioneers who described the production of thermoplastic elastomers (TPEs) by the so-called dynamic vulcanization.

A thermoplast and an elastomer are mixed at high shear rates. By adding a reactive component, the dispersed elastophase is crosslinked. Crosslinking stabilizes the highly dispersed elastophase and a compatibilizing boundary layer is formed at the same time. The realization of this idea by Radusch [22] led to practical and efficient TPEs based on polyolefins.

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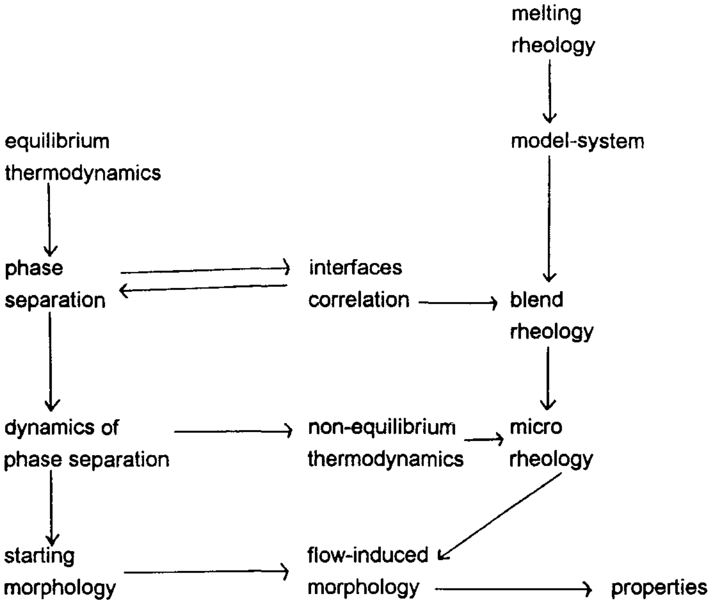
The transformation by dynamic vulcanization in polymer blending led to the development of new polymer alloys by reactive polymer blending. The aim of polymer blends is combinations of different properties. This can only be attained by preserving the primary structures of polymers in multiphase polymer alloys. It follows that the interphases in such polymer alloys are decisive.

One way of creating defined interlayers is by having a compatibilizer in the system, for instance, a graft or a block copolymer. One block or the backbone of these copolymers is compatible with one of the polymer components, and the other block or the graft is compatible with the second polymer component. Scheme 4 summarizes the factors and physical regularities which influence the properties of polymer alloys.

Equilibrium thermodynamics and melting rheology are important influences. Phase separation depends on the equilibrium thermodynamics and blend rheology depends on the interface correlations. Nonequilibrium thermodynamics influences the microrheology through the dynamics of phase separation. The starting morphology and microrheology lead to flow-induced morphology which correlates with material properties.

A second way to get new properties in polymer alloys is by using a chemical reaction for chemical coupling of the two polymers with a low molecular bi-reactive compound during mixing at high temperatures in the melt. Figure 7 shows the problems and the solutions realized by multifunctional reactions and reactive couplings in highly concentrated media, i.e., at high viscosities in the reaction mixture. Chemical reactions in the melt are typical for such highly viscous media. Problems which can be explained by hindered transport processes, by high molecule associa-



SCHEME 4. Regularities which influence the properties of polymer blends.

