EFFECT OF DYNAMIC CROSSLINKING ON MECHANICAL PROPERTIES OF PP/EPDM BLENDS

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

The effect of dynamic curing of PP/EPDM blends with sulfur and thiuram disulfide systems on their mechanical properties was studied. The results were interpreted using the knowledge of the formation of phase structure in the blends during their melt mixing. It was shown that a sufficiently slow curing reaction is necessary if a high impact strength is to be obtained. Only in such a case, a fine and homogeneous dispersion of elastomer can be formed, which is the necessary condition for high impact strength of the blend. Using an inhibitor of curing in the system and a one-step method of dynamic curing leads to an increase in impact strength of blends. From the comparison of shear modulus and impact strength values, it follows that, at the same stiffness, the dynamically cured blends have higher impact strength than the uncured ones.

Blends of isotactic polypropylene (PP) with ethylene–propylene elastomer (EPDM, EPM) are very important polymer materials. Blends with a low content of ethylene–propylene elastomer are used as high-impact polypropylene. Blends with a high content of ethylene–propylene elastomer can be used as thermoplastic elastomers. It has been shown that the blends prepared by dynamic crosslinking have better end-use properties as thermoplastic elastomers than the blends prepared only by mechanical mixing[1,2]. Similarly, dynamically crosslinked blends with a high content of polypropylene (high-impact thermoplastics) have better properties than uncrosslinked blends[3]. Higher impact strength of dynamically cured blends is a consequence of the fact that, for blends with the composition used in this study, a finer dispersion of elastomeric particles can be achieved for dynamically cured blends than for uncured ones. A great advantage of blends with crosslinked inclusions is better stability of their phase structure during further processing[3].

Preparation and properties of some dynamically cured blends were described in several patents[4–7]. Smaller attention has been focussed on basic research of the dependence of phase structure and properties of such blends on their composition and conditions of dynamic crosslinking. The effect of dynamic curing with dicumyl peroxide on the rheological properties and morphology of EPDM/PP blends was studied[8] and morphological structures of dynamically cured and uncured blends were compared[9]. The present knowledge concerning the preparation, phase structure and properties of the dynamically cured PP/EP(D)M blends is summarized in two reviews[1,2].

It is well known that a very fine dispersion of an elastomer in polypropylene matrix is a necessary condition for the achievement of high-impact strength of PP/EP(D)M blends[10,11]. The occurrence of only a small number of large elastomeric particles substantially decreases the impact strength of these blends[12]. During preparation of the dynamically cured blends, it is necessary to control the formation of a fine and homogeneous dispersion of the elastomer. Dao fulfilled this requirement by a two-step preparation of the blends[3]. On the other hand, EPDM elastomer with a higher content of diene spontaneously cures during mixing with polypropylene[13,14]. As a consequence, the blends have inhomogeneous phase structure and low impact strength[13,14]. The risk of premature curing of the elastomer and formation of inhomogeneous phase structure can be eliminated by crosslinking the elastomer phase by means of the electron beam irradiation after finishing the melt mixing[15,16]. This treatment leads to the fixation of a favourable phase structure but it is not quite convenient for industrial applications.

In this study, an attempt has been made to find such conditions of dynamic curing of the PP/EPDM blends, in which their phase structure is fixed only after obtaining a sufficiently fine dispersion of the EPDM elastomer. Dynamic curing during mixing was studies in the chamber of the Brabender Plasti-Corder. The use of curing systems must not lead to a high curing rate, because in such case, the EPDM elastomer will become highly crosslinked during the starting period of mixing. Further break-up of elastomeric domains having a high density of crosslinks is strongly restricted and a rough dispersion with numerous inhomogeneities in structure is formed. A long induction period of the curing reaction is therefore desirable for preparation of the blends with good mechanical properties.

A sulfur system without accelerator or a system based on tetramethylthiuram disulfide (TMTD) and 2-mercaptobenzothiazole (MBT) leading to poly- or monosulfide crosslinks, respectively, were used as curing systems.

