

Polymer 41 (2000) 1529–1539

# Impact fracture study of multicomponent polypropylene composites

Sz. Molnár<sup>a,b</sup>, B. Pukánszky<sup>a,b,\*</sup>, C.O. Hammer<sup>c</sup>, F.H.J. Maurer<sup>c</sup>

<sup>a</sup>Department of Plastics and Rubber Technology, Technical University of Budapest, H-1521 Budapest, P.O. Box 92, Hungary <sup>b</sup>Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary <sup>c</sup>Department of Polymer Technology, Chalmers University of Technology, S-41296 Gothenburg, Sweden

Received 14 January 1999; received in revised form 25 March 1999; accepted 8 April 1999

#### Abstract

Standard impact resistance and fracture mechanics characteristics of 17 three-component PP/BaSO<sub>4</sub>/elastomer composites and reference compounds were determined as a function of composition, dispersed phase structure and particle size of the filler. The results showed that the effect of structure is very similar on all characteristics and it influences also the temperature dependence of impact resistance. Structure was controlled by the application of functionalized polymers. The extent of encapsulation of the filler particles was estimated by calculations using the Lewis–Nielsen model and comparing calculated and measured moduli. Impact resistance increased with higher degree of encapsulation, but the crucial factor determining toughness was the prevailing micromechanical deformation process and the deforming volume. Separate distribution of the components and weak adhesion of the filler to the matrix lead to a better impact resistance than does significant encapsulation. The results prove that while stiffness of these multicomponent systems is basically determined by the extent of embedding, the correlation of toughness and structure is much more complex. The dominating role of micromechanical processes and the numerous factors influencing them (adhesion, embedding, particle size, elastomer properties, etc.) explain the contradictory results published in the literature. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Multicomponent PP composites; Impact fracture; Dispersed morphology

# 1. Introduction

Multicomponent polypropylene (PP) composites are used in large quantities in the automotive industry, amongst other applications also for the preparation of bumpers [1-3]. They usually contain an elastomer to improve the fracture, and especially the impact resistance of PP, and a filler to increase stiffness. This obvious route to improve stiffness and toughness simultaneously created much interest both industrially and academically in a number of polymers [4–11]; numerous studies have been carried out on such and similar systems in preceding years [9-16]. The results clearly showed that two types of structures can form in three-component polymer/elastomer/filler systems: separate dispersion of the minor components (elastomer, filler) in the matrix polymer [9,10,15,17,18] and embedding of the filler by the elastomer [10–12,16,18]. In polymer/polymer/filler composites a third structure was also observed where the

interphase was enriched in the filler particles [19,20]. The prevailing structure is primarily determined by thermodynamics and by surface characteristics, but it is also influenced by the rheological properties of the components and that of the composite, as well as by processing conditions [11,21,22].

Although much effort has been put into the determination of structure-property correlations in multicomponent polymer systems, much less is known about their impact resistance, in spite of the practical importance of this property. Hardly any systematic study has been carried out and the published results are contradictory. Van der Wal [23-25] carried out extensive investigations on the fracture of PP and elastomer modified PP, but their results do not help to explain the relationship between structure and impact resistance in such three-component systems. Scott et al. [26] carried out Izod impact testing combined with infrared analysis to determine the extent of embedding and its effect on impact resistance. Composites with an embedded structure possessed slightly increased impact strength and modulus, but the authors suggested further optimization of composition, component properties and technology to obtain composites with considerably improved stiffness and toughness. Faulkner [27,28] studied the impact behavior

<sup>\*</sup> Corresponding author. Department of Plastics and Rubber Technology, Technical University of Budapest, H-1521 Budapest, P.O. Box 92, Hungary. Tel.: +36-1-463-2015; fax: +36-1-463-3474.

*E-mail addresses:* pukanszky.mua@chem.bme.hu (B. Pukánszky); fm@pol.chalmers.se (F.H.J. Maurer)

Polymer	Producer	Abbreviation	MFI (g/10 min)	Molecular weight (kg/mol)		Density (g/cm <sup>3</sup> )
				M <sub>n</sub>	$M_{ m w}$	-
Stamylan P16M10	DSM	PP	5.5 <sup>a</sup>	31.0	216	0.91
Hostaprime HC5	Hoechst	MAPP	_	8.4	25	0.90
Exxcellor PE808	Exxon	EPR	5.0 <sup>b</sup>	34.7	173	0.87
Exxcellor VA1810	Exxon	EPMA	7.5 <sup>b</sup>	28.5	120	0.87

Table 1 The most important characteristics of the polymers used in the study

<sup>a</sup> 230°C/21.2 N.

