Ternary composites of polypropylene/elastomer/calcium carbonate: effect of functionalized components on phase structure and mechanical properties

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(*Received 3 September 1991; revised 24 February 1992; accepted 25 March 1992*)

Investigated ternary composites assume two phase structures: (i) ethylene–propylene elastomer (EPR) and filler are dispersed separately in polypropylene (PP) matrix; (ii) EPR encapsulates filler particles, thus forming a low-modulus interlayer between the filler and PP. Formation of these phase structures is promoted by acid–base interactions when functionalized PP or functionalized EPR is added. PP functionalized with maleic anhydride or acrylic acid enhances the interfacial adhesion between matrix and filler, which prevents dewetting of filler particles and thus accounts for higher yield stress and alteration in failure mechanism. Alternatively, the addition of 5 to 20 vol% of an analogously functionalized EPR results in extensive filler encapsulation, i.e. formation of core–shell particles. The functionalized elastomers have lower molecular mobility manifested in smaller dissipative capacity and higher glass transition temperature. Thus, it seems advisable to combine functionalized species with a standard EPR to ensure good interfacial adhesion and high molecular mobility of the interlayer. Simple model calculations indicate that virtually complete encapsulation of filler can be achieved. Composites with core–shell particles have lower yield stress and higher impact strength than composites with functionalized matrix. These two mechanical properties were found to be inversely proportional in all series of tested composites. However, core–shell particles are apparently less effective impact modifiers than elastomer inclusions, presumably because of improper size (predestined by the size of filler cores) and/or shell modulus.

(Keywords: ternary composites; polypropylene; elastomer; filler; phase structure control; acid–base interactions; mechanical properties)

INTRODUCTION

Particulate composites of polypropylene (PP) containing elastomers as impact modifiers are of ever-increasing interest because both their stiffness and toughness can be partly controlled and materials with balanced mechanical properties can be formulated. Various fillers so far have been employed in ternary polypropylene composites: talc[1–4], calcium carbonate[4–12], mica[13], etc. Toughened polypropylene composites reinforced with short glass fibres have also been investigated[14]. Ethylene–propylene (EPR) or ethylene–propylene–diene (EPDM) copolymers have been mostly used as elastomers, though the effects of polar elastomers[2,3] or block E–P copolymers[11] have also been studied. (Besides, analogous ternary composites of polyethylene/elastomer/filler have been tested[15,16].)

As shown in our earlier papers[7–12], ternary composites of PP may assume two differing phase structures: (i) elastomer and filler particles are separately dispersed in PP matrix; (ii) elastomer encapsulates filler particles thus forming core–shell inclusions. Filler particles forming cores apparently extend the elastomer volume fraction in the composites (instead of stiffening the matrix), so that the moduli of composites may even decrease with increasing filler volume fraction[7]. This finding can be explained by the theory[17] showing that the effect of spherical inclusions on the stiffness of composites depends primarily on elastic properties of the outer layer. However, it is questionable to what extent such core–shell structures enhance the impact resistance of composite materials. For instance, in composites of polystyrene/elastomer interlayer/glass beads, the elastomer did not enhance standard toughness[18]. In general, the formation of an elastomer interlayer between matrix and reinforcements has a far-reaching influence on the mechanical properties of composites, which has been investigated theoretically[17–22] as well as experimentally[18,23–29].

We have found[7,8] that the phase structure of PP/EPR/$CaCO_3$ can be controlled by several factors, the surface treatment of the filler being the most

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0032-3861/92/234961-07

important one. Particles of as-received CaCO$_3$ fillers (without any surface treatment) are extensively encapsulated by the incorporated elastomer (up to 60–70 vol% of the present filler). If the filler surface energy is gradually decreased by stearic acid treatment, fewer particles undergo encapsulation. As soon as the surface treatment (coverage) is complete, only a small percentage of particles remain encapsulated.

The reason for the encapsulation of filler particles by EPR is that the formation of an interlayer between the PP matrix and filler particles, i.e. between components with the lowest and the highest surface energy, reduces the sum of interfacial energies in a volume unit of the composite[8]. However, it is to be noted that even after complete surface treatment the filler still has considerably higher surface energy that the polymer components[8] and should remain encapsulated. In our previous paper[10] it was hypothesized that the elastomer interlayer is torn off the surface-treated filler particles (under the conditions of mixing) due to lower thermodynamic work of adhesion, which results from a reduction of the filler surface energy. Using this concept, it was also possible to explain[8] qualitatively the observed effects of particle size, shear stress and strain rate on the extent of the observed de-encapsulation. The earlier finding[2] that encapsulation of filler particles rises with the polarity of the incorporated elastomer is also in conformity with the proposed concept.