EXPERIMENTAL

Commercial EPDM elastomers Buna AP 331 (Hülls, Germany) and isotactic polypropylene Mosten 52 492 (Chemopetrol, The Czech Republic) were used. Their characteristics can be found in refs[11,12,14].

Mixtures of the elastomer with the curing system components were prepared in the W 50EH chamber of the Brabender Plasti-Corder at 60 °C. The mixtures were kneaded at 20 r.p.m. for 10 min. In sulfur curing, all the components except sulfur, were added in the third minute, sulfur was added to the mixture in the sixth minute of mixing. In thiuram disulfide curing, TMTD and MBT were added in the sixth minute, the other components in the third minute of mixing. Premixes of PP with the curing system components were prepared in the W 50EH chamber at 190 °C, at the kneading rate 30 r.p.m. for 5 min.

Curing characteristics of these rubber mixtures were determined by recording the time dependence of the torque moment during mixing the mixtures at 30 r.p.m. and 190 °C in the W 30H chamber of the Brabender Plasti-Corder. The PP/EPDM blends were mixed and simultaneously dynamically cured in the W 50EH chamber of the Brabender Plasti-Corder at 190 °C and 60 r.p.m. for 10 min. Immediately after the completion of mixing, the material from the chamber was placed in a preheated table press Fontijne. Blends were press-moulded into the shape of plates. Test specimens for the measurement of mechanical properties were cut from the plates.

Impact resistance of the blends was determined by measuring notched impact strength at 0 °C by the Charpy method and determining tensile impact strength at 23 °C. The notched impact strength was determined with a Zwick tester according to ISO R 179/2C using the pendulum with the maximum energy of 4 J. Tensile impact strength was determined with the same Zwick tester which was equipped with a special fixture for test specimens according to DIN 53 448. The maximum energy of the pendulum was again 4 J. All measurements of impact strength of materials were carried out with ten test specimens. The impact strength was calculated as an arithmetic mean of the values obtained using ten test specimens. Standard deviation was about 5 per cent.

The absolute value of complex shear modulus $|G^*|$ was measured with a Rheometrics System Four rheometer at 23 °C and angular frequency 0.1 s^{-1}.

RESULTS AND DISCUSSION

Curing characteristics, the time of minimum (t_{min}) and maximum (t_{max}) of the torque moment, were determined from the time dependence of the torque. The method is clear from Fig. 1. The time t_{min} relates to the induction period of curing reaction. The time t_{max} characterizes the highest degree of crosslinking at which the rubber can be plastically deformed and, hence, can be dispersed in polypropylene matrix. When kneading the rubber mixture for a time longer than t_{max}, a rapid mechanical destruction of the material starts followed by a steep decrease in the torque.

The rate of curing reaction, length of induction period and degree of crosslinking of the rubber component influence the impact strength of the blend. A correct and reproducible determination of the crosslink density in rubber particles dispersed in poly-

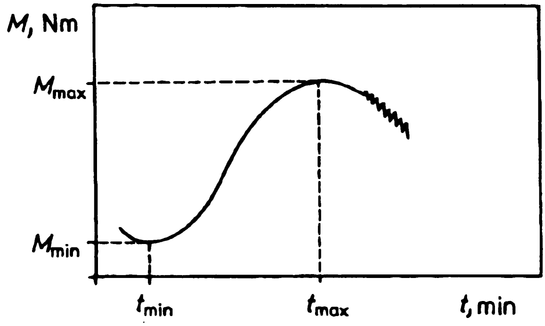

FIG. 1
Time dependence of the torque moment M of rubbers during curing

propylene matrix is very difficult. The values of crosslink density determined for rubber samples cured in the absence of polypropylene are much higher than the values obtained for rubber dispersed in polypropylene matrix and cured dynamically. This is caused by the diffusion of the components of curing system between polypropylene matrix and rubber.

The effect of length of inhibition period on impact strength was studied in dynamically cured PP/EPDM blends containing 15 and 20% rubber; the results are collected in Table I. A sulfur system inhibited by *N*-(cyclohexylthio)phthalimide (Santogard PVI, Monsanto Company, U.S.A.) was used for curing the elastomer phase.