<sup>b</sup> 230°C/100 N.

of PP/mica/elastomer composites and tried to optimize stiffness and toughness. Although he derived useful guidelines for product development, he could not determine unambiguous correlations between structure and properties. Numerous other papers also mention impact resistance of multicomponent systems, but the final conclusion is rather contradictory. Several states that fracture toughness improve with increasing extent of embedding [10,17,18,26,29], while others found the opposite, a composite where embedding was promoted by the introduction of a functionalized elastomer had lower impact strength than one with separate dispersion [30]. In another study the effect of embedding on impact resistance was shown to depend also on composition: at low filler content separate dispersion proved to be better, while at high, the embedded structure had a better impact resistance [31].

The structure-property correlations of PP/BaSO<sub>4</sub>/elastomer composites determined on injection molded bars were reported in a previous paper [32]. Beside component properties and adhesion, the particle size of the filler was also shown to influence properties significantly. In this paper attention is focused on the correlation of the same factors and the impact resistance of the composites. Fracture mechanics characteristics and standard Charpy impact resistance were determined and they are analyzed in view of structure-related phenomena, i.e. embedding and aggregation of small filler particles.

# 2. Experimental

The Stamylan P16M10 grade PP homopolymer of DSM, The Netherlands, was chosen as matrix polymer, while Exxelor PE 808 of Exxon was used as the elastomer (EPR) component. Preferential adhesion was achieved by the use of functionalized components: a maleinated PP (Hostaprime HC5, Hoechst, MAPP) was applied to improve the adhesion of the filler to the PP phase, while a maleinated EPR elastomer (Exxelor VA1810, EPMA) was selected to promote encapsulation. The most important properties of

Table 2 Composition of the investigated composites and reference compounds

Abbreviation	Elastomer		Filler		MAPP <sup>a</sup> (vol.%)	
	Туре	Amount (vol.%)	Amount (vol.%)	Size (µm)		
1a	EPR	20	10	1.0	_	
1b	EPR	20	10	1.0	1.0	
1c	EPR	20	10	1.0	2.5	
1d	EPR	20	10	1.0	5.0	
2a	EPMA	20	10	1.0	-	
2b	EPMA	20	10	0.7	-	
2c	EPMA	20	10	0.1	_	
3a	_	_	_	_	0	
3b	_	_	_	_	2.5	
3c	_	_	_	-	5.0	
4a	_	_	10	1.0	_	
4b	-	_	10	0.7	_	
4c	_	_	10	0.1	_	
5a	EPR	20	_	_	_	
5b	EPR	30	_	-	_	
5c	EPMA	20	_	_	-	
5d	EPMA	30	-	-	_	

<sup>a</sup> Volume percentage of the PP matrix.

Table 3
Fracture characteristics of the studied three-component PP/BaSO <sub>4</sub> /elastomer composites and reference compounds