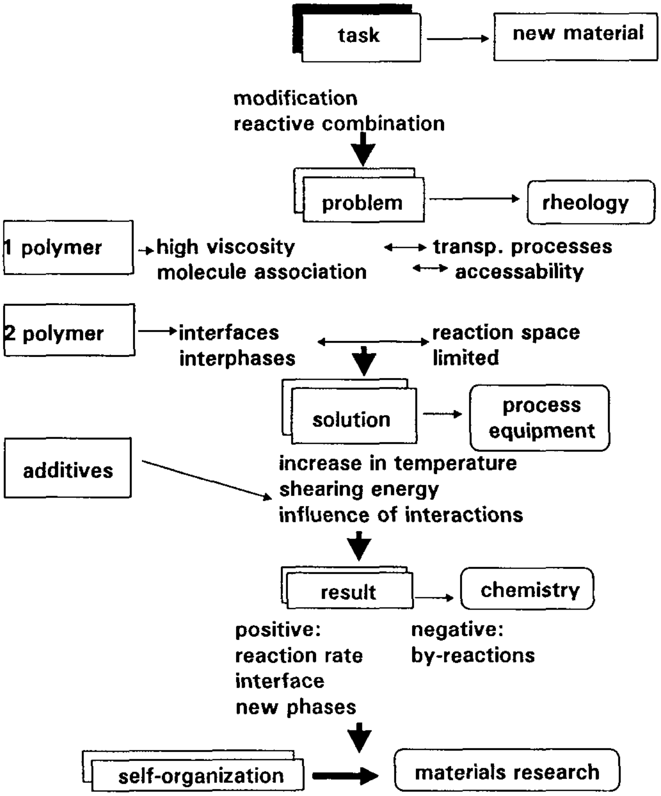


FIG. 7. Chemistry in highly viscous (highly concentrated) media.

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tions, and by limited reaction spaces between the phases derive from the high viscosity of the reaction mixture in multiphase systems.

Increasing the temperature and the shear energy in a defined residence time, which leads to acceleration of the reaction rate, can be solved with continuous-screw machines.

Boundary Layers

During so-called reactive blending, boundary layers form as an inhomogeneous third phase in the alloy. Figure 8 shows the boundary layer as an inhomogeneous third phase with a structure gradient. Parameters are the chemical composition, organization of molecules, structure (isotropy), crystallinity, morphology, and a gradient of properties such as the elasticity module, strength, viscosity, index of refraction, etc. We therefore define polymer alloys as heterophasic mixtures of polymers whose properties involve the components and the boundary layers.

Figure 9 shows the interphases realized with block copolymers. If one of the polymers has a low module, an interphase realized by a strong connection between these two polymers (upper part) will be the result. By mixing two polymers with high moduli (lower part), they must be connected (shown in a spiral) by an elastomeric

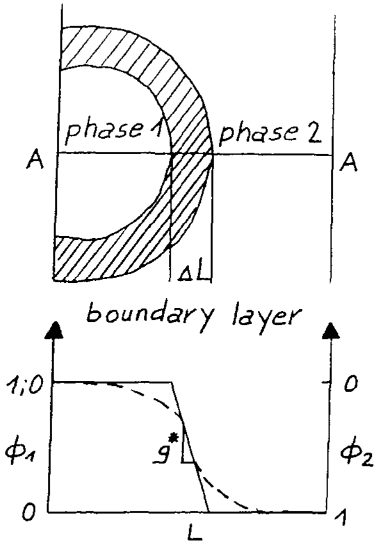

FIG. 8. Schematic graph of the boundary layer (ΔL) of Phases 1 (φ1) and 2 (φ2).

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component between the two polymers to transfer forces and reduce tension. For this, a block copolymer with elastic molecules between the two hard phases must be synthesized. Such block copolymers are expensive, but reactive polymer alloys are an alternative.

Reactive polymer alloys are a heterophasic mixture of polymers in which the compatibility of the components is increased during mixing of the polymers in the melt by chemical reactions in the interface. The two polymers can react with each other or a low molecular multifunctional substance can react with the two polymers in the interface; an interlayer results. In a polymer alloy of high modulus polymers, the resulting boundary layer has a low modulus which allows the transfer of interfaces and reduces tension. The scheme of so-called reactive blending is shown in Fig. 10. By mixing Polymer I and Polymer II in the melt, a physical blend with low interface interactions results. By adding a modifier to the mixture, a chemical reaction occurs and a reactive alloy with higher interphase interactions is obtained.

Inoue [23] demonstrated that the thickness of the layer of reactive interphases in polymer alloys is a multiple of the nonreactive interphases. The interphases are approximately 20 Å thick with nonreactive polymer alloys whereas they are 500 Å thick with reactive polymer alloys. By adding block copolymers, layer thicknesses between 50 and 100 Å are obtained, as schematically demonstrated in Fig. 11. The author demonstrated the difference between reactive and nonreactive compounding with PET/f-EPR and PET/EPR, where f-EPR is a type of rubber with reactive epoxy groups.

In Fig. 12 the thickness of the boundary layers (in nm) is shown during multireactive and reactive compounding to depend on the mixing time at a mixing temperature of 280°C. The much thicker boundary layer is the result of reactive coupling that exerts a positive effect on the toughness of the PET/EPR alloy.