It can be seen from Table I that an inhibitor concentration of 0.3 phr already leads to a double induction period and that the net time of curing ($t_{max} - t_{min}$) increases. An extension of the time period in which the rubber component can be dispersed in polypropylene matrix leads to a considerable increase in the notched impact strength of binary blends. Further extension of the induction period (the net time of curing does not change) leads to an increase in the impact strength of the blend with a lower content of elastomeric phase (85/15), but it does not practically affect the value of notched impact strength of the blend with a higher content of rubber (80/20).

No effect of the curing inhibitor (*N*-cyclohexylthio)phthalimide) was found when the other curing system, based on TMTD and MBT, was used for dynamic curing of the PP/EPDM blends. Curing characteristics of the rubber phase, cured with TMTD–BMT, are affected by the ratio TMTD/MBT in the mixture. The composition effects can be seen in Table II.

From the data in Table II it is clear that, as in the preceding case, the blends dynamically cured with thiuram disulfide systems have a substantially higher impact strength

TABLE I
Effect of the cure inhibitor concentration in the rubber phase[a] of dynamically cured 85/15 and 80/20 PP/EPDM blends on their Charpy notched impact strength, a_k, at 0 °C

CTPI[b] phr	t_{min}[c] min	t_{max}[c] min	$t_{max} - t_{min}$ min	a_k, kJ m^{-2}	
				85/15	80/20
0	0.3	1.7	1.4	13.9	24.1
0.3	0.6	2.9	2.3	14.2	38.2
0.6	1.0	3.3	2.3	17.0	39.4
1.0	2.0	4.3	2.3	19.1	37.7

[a] EPDM Buna AP 331 100, ZnO 3 phr, sulfur 1 phr, stearic acid 1 phr, and CTPI; [b] *N*-(cyclohexylthio)phthalimide; [c] curing characteristics of rubber phase, see Fig. 1.

than the uncured ones. Impact strength of the blends is considerably affected by the ratio TMTD/MBT in the rubber component of the blends. From the point of view of the maximum impact strength of a blend, the most advantageous ratio of TMTD/MBT in the rubber phase is 1 : 1. The optimum concentration of either of these components in the dispersed phase was found to be 1 phr.

The impact strength of the PP/EPDM blends dynamically cured with sulfur or thiuram disulfide systems was compared with that of the uncured blends. Dispersed rubber phase of these blends was cured with the systems described in Table III.

Dependences of the Charpy notched impact strength at 23 °C on concentration of the dispersed phase for uncured and dynamically cured PP/EPDM blends are plotted in Figs 2 and 3.

From the comparison of the concentration dependences for dynamically cured and uncured blends it follows that dynamically cured blends have a substantially higher impact strength. The highest impact strength have the blends cured with the sulfur system. The differences in the impact strength between dynamically cured and uncured blends increase with the increasing rubber content in the blends. Large differences in the impact strength for higher rubber concentrations in the blends suggest the suppression of coalescence of dispersed elastomeric particles to occur, due to their crosslinking.

It follows from Fig. 3 that the tensile impact strength reflects the method of crosslinking of the rubber phase in a blend more sensitively than the notched impact strength. From the comparison of curing characteristics of the blends dynamically cured with sulfur (formulation I) and with TMTD (formulation II, se Tables I and II), it follows that the PP/EPDM blends with a lower rate of curing of EPDM have a higher impact strength. It appears that a slower course of the curing reaction ensures a longer

TABLE II

Effect of composition of the TMTD curing system on the Charpy notched impact strength, a_k, at 0 °C for dynamically cured 85/15 and 80/20 PP/EPDM blends

ZnO phr	TMTD phr	MBT phr	t_{min}[a] min	t_{max}[a] min	$t_{max} - t_{min}$ min	a_k, kJ m^{-2}	
						85/15	80/20
1.5	0.5	0.5	2.0	12.1	10.1	12.4	24.7
3	1	1	1.5	7.2	5.7	15.6	27.3
3	3	1	0.4	3.5	3.1	12.0	17.8
3	3	2	0.4	4.0	3.6	13.8	23.7
3	3	3	1.5	7.0	5.5	17.6	23.7