Composite	LEFM parameters		Notched Charpy impact (kJ/m <sup>2</sup> ) at			
	$K_{\rm Ic} ({\rm N/mm}^{3/2})$	$G_{\rm Ic}~({\rm kJ/m^2})$	+23°C	-20°C	-40°C	
1a	$106.1 \pm 5.3$	$5.54 \pm 0.48$	$12.48 \pm 0.79$	$2.74\pm0.09$	$2.26\pm0.07$	
1b	$80.8 \pm 6.1$	$3.29 \pm 0.21$	$6.42\pm0.25$	$1.55\pm0.03$	$1.45 \pm 0.04$	
1c	$80.9\pm5.7$	$2.96\pm0.25$	$6.37\pm0.13$	$1.53\pm0.07$	$1.55 \pm 0.10$	
1d	$76.5 \pm 5.1$	$3.37\pm0.32$	$4.62\pm0.25$	$1.53\pm0.07$	$1.53\pm0.07$	
2a	$89.2 \pm 3.5$	$6.61\pm0.59$	$9.73\pm0.12$	$2.97\pm0.08$	$1.63\pm0.06$	
2b	$103.3 \pm 4.9$	$12.29\pm0.87$	$27.99\pm0.79$	$4.99\pm0.27$	$2.97\pm0.14$	
2c	$73.7 \pm 4.6$	$4.79\pm0.39$	$6.35\pm0.17$	$2.73\pm0.05$	$1.55 \pm 0.05$	
3a	$65.3 \pm 2.7$	$2.79 \pm 0.16$	$3.52\pm0.06$	$1.44 \pm 0.18$	$1.22 \pm 0.08$	
3b	$63.8 \pm 2.3$	$2.88\pm0.07$	$3.39 \pm 0.21$	$1.23\pm0.03$	$1.28\pm0.15$	
3c	$61.4 \pm 3.7$	$2.78\pm0.10$	$3.37 \pm 0.15$	$1.21 \pm 0.08$	$1.24 \pm 0.06$	
4a	$87.5 \pm 3.0$	$3.57\pm0.19$	$4.72\pm0.27$	$1.59\pm0.06$	$1.67\pm0.03$	
4b	$87.9\pm6.7$	$3.15 \pm 0.19$	$5.67\pm0.32$	$1.60 \pm 0.03$	$1.58 \pm 0.03$	
4c	$76.2 \pm 5.4$	$2.46\pm0.18$	$2.71\pm0.07$	$1.64\pm0.01$	$1.61\pm0.04$	
5a	$71.8 \pm 4.2$	$3.31 \pm 0.93$	$8.22\pm0.17$	$2.22\pm0.02$	$2.23\pm0.03$	
5b	$87.5 \pm 7.6$	$5.68 \pm 3.82$	$12.14 \pm 0.41$	$2.31 \pm 0.12$	$2.10\pm0.05$	
5c	$75.1 \pm 3.5$	$4.35 \pm 0.23$	$6.30 \pm 0.46$	$2.04 \pm 0.11$	$1.92\pm0.07$	
5d	$77.4\pm4.9$	$4.59\pm1.00$	$10.32\pm0.43$	$2.19\pm0.06$	$2.03\pm0.05$	

the polymers are listed in Table 1. Molecular weights were determined by GPC in TCB at 135°C by using PE standards. Three precipitated BaSO<sub>4</sub> fillers all produced by Sachtleben, Germany, were selected for the study. They differed in average particle size, the Blanc Fixe F grade had a particle size of 1.0  $\mu$ m, the Blanc Fixe Micro grade was somewhat smaller (0.7  $\mu$ m), while the particles of the Sachtoperse HU had the smallest dimensions (0.1  $\mu$ m).

Altogether 17 composites and reference systems were investigated; their composition is compiled in Table 2. The composites were homogenized in a Werner–Pfleiderer co-rotating twin screw extruder with an L/D ratio of 32 and screw diameter of 30 mm at 220°C. Mechanical testing was carried out on tensile bars ( $150 \times 10 \times 4 \text{ mm}^3$ ) injection molded with a Battenfeld BA 200/50 CD machine.

Scanning electron microscopic analysis was performed with a Hitachi S570 apparatus on samples taken from the fracture study. Notched Charpy impact strength was determined at a rate of 2.9 m/s on  $80 \times 10 \times 4$  mm<sup>3</sup> specimens cut from the injection molded tensile bars. Instrumented impact testing was carried out at the same rate with a span of 40 mm.  $K_{\rm lc}$  was determined from the maximum load, while the technique of Plati and Williams [33] was used for the determination of  $G_{\rm lc}$ . For this measurement the specimens were notched to different depths by a saw and sharpened by an industrial razor blade. Notch depth varied between 0.7 and 7.0 mm. Because of the high rate applied, dynamic effects occurred during fracture, which were compensated by the use of mechanical damping. The damper used was a 1 mm thick silicon rubber plate fixed to the sensor [34].

# 3. Results and discussion

In industrial practice standard impact tests (Charpy, Izod)

are used most frequently for the characterization of the impact resistance of polymers and composites. However, these methods supply size-dependent fracture characteristics, thus the application of fracture mechanics is more and more encouraged [35]. Well-established procedures exist only for rigid materials, where the principles of linear elastic fracture mechanics (LEFM) can be applied, but strict conditions must be satisfied even in this case: the geometric parameters of the specimens must exceed certain minimum values [35]. Both standard and fracture mechanics measurements have been carried out in this study in order to compare them. Moreover, notched Charpy impact resistance was determined at three practically relevant temperatures, at room temperature ( $+23^{\circ}$ C), as well as at -20 and  $-40^{\circ}$ C.

## 3.1. Fracture characteristics

The fracture characteristics determined by various methods are compiled in Table 3. Although the direct comparison of the large number of data is difficult, a few facts become evident at the first glance. The application of maleinated polypropylene (MAPP) decreases fracture resistance, while the use of EPMA increases it. Composites prepared with the filler of the smallest particle size possess the lowest fracture resistance and the selected elastomers improve impact strength only moderately. All fracture properties of a few composites, like 1a and especially 2b, exceed those of the others considerably, indicating the important effect of embedding and particle size.