To achieve better control of the phase structure and interfacial adhesion, we have attempted to exploit PP or EPR functionalized with carboxyl groups. In our preliminary communication[12] we reported that more complete encapsulation of calcium carbonate particles can be achieved by using EPR with a small percentage of grafted maleic anhydride or acrylic acid. Grafting PP with these compounds accounts for a complete de-encapsulation and for a strong matrix–filler adhesion. The latter is reflected in enhanced yield stress of ternary composites. The objective of this paper is to determine how the elastic moduli, yield stress and tensile fracture of ternary composites are affected by (i) functionalization of the matrix, (ii) various volume fractions of functionalized elastomers and (iii) varying the concentration of carboxyl groups in the PP or EPR phase when overall volume fractions of elastomer and filler are constant (e.g. in composites PP/EPR/CaCO$_3$ = 60/20/20 vol%).

EXPERIMENTAL

The following species were used for sample preparation.

Polypropylene: Mosten 52492 (Chemopetrol, Czechoslovakia), melt index 4 g/10 min (230°C, 21 N), molar mass $M_w = 450\,000$ g mol^{-1}, crystallinity 63%.

Ethylene–propylene elastomer (EPR): Dutral CO 054 (Dutral, Ferrara, Italy).

Functionalized polypropylene: maleated PP (MPP) with 0.92% of grafted maleic anhydride (a product of the Research Institute of Macromolecular Chemistry, Brno, Czechoslovakia); PP with 6% of acrylic acid (AcPP) – Polybond 1001 (BP Chemicals, UK).

Functionalized elastomers: maleated EPR (MEPR) – Dutral CO 054 with 3.7% of maleic anhydride (a laborabory product of Dutral, Ferrara, Italy); EPR with 6% of acrylic acid (AcEPR) – Polybond 1016 (BP Chemicals, UK); Dutral CO 054 with about 4% of ethylene glycol bismaleate (GEPR) (a laboratory product of the Research Institute of Macromolecular Chemistry, Brno, Czechoslovakia).

Polypropylenes or elastomers with various concentration of acrylic acid (AAc) were prepared by mixing either Mosten with Polybond 1001 or Dutral CO 054 with Polybond 1016.

Filler: microground calcium carbonate Durcal 2 (Omya, Switzerland), average particle diameter 3.6 μm, specific surface area 3.3 m^2 g^{-1}, surface-treated with 0.3 of stearic acid.

The components were mixed in a PLE 651 Brabender Plasticorder (chamber W-50 H, charge volume 47 ml, 200°C, 50 rev min^{-1}, 10 min). Plates 150 mm × 150 mm × 1mm were compression moulded at 200°C (5 min without pressure, 2 min at 6 MPa) and then cooled down (about 100°C min^{-1}) under a pressure of 6 MPa. The cut-off samples for mechanical measurements were annealed at 114°C for 90 min and slowly cooled to room temperature.

Dynamic mechanical measurements were carried out with the aid of a freely oscillating torsional pendulum (frequency about 1 Hz; heating rate about 0.9–1°C min^{-1}). Stress–strain dependences were determined with an Instron Tensile Tester TT-CM at room temperature (dumbbell specimens: gauge length 45 mm, width 10 mm, thickness 1 mm, strain rate 300% min^{-1}). Tensile impact strength (*TIS*) was measured with Zwick Impact Tester at room temperature (impact speed 2.6 m s^{-1}) using the same specimens as for the stress–strain measurements.

RESULTS AND DISCUSSION

Phase structure analysis

Temperature dependences of storage and loss shear moduli of ternary composites consisting of standard (non-functionalized) polymer components are shown in *Figure 1*. The loss modulus peaks located at about −3°C and −65°C correspond to the glass transitions of PP and EPR, respectively, detected at a frequency of about 1 Hz. The flat maximum of the loss modulus at about −150°C is induced by local rotatory motions of short backbone segments in both polymers[30]. While the T_g of the matrix is constant, a small drop in the T_g of EPR with decreasing elastomer volume fractions, v_e, can be observed. The latter effect has been ascribed[31] to negative compression, which acts on elastomer particles due to their faster shrinkage in comparison with the PP matrix. (For this reason, the T_g values of various