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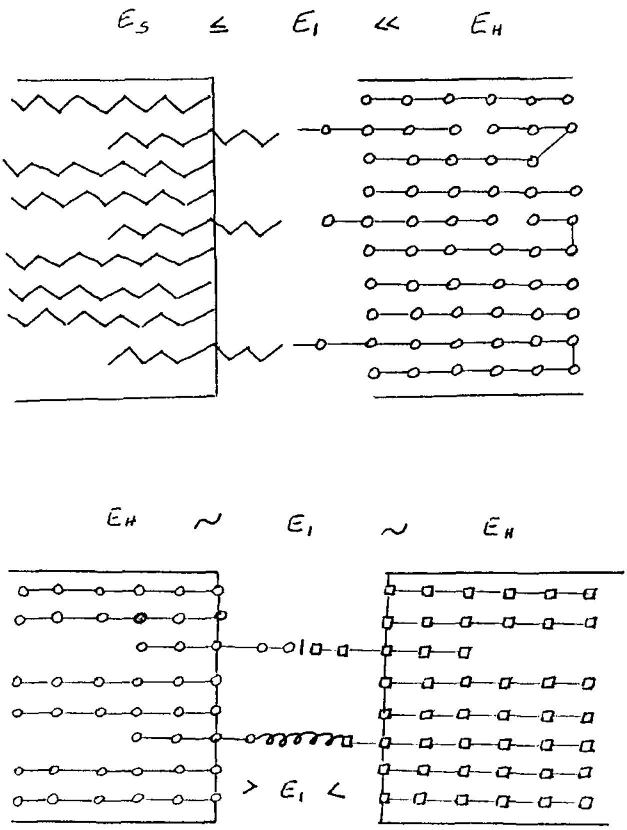

FIG. 9. Interphases with block copolymers.

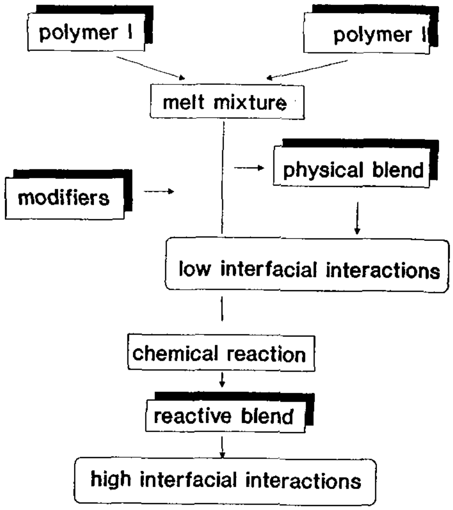

FIG. 10. Reactive compounding.

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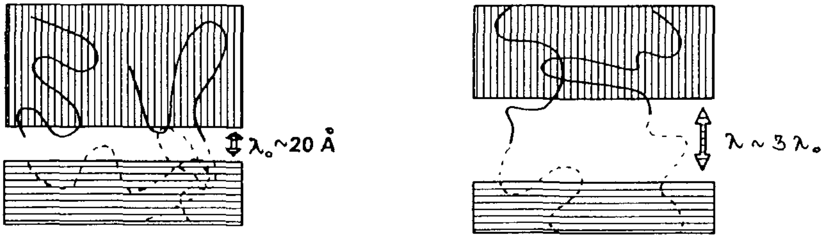
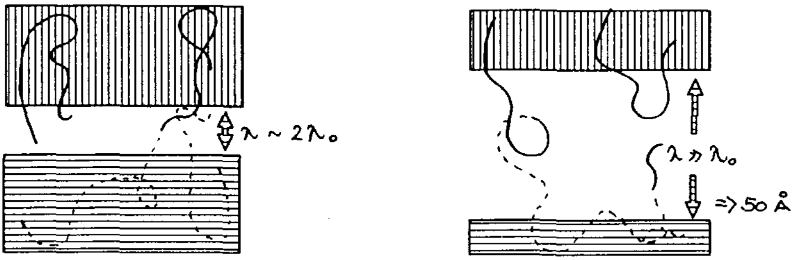


(a) A/B (non-reactive) **(b) A-B**



(c) A/B/A-B **(d) reactive A/B**

(a): between polymers A and B (non-reactive)
(b): between microdomains of neat A-B block copolymer
(c): consisting of polymer A, polymer B, and A-B block copolymer and
(d): generated by reaction between polymers A and B

FIG. 11. Schematic illustrations of polymer–polymer interphases.