As it was indicated earlier, LEFM can be applied only under strict conditions, thus a validity check was carried out for the measured quantities,  $K_{Ic}$  and  $G_{Ic}$ . The direct application of the principles developed for homogeneous materials showed that apparently none of the composites and reference compounds satisfies the required size criteria: the



Fig. 1. Load vs. deflection trace of a two-component  $PP/BaSO_4$  composite containing 10 vol.% filler of 1.0  $\mu$ m average particle size (composite 4a).

calculated minimum required thickness of the specimens (B) would range from 7 to 50 mm, while the actual size was 4 mm. However, it was shown earlier [36] that in heterogeneous systems yield stress ( $\sigma_y$ ) must be corrected by the effective load-bearing cross-section, since  $\sigma_y$  usually decreases in such composites even when their stiffness increases [37,38]. Correction of minimum thickness both for the effective load-bearing cross-section and the different rate of the tensile and impact measurements showed that all composites satisfy LEFM conditions: the corrected minimum thickness varied between 0.5 and 1.9 mm.

Although the corrected thicknesses indicated valid LEFM conditions, the results must be treated with care. Most of the composites failed in a brittle manner, indeed, yielding



Fig. 2. Increased plastic deformation of a PP/elastomer blend containing 30 vol.% EPR (composite 5b).



Fig. 3. Correlation of strain energy release rate ( $G_{Ic}$ ) and notched Charpy impact strength (+23°C) for the studied composites and reference compounds. Symbols: ( $\bullet$ ) PP(MAPP)/BaSO<sub>4</sub>/EPR, ( $\blacksquare$ ) PP/BaSO<sub>4</sub>/EPMA, ( $\times$ ) PP(MAPP), ( $\blacktriangle$ ) PP/BaSO<sub>4</sub>, ( $\bullet$ ) PP/elastomer.

triangular load vs. deflection traces similar to the one presented in Fig. 1. However, the introduction of the elastomer led to increased deflection and the PP/elastomer blends underwent larger plastic deformation (Fig. 2). Comparison of all data and the instrumented impact traces showed that all composites satisfied LEFM conditions except the PP/elastomer blends containing 30 vol% EPR or EPMA.

All properties, including fracture characteristics, obviously depend on the structure of the composites. The similar dependence of the various fracture properties in Table 3 on composition indicates that structure influences them more or less the same way. Further proof of this similarity is given in Fig. 3, where  $G_{Ic}$  is plotted against the notched Charpy impact resistance measured at +23°C. Although some deviations can be observed from the straight line drawn, these are not significant and they are in the range of the standard deviation of the measurements. Similar correlations could be observed also among the other quantities measured, including  $K_{\rm Ic}$ , although the deviations from the general tendency were occasionally larger than in Fig. 3. These results clearly corroborate previous observations showing that most fracture characteristics are influenced by structure similarly, any of them can be used in such studies or for the optimization of composition and structure [36].

#### 3.2. Temperature

The effect of temperature on impact resistance is very important in practice especially in such applications as the bumper. Sufficient toughness must be maintained also at subambient temperatures and impact resistance is usually



Fig. 4. Temperature dependence of notched Charpy impact strength for selected composites; ( $\bullet$ ) PP/EPR/BaSO<sub>4</sub> (1.0 µm), 1a; ( $\blacksquare$ ) PP/EPMA/BaSO<sub>4</sub> (0.7 µm), 2b; ( $\blacktriangle$ ) PP, 3a.

measured at temperatures as low as  $-40^{\circ}$ C. The combined effect of temperature and structure is obviously interesting both for theory and practice. The notched Charpy impact resistance of three selected composites is plotted against temperature in Fig. 4. The results indicate that the influence of temperature is stronger in the composites which contain an elastomer. The impact resistance of these systems increases considerably above  $-20^{\circ}$ C; the glass transition temperature of the elastomer seems to be around this temperature at the high deformation rate used. Valid LEFM conditions and the related constraint may also influence the deformation of the samples and the apparent shift of  $T_{e}$ . These results completely correspond to expectations



Fig. 5. Correlation of notched Charpy impact resistance measured at two different temperatures. Symbols are the same as in Fig. 3.

and are in accordance with earlier observations. However, structure plays an important role as well, since the replacement of EPR by EPMA leads to a significant increase of impact strength at all temperatures. The influence of structure on notched Charpy impact resistance is practically the same at all temperatures. This is proved also in Fig. 5, where  $a_n$  values, defined as the fracture energy normalized to the ligament area, measured at +23°C and -40°C, respectively, are plotted against each other.