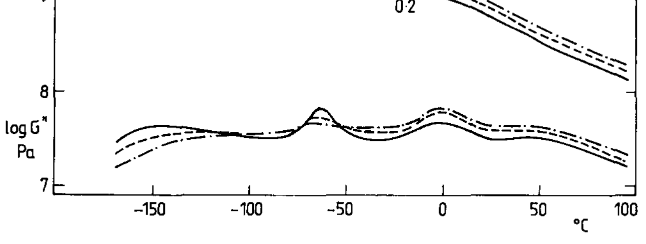

Figure 1 Temperature dependence of the storage and loss shear moduli of composites polypropylene/elastomer/calcium carbonate (20 vol%). Elastomer: Dutral CO 054 (volume fractions indicated)

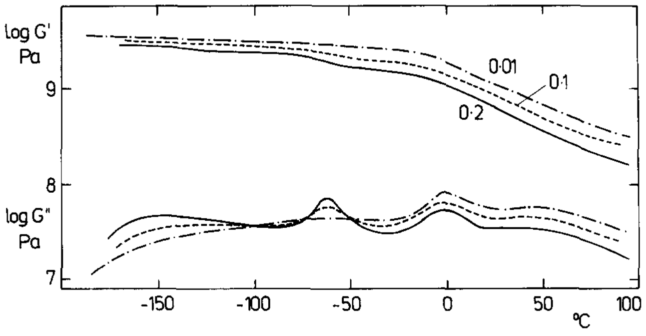

Figure 2 Temperature dependence of the storage and loss shear moduli of composites polypropylene/elastomer/calcium carbonate (20 vol%). Elastomer: Dutral CO 054 (volume fraction indicated). Polypropylene modified by maleic anhydride (0.002 wt% of maleic anhydride related to incorporated filler)

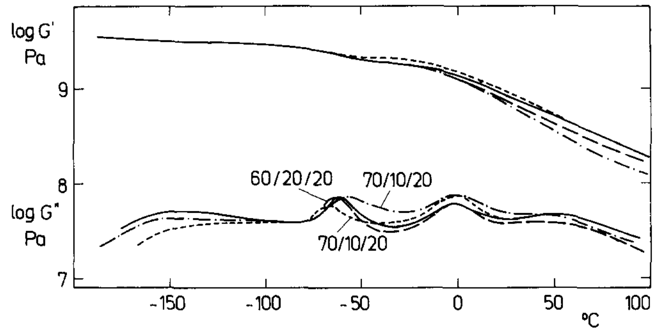

Figure 3 Temperature dependence of the storage and loss shear moduli of composites polypropylene/elastomer/calcium carbonate (20 vol%). Elastomer: Dutral CO 054. Concentration of acrylic acid in polypropylene: composites 60/20/20, 6% (——), 1.2% (— — —); composites 70/10/20, 1.2% (------), 0%, but 0.48% of AAc in elastomer (—·—)

elastomers should be compared at the same elastomer volume fraction in composites.)

To strengthen the matrix–filler interaction and, consequently, to suppress any encapsulation of the dispersed filler by the elastomer, PP functionalized with maleic anhydride (*Figure 2*) or acrylic acid (*Figure 3*) was added to the PP matrix (the concentrations of maleic anhydride were selected on the basis of our previous results[18,32]). The patterns in *Figure 2* can be regarded as an upper limit for G' and a lower limit for G'' because any encapsulation of filler particles by elastomer makes the G' drop at T_g(EPR) more profound and magnifies the concomitant loss modulus peak (filler cores apparently 'extend' the elastomer). Obviously, the used fractions of MPP or AcPP do not appreciably affect the T_g of the matrix. The glass transition loss peaks of the elastomers in the 60/20/20 composites in *Figures 1* and *2* are of equal size, which means that the filler and elastomer are dispersed separately also in the composites consisting of standard polymers, obviously due to filler surface treatment, as has been demonstrated earlier[7,8].

Contrasting phase structures, presumably with a maximum achievable encapsulation of filler particles with the elastomer (at given volume fractions of both dispersed phases), were prepared by using maleated EPR (MEPR) or EPR with acrylic acid (AcEPR) (*Figures 4* and *5*). The functionalized elastomers were used as received (not diluted by a standard elastomer) in order to assure their strong adhesion to the calcium carbonate filler. These elastomers exhibit higher T_g than the standard elastomer, i.e. -41°C or -42°C, respectively. Furthermore, the loss peaks become lower and broader, reflecting a broader distribution of relaxation times. To evaluate the effect of functionalization on the extent of relaxation processes and/or the extent of encapsulation, it is necessary to select a suitable parameter sensitive to these changes. SEM micrographs of the phase structures of the ternary composites (containing functionalized components) published in our previous paper[12] have presented convincing evidence of complete encapsulation of filler particles by functionalized elastomers or of de-encapsulation in composites with functionalized PP matrix. However, SEM can hardly be used for quantitative estimation of the extent of encapsulation. Dynamic mechanical data seem to be more convenient for this purpose because they can be confronted with predictions of a series of models related to various phase structures[31].