[a] Curing characteristics of rubber phase, see Fig. 1.

time period in which rubber is being dispersed and simultaneously coalescence of the dispersed rubber particles is efficiently blocked. Lower values of impact strength for the PP/EPDM-II, containing rubber phase crosslinked with TMTD, are not apparently caused by the effect of coalescence of rubber particles, as in the case of uncured blends, but by imperfect dispersion of the rubber phase, caused by a too rapid start of the curing reaction. For dynamic curing of PP/EPDM blends diffusion of curing agents between phases during mixing can be used. If the components of a curing system will diffuse from polypropylene matrix into discrete rubber phase, it can be assumed that the concentration of curing agent will increase more quickly in small than in large rubber particles, because small particles have a higher surface-to-volume ratio. In large particles, the concentration of the curing agent and also crosslink density will increase more slowly than in small particles. In conditions of continuous shear, large particles will be for a longer time in the state in which their further break-up is possible. An assumption can be made that blends with a more homogeneous phase structure and therefore with a higher impact strength will be formed under conditions of diffusion of the curing system components from polypropylene to rubber phase, than with the blends where the rubber component contains the curing system from the very beginning. With the aim to verify this assumption, a set of blends was prepared where the curing system components were premixed either with the polypropylene phase or with the rubber phase, or one-step mixing was used, i.e. all the blend components (including curing system) were charged into the mixing chamber at once. The data correlating the method of blend preparation with the values of the Charpy impact strength at 0 °C are given in Table III.

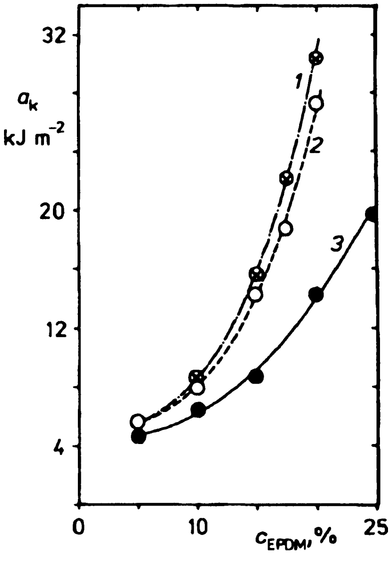

FIG. 2

Dependence of the Charpy notched impact strength, a_k, at 0 °C on rubber concentration c_{EPDM} for dynamically cured blends PP/EPDM-I (*1*) and PP/EPDM-II (*2*) and uncured blend PP/EPDM (*3*) (for EPDM-I and EPDM-II see Table III)

From the data it follows that the blends of polypropylene containing the curing system components (B, E) or mixed by the one-step method have higher impact strength than blends prepared by mixing neat polypropylene and a mixture of rubber and curing system (A, D). Higher values of impact strength for the blends, where the curing system components can diffuse into the rubber phase until mixing is started, manifest a

TABLE III
Effect of the method of preparation of dynamically cured 80/20 PP/EPDM blends on their Charpy notched impact strength, a_k, at 0 °C

Blend	Curing system[a]	Premixed with	a_k, kJ m^{-2}
A	I	EPDM	30.4
B	I	PP	37.7
C[b]	I	–	40.8
D	II	EPDM	27.3
E	II	PP	30.9
F[b]	II	–	31.0

[a] I: ZnO 3 phr, stearic acid 1 phr, sulfur 1 phr, *N*-(cyclohexylthio)phthalimide 0.3 phr; II: ZnO 3 phr, TMTD 1 phr, MBT 1 phr; [b] mixed in one step.