### 3.3. Effect of embedding

Earlier analysis of the experimental data showed that two structure-related phenomena determine properties in the investigated composites, embedding of the filler by the elastomer and aggregation of small filler particles [32]. In order to discuss the effect of embedding we must have some idea about its extent. The simplest way to estimate embedding is the comparison of the measured modulus of the composites to values calculated under the assumption of additive effects, i.e. for separately dispersed components, by the application of an appropriate model. The use of such calculations have been demonstrated before and the changes in the calculated extent of embedding showed always a strong correlation with factors influencing structure and properties (surface treatment of the filler, use of functionalized polymers, particle size, etc.) [12,30,39–41].

By using the above-mentioned principles the extent of embedding was calculated for our seven three-component systems (composites 1a-d, 2a-c). The Lewis-Nielsen, or modified Kerner equation was used as before [39-41]. The results of the calculations are collected in Table 4. The amount of encapsulated filler was calculated from, and is proportional to, the difference of the measured and calculated Young's moduli. In accordance with our previous results, only a small amount of the filler is embedded in the PP/BaSO<sub>4</sub>/EPR composite and when MAPP is used; the prevailing structure is separate dispersion of the components in this case. The introduction of EPMA, on the other hand, leads to increased embedding. The large specific surface area of the smallest particles and their aggregation tendency lead to a smaller extent of encapsulation, though. The results presented in Table 4 are in accordance with expectation and with previous observations, and they seem to reflect the extent of encapsulation, indeed. However, attention must be called here to the fact that they are not at all absolute values, but indicate only the relative extent of embedding.

Since the amount of embedded filler expresses the changes in the structure in quantitative terms, fracture toughness ( $G_{Ic}$ ) was plotted against this quantity in Fig. 6. Although a clear tendency can be observed in the figure shown by the thin solid line, i.e. toughness increases with the extent of embedding, it is obvious that encapsulation alone does not explain the variation of impact resistance: other factors must also influence it. Increased adhesion of

Composite	Elastomer	Filler, $d$ (µm)	MAPP (%)	Modulus (GPa)		Embedded filler (%)
				Calculated	Measured	
1a	EPR	1.0	0	1.84	1.70	10
1b	EPR	1.0	1.0		1.66	
1c	EPR	1.0	2.5	1.79	1.69	7
1d	EPR	1.0	5.0		1.68	
2a	EPMA	1.0	_		1.14	67
2b	EPMA	0.7	_	1.81	1.10	73
2c	EPMA	0.1	_		1.33	48

Estimation of the amount of encapsulated filler in three-component PP/BaSO<sub>4</sub>/elastomer composites

the filler and the polymer leads to decreased impact strength (1b-d) and aggregation has a similar effect (2c), while impact resistance exhibits a maximum as a function of particle size (2b).

The effect of all factors influencing impact resistance is demonstrated well in Fig. 7. Low impact resistance and a maximum as a function of particle size, is measured in the two-component PP/BaSO<sub>4</sub> composites. These materials are very brittle (see Fig. 1), the relatively large particles debond easily from the matrix (Fig. 8), fracture resistance is low.

The introduction of EPR leads only to a small increase in impact resistance when also some MAPP is added (see composite 1b). For practical purposes, the selection of this elastomer is not appropriate, since its incorporation does not result in significant impact modification. Strong adhesion between the filler and the matrix PP was previously shown to lead to decreased impact resistance [7,42]. The role of adhesion is further demonstrated by the behavior of composite 1a. The absence of MAPP lead to a significant increase of  $a_n$ , as the comparison of composites 1a and 1b shows (see Table 3 and Fig. 7). The improved impact



Fig. 6. Effect of embedding on the fracture toughness ( $G_{Ic}$ ) of three-component PP/elastomer/BaSO<sub>4</sub> composites ( $\bullet$ ) PP/EPR/BaSO<sub>4</sub> (MAPP), ( $\blacksquare$ ) PP/EPMA/BaSO<sub>4</sub>.

strength is caused by the increased deformability of the sample, deflection of this compound is considerably larger than that of composite 4a (compare Figs. 1 and 9). As the SEM micrograph of Fig. 10 shows the dominating deformation process is debonding in this material. Both the filler particles and the elastomer detach themselves from the matrix during fracture as shown by the clean surfaces of the particles and the numerous holes left behind. The filler and the elastomer can be hardly distinguished from each other, but the particles of the latter have a more regular shape and smoother surface. The above-presented results call attention to the importance of micromechanical deformation processes. The improved adhesion of the filler and PP hinders debonding, thus the filler cannot contribute to energy absorption in composites 1b-d, while it absorbs considerable impact in composite 1a. Changing particle size has a twofold effect, it changes the energy necessary for debonding [43,44] and influences the extent of aggregation [45].