The extent of molecular motions that set in over a temperature (or frequency) interval of a glass or secondary transition can be characterized with the aid of 'relaxation strength' defined as[33]:

$$S_\mathrm{l} = (G_\mathrm{u} - G_\mathrm{r})/G_\mathrm{r} = G'(-90°\mathrm{C})/G'(-30°\mathrm{C}) - 1 \qquad (1)$$

where the unrelaxed, G_u, and relaxed, G_r, moduli are approximated – in the case of the glass transition of the elastomers used – by values at -90°C and -30°C, respectively, which are well below and above the glass transition temperature. It is to be noted, however, that S_l thus defined is always greater than zero owing to a modulus decrease produced by thermal expansion, even if no relaxation process is involved. In multiphase

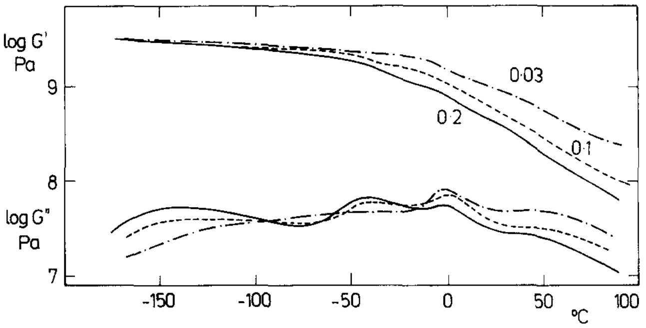

Figure 4 Temperature dependence of the storage and loss shear moduli of composites polypropylene/maleated elastomer/calcium carbonate (20 vol%). Elastomer volume fractions indicated in the figure

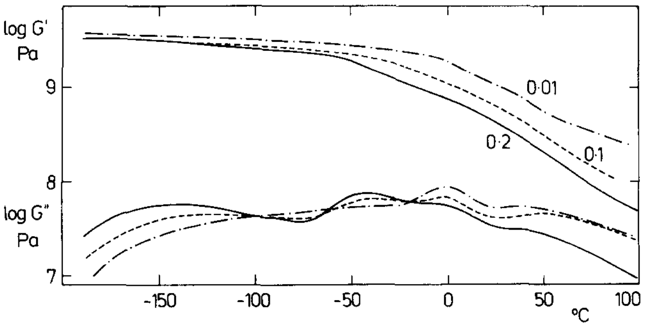

Figure 5 Temperature dependence of the storage and loss shear moduli of composites polypropylene/Polybond 1016/calcium carbonate (20 vol%). Elastomer volume fractions indicated in the figure

Table 1 Calculated values of the elastomer glass transition relaxation strength in ternary composites polypropylene/elastomer/filler = 60/20/20

Apparent elastomer vol. fract.	0.20	0.30	0.35	0.40
Apparent filler vol. fract.	0.20	0.10	0.05	0.00
Amount of encapsulated filler (%)	0	50	75	100
$S_I = G'(-90°C)/G'(-30°C) - 1$	0.48	0.68	0.81	1.41

systems, S_I is proportional to the volume fraction of the component undergoing the transition.

S_I of various phase structures can be semiquantitatively calculated by using existing models predicting the shear modulus of particulate composites or blends. The Kerner–Nielsen equation[34] has been shown[7] to be convenient for the description of the effects of fillers and elastomers on the modulus of ternary composites. Model calculations can be done in two steps: (1) inclusions of an elastomer are embedded in PP; (2) filler particles are added to the two-phase matrix under the assumption that they do not interact with the elastomer inclusion already present, so that both dispersed phases affect the resulting modulus independently. Under these assumptions, the following equation can be used to calculate the shear modulus of ternary composites:

$$G_{tc} = G_m \frac{1 - F_e B_e v'_e}{1 + A_e B_e v'_e} \frac{1 + A_f B_f v_f}{1 - F_f B_f v_f} \qquad (2)$$

where

$$A_e = (8 - 10\nu_m)/(7 - 5\nu_m)$$
$$B_e = (G_m/G_e - 1)/(G_m/G_e + A_e)$$
$$F_e = 1 + [(1 - V_e)/V_e^2]v'_e$$
$$v'_e = v_e/(1 - v_f)$$
$$A_f = (7 - 5\nu_{me})/(8 - 10\nu_{me})$$
$$B_f = (G_f/G_{me} - 1)/(G_f/G_{me} + A_f)$$
$$F_f = 1 + [(1 - V_f)/V_f^2]v_f$$
$$\nu_{me} = \nu_m(1 - v'_e) + \nu_e v'_e$$