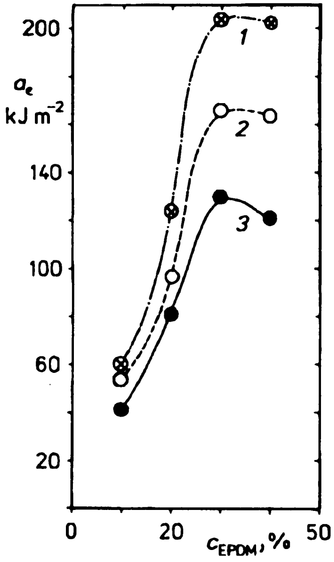

FIG. 3
Dependence of the tensile impact strength, a_ε at 23 °C on rubber concentration, c_{EPDM}, for dynamically cured blends PP/EPDM-I (*1*) and PP/EPDM-II (*2*) and uncured blend PP/EPDM (*3*) (for EPDM-I and EPDM-II see Table III)

favourable effect of the longer period between the start of mixing and the achievement of a high crosslink density in the rubber phase. This result confirmed our assumption on phase structure formation in the PP/EPDM blends during dynamic crosslinking.

For practical application of high-impact polypropylene blends it is useful to know their stiffness. Stiffness of a material can be well characterized by dynamic shear modulus. In Fig. 4, the dependence of tensile impact strength on the absolute value of complex shear modulus, $|G^*|$, is plotted for dynamically cured blend PP/EPDM-I and PP/EPDM-II (cured with formulations I and II, respectively) and for the uncured PP/EPDM blend. From the dependence in Fig. 4, it follows that for obtaining a material with the highest impact strength and the smallest loss of modulus, dynamically cured blends are undoubtedly more advantageous than uncured ones.

CONCLUSIONS

It was shown that the impact strength of the PP/EPDM blends can be significantly improved by dynamic crosslinking of dispersed elastomeric particles. Differences in impact strength of dynamically cured and uncured blends increase with increasing concentration of rubber in the blend. To achieve the maximum level of impact strength of a dynamically cured blend, it is necessary that a high crosslink density should be reached only after obtaining a sufficiently fine dispersion of elastomer in the polypropylene matrix. It was shown that it is advantageous to include an inhibitor of curing into the curing system. The inhibiting effect of *N*-(cyclohexylthio)phthalimide on the

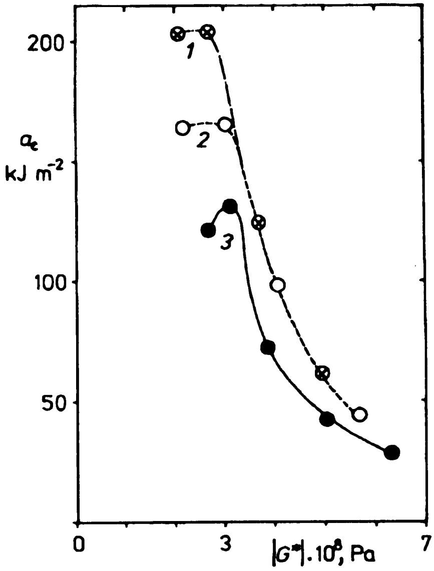

FIG. 4

Dependence of the tensile impact strength, a_t on absolute value of complex shear modulus, $|G^*|$ measured at angular frequency ω = 0.1 s^{-1}) at 23 °C, for dynamically cured blends PP/EPDM-I (*1*) and PP/EPDM-II (*2*) and for uncured blend PP/EPDM (*3*) (for EPDM-I and EPDM-II see Table III) course of curing reaction of EPDM leads to a higher impact strength of dynamically cured PP/EPDM blends.

Another method which can extend the time interval between the start of blend mixing and complete curing of its elastomer phase, is diffusion of the curing system components into rubber phase during blend mixing. It was shown that the one-step method of blend preparation, when all components (including the curing system) are charged into a chamber of a kneader simultaneously at the start of mixing, has an especially favourable effect on impact strength of the blend.

From comparison of dependences of the tensile impact strength for dynamically cured and uncured PP/EPDM blends on the absolute value of complex shear modulus, it follows that dynamically cured blends have substantially higher impact strength at the same level of stiffness. Therefore, dynamically cured blends are undoubtedly more advantageous than uncured ones.

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