The other correlation in Fig. 7, and especially the impact resistance of composite 2b, demonstrates the combined



Fig. 7. Notched Charpy impact resistance  $(+23^{\circ}C)$  of the composites plotted against the particle size of the filler; ( $\blacktriangle$ ) PP/BaSO<sub>4</sub>, ( $\textcircled{\bullet}$ ) PP(MAPP)/EPR/BaSO<sub>4</sub>, ( $\textcircled{\bullet}$ ) PP/EPR/BaSO<sub>4</sub>, ( $\textcircled{\bullet}$ ) PP/EPR/BaSO<sub>4</sub>.



Fig. 8. SEM micrograph taken from the fracture surface of composite 4a,  $PP/BaSO_4$  (1.0  $\mu m).$ 

effect of encapsulation and particle size, of which the latter is dominant. The debonding of EPMA is obviously easier than that of the filler covered by MAPP and the elastomer somewhat increases plastic deformation as well (see composites 1c and 2c). However, in the present system, the contribution of the filler to improved impact resistance is larger than that of the elastomer and separate dispersion leads to a better combination of properties as shown by the comparison of composites 1a and 2a. In the case of composite 2b deformability increases further (Fig. 11) compared to the previously presented load vs. deflection traces (see Figs. 1 and 9). The larger deformation is accompanied by a more



Fig. 9. Load vs. deflection trace of composite 1a, PP/EPR/  $BaSO_4\,(1.0~\mu m),$  0% MAPP.

homogeneous fracture surface (Fig. 12), where a smaller number of debonded filler particles and fewer holes can be observed than in the previous SEM micrograph (see Fig. 10). Obviously, the combined effect of evenly distributed smaller particles and the higher extent of encapsulation leads to a synergetic increase of impact resistance [18,45]. Apparently the volume affected by the micromechanical deformation processes—mainly debonding and some shear yielding—is much larger in composite 2b than in any of the other materials.

It seems to be appropriate to discuss here the possible relevance of the recently published approach of Bartczak et al. [46-48] developed for the explanation of improved impact resistance in crystalline polymers. This approach is based upon the theory of Wu [49,50], as well as on the observations of Muratoglu et al. [51]. It states that preferential orientation of crystallites occurs near the surface of heterogeneities and below a critical interparticle distance the overlapping of oriented layers leads to the slipping of weak crystalline planes. They conclude that the properties of the inclusions are of secondary importance and the deformation of the matrix polymer absorbs most of the energy during fracture. This latter statement is obviously true, however, the approach leaves the effect of several factors unexplained in our case. Decreasing particle size and separate dispersion of the components should increase fracture resistance, since both decrease interparticle distance. The poor performance of the smallest particles might be explained by the disadvantageous effect of aggregation, but the strong influence of encapsulation (see Fig. 6) cannot. The size of the dispersed particles increases, while their number decreases as a result of encapsulation. Both should lead to decreased fracture resistance, which is clearly not the



Fig. 10. Fracture surface of composite 1a, debonding of filler and elastomer.

case. Further questions could be raised about the effect of adhesion, the different influence of the elastomer and the filler, the role of stress distribution, interphase formation, etc. The approach clearly needs further refinement in order to answer these questions. Nevertheless, the results presented earlier prove that in multicomponent polymer systems the main factor determining impact resistance is the type and extent of the prevailing micromechanical deformation process. As a consequence, a composite with either a separately distributed or an embedded structure may possess higher impact resistance than the other, which explains the contradictory observations published in the literature.

# 3.4. Aggregation

The possible role of aggregation was mentioned several times during the previous discussion. Published results prove that aggregates act as fracture initiation sites and decrease strength and fracture resistance [52,53]. In the present series of experiments the composites containing the smallest filler particles exhibit clearly lower impact strength than similar composites differing only in particle size (see Table 3). The presence of aggregates in composites and their role in the fracture process is demonstrated excellently in Fig. 13. A large aggregate can be clearly distinguished in the SEM micrograph of the fracture surface and it is also clear that the crack propagated through it. Similar formations can be seen also in Fig. 14 showing the fracture surface of composite 2c. Although a considerable part of the filler is embedded into the elastomer (Table 4), the presence of aggregates on the fracture surface is unambiguous.