Here ν is the Poisson ratio, V is the maximum packing fraction, and indices m, e, f, me stand for PP, elastomer, filler and two-phase matrix. $V_f = V_e = 0.64$ has been used, which corresponds to random packing of single-size spheres. (This value of V_e cannot be achieved in real blends owing to phase inversion; however, it was obtained for PP/EPR and PE/EPR blends by extrapolation[31].) v'_e and ν_{me} represent the actual volume fraction of elastomer in the matrix and the Poisson ratio of the two-phase matrix prior to the addition of filler.

To calculate S_I related to the elastomer glass transition, we used the following experimental data[7,8,31,32] for the polymers at −90°C and −30°C: $G_m = 2.13$, 1.72 GPa; $G_e = 510$, 5 MPa; $\nu_m = 0.3$, 0.35; $\nu_e = 0.3$, 0.499; $V_e = V_f = 0.64$; $G_f = 11$ GPa. The PP matrix is then marked with an apparent $S_I = 0.21$, which is a result of the modulus drop due to thermal expansion, not due to a relaxation process. The 60/20/20 composite (*Table 1*) with separated elastomer and filler is characterized by a theoretical value of $S_I = 0.48$, which is in good accord with experimental data that range from 0.48 to 0.54 (*Tables 2* and *3*) for the composites with no functionalized component or with functionalized PP matrix. Thus, filler encapsulation in these composites can be regarded as negligible.

A quantitative estimate of the percentage of encapsulated filler particles from the results of dynamic mechanical measurements is rather difficult because the modulus of the core–shell particles is not known. Under a simplifying assumption that their modulus is equal to that of the elastomer itself, the apparent volume fraction of the elastomer (extended by filler) can be calculated. *Table 1* shows how the theoretical values of S_I for the 60/20/20 composites rise with advancing encapsulation. The experimental values found for MEPR, AcEPR and GEPR were 0.79, 0.86 and 0.72 (*Table 2*), which corresponded to 75% encapsulation, though a maximum degree of encapsulation was expected. However, as the actual modulus of core–shell particles is likely to be somewhat higher than G_e, the actual percentage of encapsulated filler particles is higher than that predicted in this simplified way. This discrepancy may also be partly ascribed to lower molecular mobility and higher modulus of functionalized elastomers.

To diminish the effect of lower molecular mobility and to estimate approximately the minimum concentration of carboxyl groups, necessary for complete filler

Table 2 Effect of functionalized components on mechanical properties of composites polypropylene/elastomer/calcium carbonate (20 vol%)

Elastomer (vol%)	s_{yc}[a] (MPa)	e_{uc}[b] (%)	*TIS*[c] (kJ m^{-2})	S_I[d]
Dutral CO 054, no functionalized component				
0	23.5	50	70	
1	24.7	90	56	
3	22.2	24	54	
5	21.2	250	140	0.29
10	19.2	350	266	0.33
15	16.9	160	257	
20	14.4	290	454	0.53
Dutral CO 054, 0.2% maleic anhydride (Manh) in PP matrix				
0	37.0	7.5	37	
1	30.8	7.5	73	0.21
3	33.6	10	80	
5	31.8	7.5	73	
10	27.5	9.5	70	0.35
15	22.5	35	192	
20	20.7	70	199	0.54
Dutral CO 054 with 3.6% MAnh				
1	25.5	120	87	
3	24.8	110	87	0.25
5	24.2	130	104	
10	21.6	80	131	0.47
15	18.8	110	149	
20	17.3	120	190	0.79
Polybond 1016 with 6% acrylic acid				
1	23.4	55	54	0.24
2	23.6	40	57	0.27
5	23.7	23	76	0.34
10	20.5	21	82	0.50
20	15.9	39	139	0.86
Dutral CO 054 with 3.9 wt% of ethylene glycol bismaleate				
1	33.4	7.3	57	0.23
3	30.3	8.5	64	
5	30.0	9.0	72	
10	25.3	17	71	0.38
15	20.7	100	133	
20	16.7	280	271	0.72

[a] Yield stress of composites
[b] Strain at break of composites
[c] Tensile impact strength of composites
[d] Relaxation strength associated with the elastomer glass transition

Table 3 Effect of the acrylic acid concentration in polypropylene or in elastomer on mechanical properties of ternary composites