Experimental Results

In Fig. 13 a property multigraph of PP/PA-alloys with 30% glass fibers in the mix is presented as an example of a polymer alloy with a reactive block copolymer. It was commercialized by Altendorfer and colleagues [24] in PP with glass fiber compounds (the cross-hatched area). The dimensional changes and the water absorption for the molding products are very low. The tear strength, flexural modulus, heat distortion temperature, and especially the impact strength at −20°C are relatively low in comparison to PA-6 with 30% glass fibers. PA-6 with 30% glass fibers has higher values in all properties (diagonal line area). The negative properties of the PA-6–glass fiber compounds are the high values in water absorption and the dimensional change. The solid area illustrates a 50:50 PP/PA alloy with 30% glass fiber and a reactive compatibilizer. The result is convincing. The alloy shows a significant increase of the HDT, modulus, tear strength, and impact strength in comparison to PP glass fibers, and a overproportioned reduction of water absorption and dimensional change in comparison to PA-6–glass fiber alloys.

We, too, have been led by Coran's and Patel's basic idea in our research work. Our work on reactive blending has been based on developing new polymer alloys. Initially, we added only radical formers to the melting mixtures of PA-6 and TPU. We improved the properties of the alloys by radical coupling in the boundary areas between the polymer phases [25].

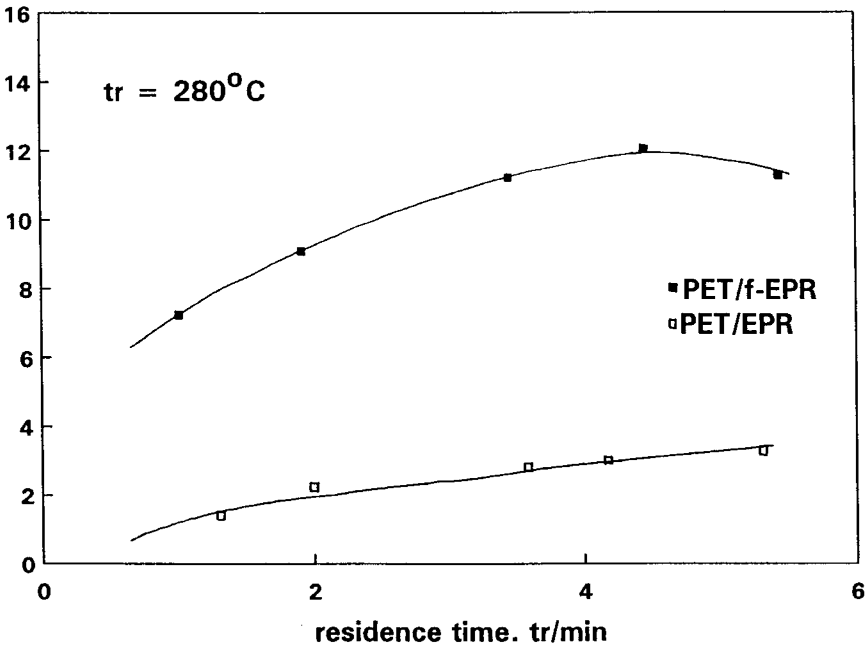


FIG. 12. Time variation of volume fraction of interphases during melt mixing.