# 4. Conclusions

Impact fracture characterization of various three-component PP/BaSO<sub>4</sub>/elastomer composites showed that the effect of structure is very similar on all characteristics. Also the temperature dependence of impact resistance is influenced by structure. In accordance with previous results published in the literature, the structure of such multicomponent systems can be controlled by the application of functionalized polymers. The use of MAPP led to separate distribution of the components, while the introduction of EPMA promoted embedding of the filler into the elastomer. The



Fig. 11. Load vs. deflection correlation of composite 2b, PP/EPMA/BaSO<sub>4</sub>  $(0.7 \mu m)$  measured in instrumented impact test.



Fig. 12. SEM micrograph taken from the fracture surface of composite 2b.

extent of encapsulation was estimated by calculations using the Lewis–Nielsen model and comparing calculated and measured moduli. Although impact resistance increased with higher degree of encapsulation, the crucial factor determining toughness was the prevailing micromechanical deformation process and the deforming volume. Separate distribution of the components and weak adhesion of the filler to the matrix led to a better impact resistance than significant encapsulation at a particle size of  $1.0 \,\mu\text{m}$ . Optimum performance was achieved by the encapsulation and even distribution of 0.7  $\mu$ m BaSO<sub>4</sub> particles in PP. The results clearly show that while stiffness of these multicomponent systems is basically determined by the extent of embedding, the correlation of toughness and structure is much more complex. The dominating role of micromechanical processes and the numerous factors influencing them (adhesion, embedding, particle size, elastomer properties, etc.) explain the contradictory results published in the literature.



Fig. 13. Large aggregate located on the fracture surface of the two-component  $PP/BaSO_4$  composite (4c) containing the filler of the smallest particle size (0.1  $\mu$ m).



Fig. 14. Fracture surface of composite 2c, PP/EPMA/BaSO<sub>4</sub> (0.1 µm); presence of aggregates.

#### Acknowledgements

The authors gratefully acknowledge the National Swedish Board for Industrial and Technical Development (NUTEK) as well as the National Scientific Research Fund of Hungary (OTKA grant no T 016500) and the Varga József Fund of the Faculty of Chemical Engineering, TUB for the financial support of this work. We are also grateful to V. Blomquist for her assistance in the preparation of the composites, as well as to L.I. Kulin and M. Björklund for the GPC measurements.

#### References

- JP 07118462, Impact-resistant and rigid automobile bumpers made of polyolefin compositions, Mitsubishi Kagaku Kk, Japan; Nissan Motor (CA 123: 288904).
- [2] EP 580069, Injection molding compositions for automobile bumpers, Sumitomo Chemical, Japan; Toyota Jidosha Kabushiki Kaisha (CA 122: 57706).
- [3] JP 02251547, Polyolefin compositions for automobile bumpers, Idemitsu Petrochemical, Japan (CA 114: 165755).
- [4] Peiffer DG, Nielsen LE. J Appl Polym Sci 1973;23:2253.
- [5] Speri WM, Patric GR. Polym Engng Sci 1975;15:668.
- [6] Dekkers MEJ, Dortmans JPM, Heikens D. Polym Commun 1983;26:145.
- [7] Galeski A, Kalinski R. In: Martuscelli E, Palumbo R, Kryszewsky M, editors. Polymer blends, processing, morphology, properties, 1. New York: Plenum, 1980. p. 431.
- [8] Comitov PG, Nicolova ZG, Siméonov IS, Naidenova KV, Siarova AD. Eur Polym J 1984;20:405.
- [9] Dao KC. J Appl Polym Sci 1982;27:4799.
- [10] Stamhuis JE. Polym Compos 1984;5:202.
- [11] Stamhuis JE. Polym Compos 1988;9:72.
- [12] Scott C, Ishida H, Maurer FHJ. In: Ishida H, Koenig JL, editors. Composite interfaces, New York: Elsevier, 1986. p. 177.