F.c.[a] (%)	s_{yc}[b] (MPa)	e_{uc}[c] (%)	*TIS*[d] (kJ m^{-2})	S_l[e]	G'(22°C) (MPa)
Composites with AcPP (Polybond 1001), composition 60/20/20					
20	18.6	26	137	0.48	974
25	19.8	36	164	–	901
65	19.9	41	208	–	935
100	20.2	11	151	0.48	938
composition 70/10/20					
20	24.8	3.6	–	0.33	1040
25	25.5	17	–	–	1068
65	27.6	13	–	0.31	1072
Composites with AcEPR (Polybond 1016), composition 60/20/20					
8	12.6	250	277	1.22	386
27	13.1	250	181	1.29	399
75	13.0	220	264	1.24	405
100	16.3	46	127	0.96	452
composition 70/10/20					
8	16.7	100	138	0.51	602
27	16.8	190	117	–	–
75	17.9	120	131	0.58	654
100	19.6	40	96	0.55	650

[a] Percentage of functionalized component (containing 6% of acrylic acid) in PP matrix or in EPR elastomer

[b] Yield stress

[c] Strain at break

[d] Tensile impact strength

[e] Relaxation strength of the elastomer glass transition

encapsulation, we have prepared four series of samples (*Table 3*, *Figure 6*) with varying concentration of acrylic acid either in the elastomer or in the PP matrix. If 25% of the AcEPR is replaced by standard EPR, both the storage and loss moduli dependences on temperature are markedly modified in the −80°C to 30°C region: (i) G' drops deeper; (ii) the glass transition loss peak is magnified; (iii) the T_g decreases from −44°C to −55°C. All these effects provide evidence of increasing molecular mobility of the elastomer interlayer. Such intensification of relaxation processes can occur only if the amount of filler 'extending' the elastomer phase is not perceptibly diminished. If the number of encapsulated filler particles was perceptibly reduced, it would cause an increase of the modulus and reduction of the intensity of relaxation phenomena[5–7]. (In our previous publication[7], we confronted the room-temperature modulus with model calculations to estimate the percentage of encapsulated filler particles.)

A further decrease in the concentration of AAc in EPR (down to 0.5%) does not appreciably affect the storage modulus in the interval −90°C to −30°C, while the loss peak rises slightly and shifts down to −60°C (*Figure 6*, *Table 3*). The values of S_l for the 60/20/20 composite approaches the limit 1.41 calculated under the assumption of total encapsulation of filler particles with the standard elastomer. The modulus G'(22°C) also decreases, which can be explained by 'softening' of the core–shell inclusions. Thus, the added standard EPR plays a dominant role in the elastic properties of core–shell inclusions, in accord with model calculations[17], which show that elastic properties of a particle are primarily determined by those of the outer layer. Our results, in conformity with SEM micrographs[12], indicate that the functionalized EPR ensures encapsulation of filler particles, while the standard elastomer imparts higher molecular mobility to the outer shell layer. The arbitrarily selected lowest concentration of AAc, i.e. 0.5% (8% of Polybond 1016 in the elastomer phase), is obviously sufficient to achieve complete encapsulation.

On the other hand, $S_l = 0.48$ (*Table 3*) and $T_g = -65$°C of non-functionalized elastomer in the 60/20/20 composites are not affected by the concentration of acrylic acid in the PP matrix, which was to be expected because the carboxyl groups are concentrated at the matrix/filler interface and cannot influence the molecular mobility of the separately dispersed elastomer. *Figure 3* reveals that dilution of AcPP from 6% to 1.2% of AAc does not have any profound effect on the dynamic mechanical behaviour of the composites, indicating that the phase structure has not been changed. Besides, as the molecular mobility of PP is rather limited owing to a high crystalline fraction, the effect of AcPP on the extent and temperature location of the glass transition loss peak is hardly perceptible.

For illustration, two 70/10/20 composites with contrasting phase structures are included in *Figure 3*. The sample containing 1.2% of AAc in PP matrix displays a small loss maximum at −67°C because hardly any encapsulation can occur in this case. However, if 0.48% of AAc is present in the EPR phase, the loss peak becomes larger than that of the 60/20/20 sample with the standard elastomer. These results clearly document the effect of AAc, leading to extensive encapsulation and, consequently, to an increase in apparent volume fraction of the elastomer due to the formation of core–shell structures.