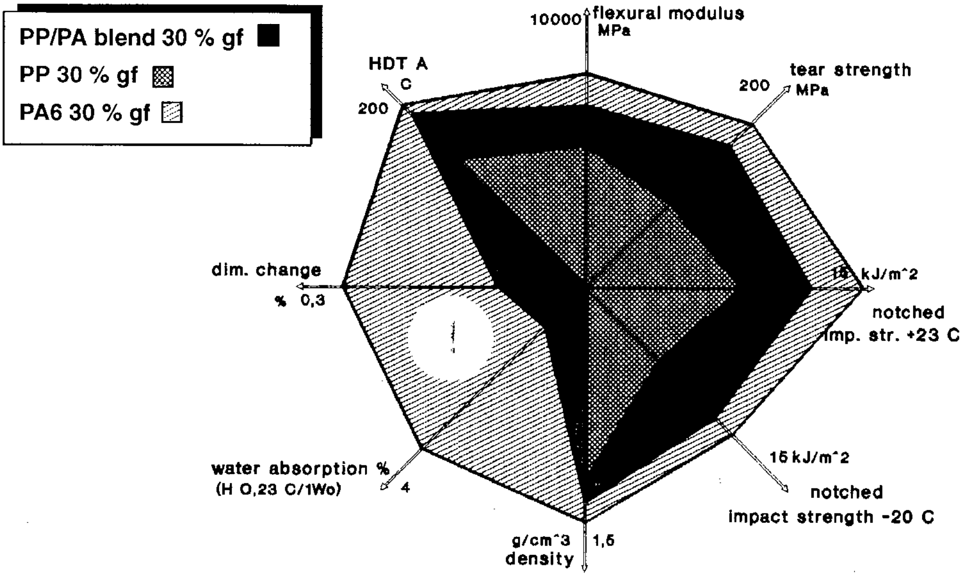


FIG. 13. Property multigram of PP, PA-6, and PP/PA blend with 30% glass fibers.

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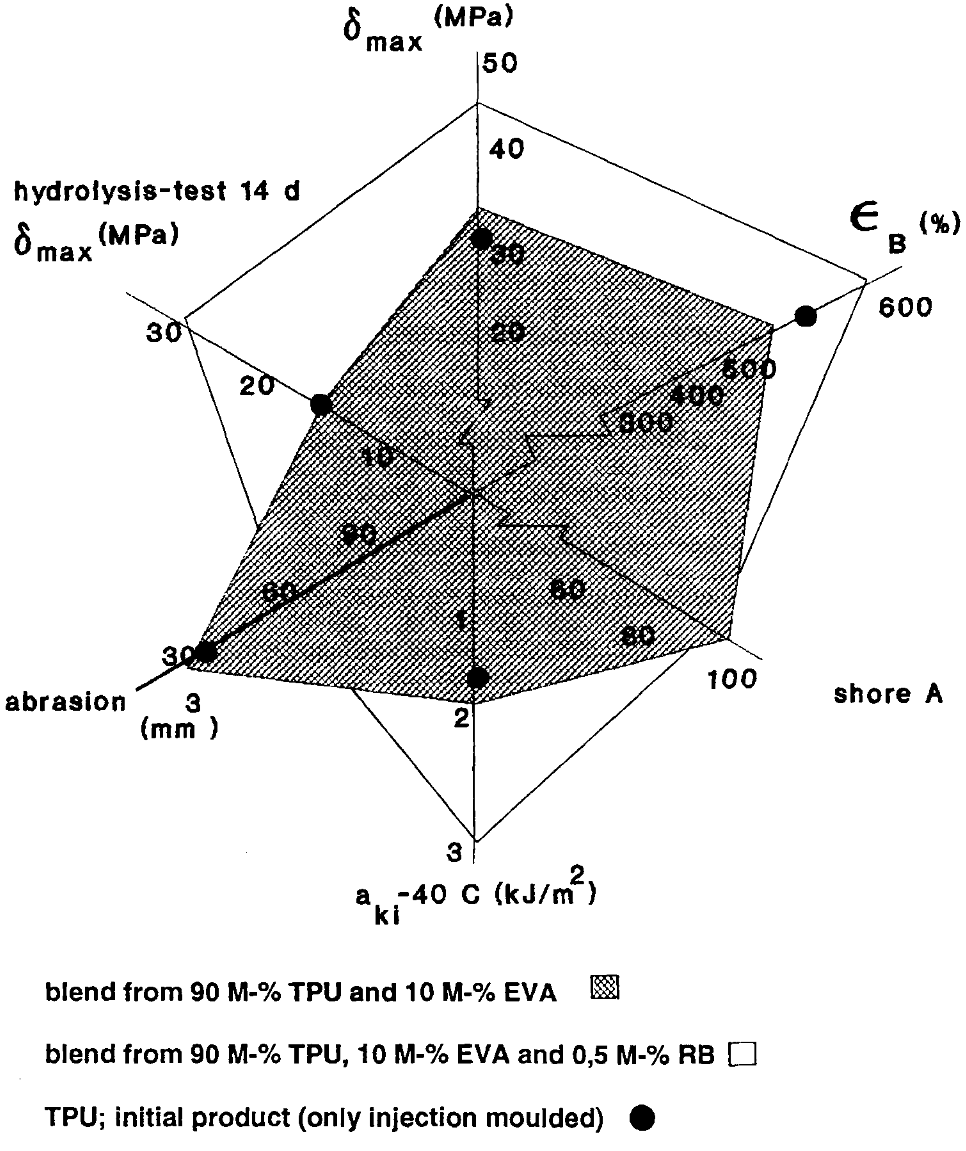