- [13] Rusznák I, Bertalan Gy, Anna P, Marosi Gy, Molnár I. Plaste Kautsch 1985;32:254.
- [14] Marosi Gy, Bertalan Gy, Anna P, Rusznák I. J Polym Engng 1993;12:33.
- [15] Kolarík J, Lednický F. In: Sedlácek B, editor. Polymer composites, Berlin: Walter de Gruyter, 1986. p. 537.
- [16] Pukánszky B, Kolarík J, Lednický F. In: Sedlácek B, editor. Polymer composites, Berlin: Walter de Gruyter, 1986. p. 553.
- [17] Kitamura H. In: Hayashi T, Kawata K, Umekawa S, editors. Progress in Science and Engineering of Composites, Tokyo: Japanese Society of Composite Materials, 1982. p. 1787.
- [18] Nakagawa H, Sano H. Polym Prepr 1985;26:249.
- [19] Sumita M, Sakata K, Asai S, Miyasaka K, Nakagawa H. Polym Bull 1991;25:265.
- [20] Hammer CO, Maurer FHJ. Polym Compos 1998;19:116.
- [21] Stamhuis JE. Polym Compos 1998;9:280.
- [22] Pukánszky B, Tüdos F, Kolarík J, Lednický F. Polym Compos 1990:11:98.
- [23] van der Wal A, Mulder JJ, Thijs HA, Gaymans RJ. Polymer 1998;39:5467.
- [24] van der Wal A, Mulder JJ, Gaymans RJ. Polymer 1998;39:5477.
- [25] van der Wal A, Mulder JJ, Oderkerk J, Gaymans RJ. Polymer 1998;39:6781.
- [26] Scott C, Ishida H, Maurer FHJ. J Mater Sci 1987;22:3963.
- [27] Faulkner DL. J Appl Polym Sci 1988;36:467.
- [28] Faulkner DL. Polym Mater Sci Engng 1988;59:436.
- [29] Jancar J, DiBenedetto AT. J Mater Sci 1995;30:2438.
- [30] Kolarík J, Jancar J. Polymer 1992;33:4961.
- [31] Chiang WY, Yang WD, Pukánszky B. Polym Engng Sci 1992;32:641.
- [32] Hammer CO, Maurer FHJ, Molnár Sz, Pukánszky B, Control of the structure and properties of barium sulphate-filled blends of polypropylene and ethylene propylene copolymer. J Mater Sci, submitted for publication.
- [33] Plati E, Williams JG. Polym Engng Sci 1975;15:470.
- [34] Bezerédi A, Vörös Gy, Pukánszky B. J Mater Sci 1997;32:6601.
- [35] Williams JG. Fracture mechanics of polymers, Chichester: Ellis Horwood, 1984.
- [36] Pukánszky B, Maurer FHJ, Boode J-W. Polym Engng Sci 1995;35:1962.

- [37] Pukánszky B, Turcsányi B, Tüdos F. In: Ishida H, editor. Interfaces in polymer, ceramic, and metal matrix composites, New York: Elsevier, 1988. p. 467.
- [38] Pukánszky B. In: Karger-Kocsis J, editor. Polypropylene. Structure, blends and composites, 3. London: Chapman and Hall, 1995. p. 1.
- [39] Kolarík J, Lednický F, Pukánszky B. In: Matthews FL, Buskell NCR, Hodgkinson JM, Morton J, editors. Proceedings of the 6th ICCM/2nd ECCM, vol. 1. London: Elsevier, 1987:452.
- [40] Kolarík J, Lednický F, Pukánszky B. Compos Polym 1990;3:271.
- [41] Pukánszky B, Tüdos F, Kolarík J, Lednický F. Compos Polym 1989;2:491.
- [42] Pukánszky B, Maurer FHJ. Polymer 1995;36:1617.
- [43] Vollenberg P, Heikens D, Ladan HCB. Polym Compos 1988; 9:382.

- [44] Pukánszky B, Vörös Gy. Compos Interfaces 1993;1:411.
- [45] Michler GH, Tovmasjan JM. Plaste Kautsch 1988;35:73.
- [46] Bartczak Z, Argon AS, Cohen RE, Weinberg M. Polymer 1999;40:2331.
- [47] Bartczak Z, Argon AS, Cohen RE, Weinberg M. Polymer 1999;40:2347.
- [48] Bartczak Z, Argon AS, Cohen RE, Kowalewski T. Polymer 1999;40:2367.
- [49] Wu S. Polymer 1985;26:1855.
- [50] Wu S. J Appl Polym Sci 1988;35:549.
- [51] Muratoglu OK, Argon AS, Cohen RE, Weinberg M. Polymer 1995;36:921.
- [52] Pukánszky B, Fekete E. Polym Polym Compos 1998;6:313.
- [53] Svehlova V, Poloucek E. Angew Makromol Chem 1987;153:197.