The data obtained so far allow the following tentative conclusion to be made: if a sufficient amount of elastomer – in relation to filler content – is present in a composite, extensive encapsulation of filler can be achieved with the aid of added carboxylated EPR. The core–shell particles affect the elastic properties of the composites in a similar way as the pure elastomer. Small amounts of elastomers (1–3%) do not show any noticeable effect on elastic properties, e.g. no perceptible loss peak can be seen, even if the tendency to encapsulation is supported by high concentrations of carboxyl groups. Obviously, the encapsulation is far from complete and/or the elastomer layer is too thin to control the elastic properties of the core–shell inclusion. (The small effects on the elastic behaviour were expected and low fractions of elastomers were used in an attempt to improve the impact properties of composites.)

Yield stress and ultimate properties

Yield stress is an important characteristic of polymeric materials because it indicates the limit of allowable tensile

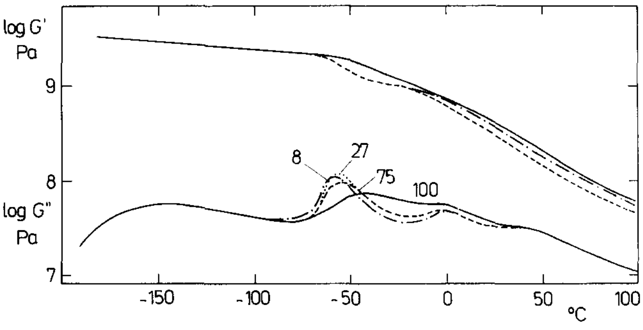

Figure 6 Temperature dependence of the storage and loss shear moduli of composites polypropylene/elastomer/calcium carbonate 60/20/20. Concentrations (%) of Polybond 1016 in the elastomer phase (batch with Dural CO 054) are indicated

Table 4 Effect of the concentration of maleic anhydride on mechanical properties of polypropylene

Amount of of maleic anhydride (%)	s_y[a] (MPa)	e_y[b] (%)	*TIS*[c] (kJ m^{-2})
0	33.2	15	104
0.01	37.0	14	86
0.40	37.6	9.5	80
0.92	37.6	8.7	55

[a] Yield stress
[b] Yield strain
[c] Tensile impact strength

stress in most applications. The yield stress of the PP matrix is $s_{ym} = 33.2$ MPa (*Table 4*); the addition of 20 vol% of calcium carbonate causes the yield stress to drop to 23.5 MPa (*Table 2*), which is a result of poor interfacial adhesion between matrix and filler (in the absence of functionalized PP). Similarly, the yield stress is also reduced by elastomers[31]. As all interfaces present in the standard ternary composites (i.e. PP/EPR, PP/calcium carbonate and EPR/calcium carbonate) are too weak to sustain stress transfer between phases, the effects of filler and elastomer on the yield stress are reported to be approximately additive[6,35].

The decrease in the yield stress of ternary composites, s_{yc}, brought about by dispersed components, can be partly prevented by using functionalized PP (*Table 3*). The value of s_{yc} of the 60/20/20 species increases from 14.4 MPa for the standard PP (*Table 2*) to 20.2 MPa for the matrix containing 6 wt% of AAc (as-received Polybond 1001) or to 20.7 MPa for the matrix containing 0.2 wt% of MPP. However, a substantial increase in s_{yc} is achieved at a concentration of about 1.5 wt% of AAc in the matrix. Similarly, 0.2% of maleic anhydride (related to the amount of incorporated filler) ensures good adhesion at the matrix/filler interface and prevents dewetting of filler particles[32]. For instance, the composite with 20 vol% of CaCO$_3$ retains the same yield stress as the matrix itself (*Table 2*), i.e. about 37 MPa. (A small percentage of MPP in standard PP can cause a slight increase in s_{ym} (*Table 4*); a likely reason has been sought[32] in the effects of MPP on nucleation and crystallization processes.) In ternary composites with functionalized PP, the yield stress is then predominantly decreased by rising elastomer content because of poor PP/EPR interfacial adhesion. Thus, s_{yc} remains higher by 5–6 MPa than that of analogous standard composites (*Table 2*) with separately dispersed filler and elastomer.

On the other hand, the addition of functionalized EPR, which accounts for complete encapsulation in the 60/20/20 composites, does not result in the lowest yield stress of about $s_{yc} = 14$ MPa (characterizing non-functionalized composites with separated dispersed phases), but somewhat higher values ranging from 15.9 to 17.3 MPa can be observed for $v_e = v_f = 0.2$ (*Table 2*). This difference can hardly be due to enhanced adhesion between EPR and CaCO$_3$ inside the core–shell inclusions; rather, it may be ascribed to alterations in the micromechanics of yielding in the presence of relatively voluminous core–shell inclusions.