FIG. 14. Property multigram of TPU/EVA alloys with and without chemical coupling with 0.5 mol% peroxide (RB) after extrusion and injection molding.

We found it was important for the radical former to be concentrated in the interfaces, i.e., it showed very little solubility in the polymers and it only split when PA-6 was in the melted form. This principle of partial compatibility of the radical former in the polymers is analogous to the use of block or graft copolymers as compatibilizers. On the contrary, if one reactive compatibilizer is dissolved in one of the polymer components, the polymer is modified and is unsuitable for compatibilizing. Otherwise, partial solution in or at the polymer surfaces is necessary for a

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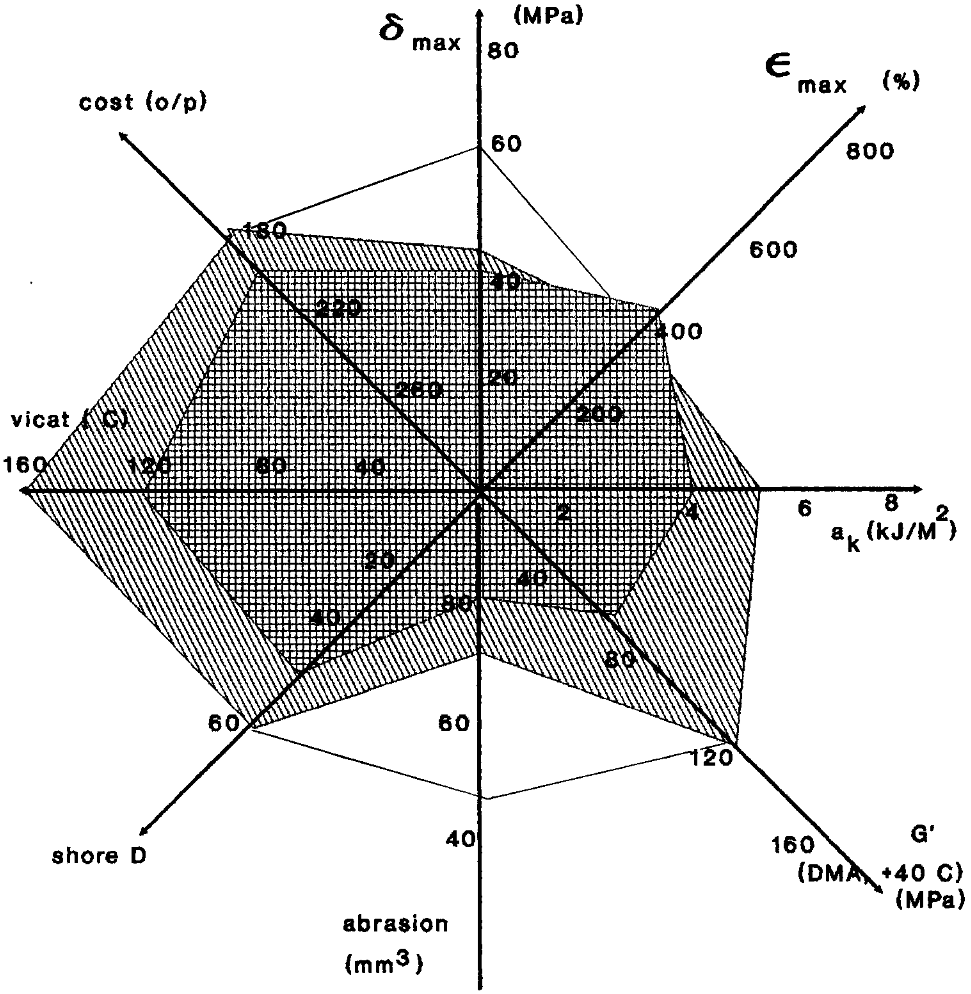