The tensile impact strength (*TIS*) of PP matrix drops by about 20 or 50%, if 0.01 or 0.1% of maleic anhydride is incorporated (*Table 4*). Obviously, the morphological changes leading to higher yield stress bring about a drop in *TIS*. Incorporation of 20 vol% of calcium carbonate in the standard PP accounts for a slight decrease in *TIS* (*Table 2*). However, if the amount of maleic anhydride in the PP matrix equals 0.2 wt% of incorporated calcium carbonate, *TIS* is appreciably lowered in the whole range of elastomer volume fractions used in this paper, i.e. 1 to 20 vol%. The reason can be seen in the fact that the dewetting of filler particles is prevented (as demonstrated by an increment of yield stress and by a drop of strain at break, *Table 2*) and adhesive fracture if partly replaced by cohesive fracture, as has been found earlier[32].

Composites with core–shell particles containing functionalized elastomers have lower *TIS* and e_{uc} than composites with the standard matrix and elastomer (*Tables 2* and *3*) where elastomer and filler particles are dispersed separately (due to filler surface treatment[7,8]) and where all interfaces are weak. (The strain at break can also be regarded as an approximate measure of the work to fracture because its changes dominate over the concurrent opposite changes of yield stress.) Moreover, increasing concentration of AAc in the elastomer phase is manifested – along with slightly rising modulus and yield stress – in decreasing *TIS* and strain at break. This tendency may partly be caused by step-by-step drop of molecular mobility with increasing percentage of carboxyl groups. The differences between the properties of these two types of composites are very small at 1 or 3 vol% of elastomers, but they become more pronounced with rising elastomer content. We can infer that small concentrations of elastomers do not have any beneficial influence on *TIS* regardless of whether they are dispersed separately or are bound to the filler surface. At higher EPR volume fractions, separately dispersed phases of EPR and filler are apparently more effective impact modifiers than core–shell inclusions of the same overall composition (in the 60/20/20 composites, the volume fraction of core–shell inclusions is twice as high as that of the elastomer itself). There are several likely causes of this phenomenon: (i) the core–shell particle size predestined by the size of filler cores and its elastic properties are less convenient for interconnection of local microzones of yielded matrix than smaller particles of elastomers; (ii) as the tendency for encapsulation diminishes with increasing size of filler particles[8], the fraction of big filler particles (which reduce the critical failure stress) retains its detrimental effect on ultimate properties; (iii) the interparticle distance, which is believed[36] to control fracture processes during impact, is much larger in composites (of a given composition) with core–shell particles.

CONCLUSIONS

Ternary composites PP/EPR/CaCO$_3$ assume two contrasting phase structures: (i) ethylene–propylene elastomer and filler particles are dispersed separately in PP matrix; (ii) elastomer encapsulates filler particles, thus forming a low-modulus interlayer between the filler and PP matrix. Formation of these phase structures is promoted by the addition of functionalized PP or of functionalized EPR, respectively, due to acid–base interactions with the filler surface. PP functionalized by maleic anhydride or acrylic acid enhances the interfacial adhesion between matrix and filler, which prevents dewetting of filler particles and thus accounts for the relatively higher yield stress and lower impact strength. Alternatively, the addition of an analogously functionalized elastomer to a standard EPR results in extensive filler encapsulation, i.e. formation of core–shell particles.

Functionalization of elastomers leads, however, to lower molecular mobility manifested in smaller dissipative capacity and higher glass transition temperature. A comparison of dynamic mechanical experimental data with simple model calculations indicates that virtually all filler particles are encapsulated by the elastomer phase if the volume fraction of the elastomer approaches that of the filler, e.g. in the 60/20/20 composites. About 0.5% of acrylic acid in EPR ensures complete filler encapsulation in these composites. Small fractions of elastomers, i.e. 1 to 3 vol%, do not appreciably affect mechanical properties of composites. Composites with core–shell particles have lower yield stress and higher tensile impact strength than composites with functionalized matrix, i.e. with separately dispersed phases and strong matrix–filler adhesion. However, the highest tensile impact strength has been found for composites with separately dispersed filler and standard elastomer particles where the separation is achieved with the aid of filler surface treatment (low interfacial adhesion does not prevent the dewetting of filler particles in the course of deformation). Thus, a tentative conclusion can be drawn that the core–shell particles are less effective impact modifiers than elastomer inclusions, presumably because of improper size (predetermined by the size of filler cores), larger interparticle distance and detrimental effect of big filler particles, which are difficult to encapsulate. The tensile impact strength and yield stress are inversely proportional in all series of tested composites, irrespective of structural reasons.

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