TPU ▦

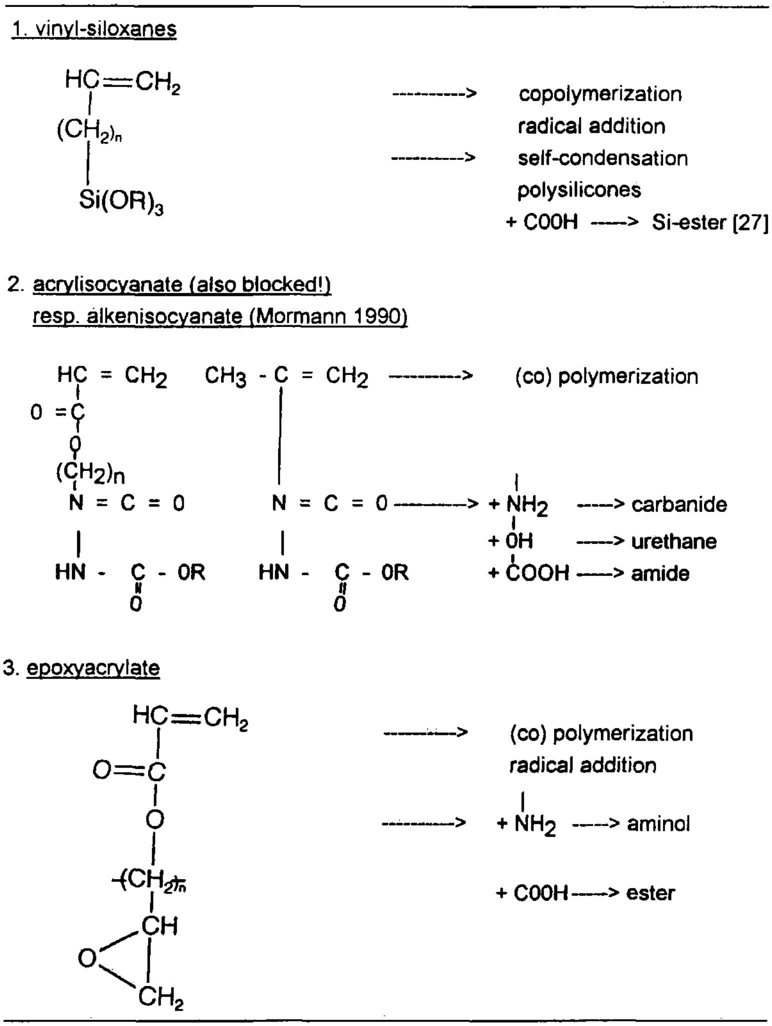
TPU/PET - 80/20 blends ▧

TPUpet/ - 80 20 blend + 1 wt. MDI ☐

FIG. 15. Property multigram of TPU/PET alloys with and without reactive coupling with 1 wt% MDI after extrusion and injection molding.

chemical reaction with both polymer chains. Thus, the reactive compatibilizers act as tensides which stabilize their dispersing function in a chemical side-reaction. These so-called "reactive tensides" stabilize the dispersity above the equilibrium because of their chemical coupling. That can be reached by high shear powers in melt/mixing machines. The know-how of the experiment involved grafting and coupling reactions in an extruder with a defined retention time, shear power, and

TABLE 2A. Vinyl Compounds



temperature distribution so the desired dispersity of one polymer is reached in the second polymer phase. We investigated this principle in the TPU/EVA and TPU/PET systems.

In Fig. 14 a TPU alloys with 10% EVA in compared with pure TPU (large black dots) to which 10% EVA was added. No significant changes can be seen. By adding 0.5 mol% of a special radical-former (a peroxide), a slight decrease of abrasion, a significant increase of the notched impact bending strength at −40°C, an increase of the modulus, and an unexpected increase in hydrolysis stability resulted. Figure 15 demonstrates the synthesis of TPU/PET alloys as carried out by Pötschke and Pionteck. It was found out that by adding 20% PET to TPU [26] based on a polyester, an increase in toughness and heat resistance time compared to pure TPU (cross-hatched area) was found. If 1% by weight methylenebisdiiocyanate

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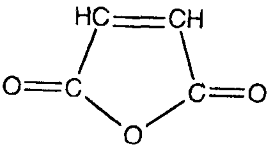
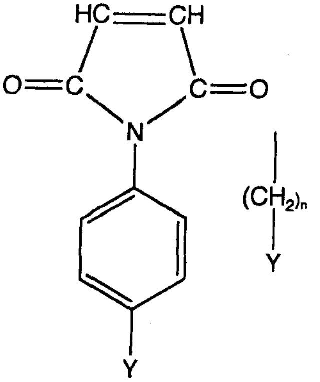
TABLE 2B. Maleic Anhydride Substitutes

maleic anhydride 	--------->	radical addition (copolymerization) (Diels-Alder-addition, EN-reaction
	--------->	+ - OH (aliph.) ----> half-ester
	--------->	+ - NH$_2$ -----> amide acid ----> imide
maleimides 	--------->	radical addition (copolymerization) Diels-Alder-addition Michael-addition
	--------->	Y-functionality e.g. -COX -Si(OR)$_3$
copolymaleic anhydrides	--------->	half-ester amid acids ----> imides
copolymaleinimides	--------->	Y-functionality

(MDI) is added to the melting mixture as a reactive compatibilizer, the tensile strength is increased and the abrasion is decreased. These two characteristic values demonstrate the importance of the use of such alloys. Morphologic examination of this alloy showed that separate crystal phases of PET are formed in TPU, which reinforce the TPU phase. The potential of these alloys has not been exhausted with the experimental facilities available to us. This is true of both the polymer compounds used, the reactive compatibilizers, and the reaction conditions. However, these examples show the possibilities upon which reactive polymer alloys are based.

In conclusion, we show some of the well-known bireactive compounds used as compatibilizers (Tables 2A, 2B, and 2C). Various functional limits are given for combinations of polymers whose structures might be useful as compatibilizers. Their suitability can only be determined by experimental examination.

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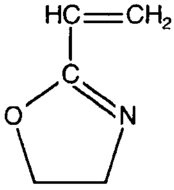
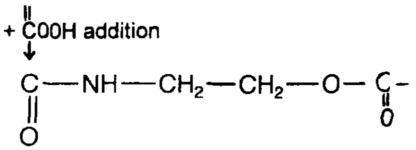
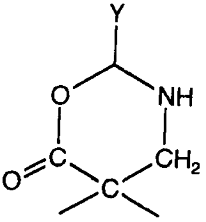
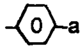
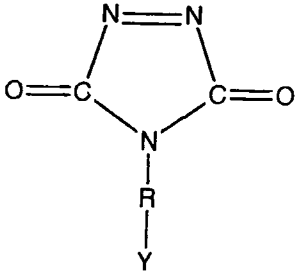
TABLE 2C. Heterocycles

vinyloxazoline 	---------> copolymerization radical addition --------->  $+\ \overset{\|}{\mathrm{C}}\mathrm{OOH}$ addition $-\underset{\|\|}{\overset{}{\mathrm{C}}}(\mathrm{=O})-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\mathrm{C}(\mathrm{=O})-$
2-oxazoline-5-on 	---------> Y-functionality ---------> + HO  -addition [28]
1, 2, 4-triazoline-3,5-dione 	---------> aromates Diels-Alder-addition ---------> Y-functionality [29]

CONCLUSIONS

IPNs offer new material properties, especially when they include a radical polymerization mechanism.

Semi-IPNs show improved morphologies together with thermoplastic processibility.

Preconditions are the solubility of the polymerizable monomer in a second crosslinked polymer and nonmiscibility of the polymers.

Grafting reactions and the mechanism of chain termination decisively influence the properties of IPNs.

Improvement of the concept of reactive blending with bifunctional heteroreactive low-molecular, oligomer, and high-molecular compatibilizers as well as with co-reactive groups of polymer components allow the development of new polymer alloys with outstanding properties.

The influence of molecular parameters, interfacial tensions, zero shearing viscosities, and shearing rates (microrheology) on the morphology of blends and their stability are necessary parameters for theoretical interpretations and properties of polymer alloys.

Technological developments of extruders allow descriptions of material and heat transport processes in investigations of chemical reactions.

Prediction of the material properties based on the morphology of polymer alloys made from two high-modulus polymers is not yet possible. The development of calculation models for energy dissipation in blends between high-modulus (also partially crystalline) polymers will help the question of the necessity of elastic dumping elements.

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