HANS-JOACHIM RADUSCH[1)*)], PETER DOSHEV[1)], GERD LOHSE[2)]

Phase behavior and mechanical properties of heterophasic polypropylene — ethylene/propylene copolymers systems

Summary — In the following study the interactions between the phases, the morphology development and the resulting mechanical performance of the heterophasic polypropylene—ethylene/propylene copolymers (PP/EP) systems were investigated with respect to EP composition and matrix and dispersed phase molecular weights. It was shown that the compatibility between the components forming the matrix and the dispersed phase, as well as the dimensions of the dispersed domains were primarily controlled by ethylene content in EP. The decrease of ethylene content in ethylene/propylene copolymer was found to produce a strong refinement of the dispersed particle size and accordingly a reduction of the brittle to ductile transition temperature (T_{BDT}) of the materials, as defined by conventional impact testing. However, the general fracture energy level was found to be governed by the molecular weights of the blend components. Increasing molecular weight of EP as well as of PP showed a beneficial effect on the toughness of the investigated blends.

Key words: polypropylene, ethylene/propylene copolymers, blends, heterophasic systems, dynamic mechanical analysis, morphology, impact strength.

The continuous growth and extension of the application field of the impact modified polypropylene requires improved understanding of the structure-property relationship concerning these materials. The microstructure as well as the compatibility of the phases have been considered playing the decisive role for the morphology development and subsequently for the end-use properties of the blends of polypropylene with ethylene-propylene rubber [1]. This is also valid and even amplified for the materials where the structure heterogeneity of the dispersed phase should also be taken into account. In this study the phase behavior and impact properties of polypropylene heterophasic polypropylene-ethylene/propylene copolymers (PP/EP) systems were investigated with respect to EP composition as well as to PP-matrix and dispersed phase (EP) molecular weights. The compatibility and the interactions between the matrix and the dispersed phase were discussed in connection with the observed mode and state of dispersion of EP and the resulted mechanical performance of the materials.

Table 1. Materials characteristics[*)]

Materials		MFR_{matrix} g/10 min	MFR_{total} g/10 min	XS wt. %	IV (of XS) dl/g	D_w µm
symbols	ethylene content in EP (calculated values) wt. %					
PP/EP82	82	~20	4.7	20.4	3.4	4.50
PP/EP70	70	~20	8.1	20.5	2.4	1.59
PP/EP50	50	~20	9.35	20.3	2.5	1.40
PP/EP30	30	~20	11.1	19.2	2.4	1.02
PP/EP17	17	~20	9.7	25.2	1.6	0.20
PP/EP$_L$	50	~25	20	17.2	1.5	0.40
PP/EP$_M$	50	~25	11.5	18.8	2.4	1.37
PP/EP$_H$	50	~25	7.9	18.2	4.5	1.32
PP$_L$/EP	50	~85	44	13.6	2.5	1.60
PP$_M$/EP	50	~30	21	13.6	2.7	1.35
PP$_H$/EP	50	~22	12	13.7	3.3	1.30

[*)] MFR_{total} — melt flow rate of the blend, determined according to ISO 1133; MFR_{matrix} — melt flow rate of the matrix; XS — xylene soluble fraction; IV — intrinsic viscosity value, measured in decalin at 135 °C; D_w — weight average particle diameter.

EXPERIMENTAL

Materials

The heterophasic systems used in this study are research materials provided by Dow Chemical. They were

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[1)] Martin Luther University Halle-Wittenberg, Institute of Materials Science, D-06099 Halle (Saale), Germany.

[2)] Dow Olefinverbund GmbH, D-06258 Schkopau, Germany.

[*)] Corresponding author: e-mail: Hans-Joachim.Radusch@iw.uni-halle.de

produced by a sequential polymerization process in a reactor cascade by means of commercial fourth generation Ziegler-Natta catalyst. The characteristics of the investigated materials are summarized in Table 1.

The molecular parameters of PP matrix and EP are reflected by MFR_{matrix} and intrinsic viscosity (*IV*) values, while the indexes L, M and H indicate low, medium and high molecular weight respectively. The amount of ethylene/propylene copolymer is roughly illustrated by the amount of xylene soluble fraction (XS). For the sake of systematics, only a single parameter was varied within each of the series, namely ethylene content in EP, molecular weight of EP and molecular weight of PP.

After the synthesis step the materials were compounded with a standard additive package in PlastiCorder PL2100 single screw extruder (Brabender) with screw speed of 100 rpm and barrel zone temperatures from 210 to 230 °C. The test specimens were produced using BA 100 injection molding machine (Battenfeld) at barrel temperature of 200 °C and mold temperature of 40 °C.

Method of testing

The mechanical relaxation behavior of the blends and the glass transition temperatures (T_g) of the components were measured by means of Mark II dynamic mechanical analyzer (Rheometric Scientific). Rectangular bars with dimensions 40 × 10 × 4 mm were tested using torsion pendulum at frequency of 1 Hz and heating rate of 1 K/min. The storage (*G'*) and loss moduli (*G''*) as well as the loss tangent (tan δ) were determined in the temperature range of -100 to 150 °C.

Impact testing was performed using conventional Charpy device type 5102 (Zwick) equipped with 4 J pendulum according to DIN EN ISO 179. In order to obtain the brittle to ductile transition (T_{BDT}), the test was performed at least at five different temperatures for each material and the temperature of step growth of notched impact strength (a_{CN}) was found.

Morphology observations were accomplished by means of scanning electron microscope JSM 6300 (Jeol). Micrographs were taken from sections of the injection molded dumbbell specimens. The sections were subjected to permanganic etching in order to degrade the amorphous ethylene/propylene copolymer and were gold-coated before viewing.

RESULTS AND DISCUSSION

Phase behavior and dynamic mechanical properties

In previous studies [2—4] it has been demonstrated that the structure of the "in reactor" produced blends was rather complex, comprising a wide range of fractions of different compositions. The main constituents of these materials could be identified as polypropylene matrix, amorphous ethylene/propylene copolymer and, depending on EP composition, also some amount of crystallizable ethylene/propylene copolymer. The latter is favored at high ethylene contents and was found to influence strongly the phase behavior and interfacial adhesion between the matrix and the dispersed phase.

In this study, the compatibility and the interaction between the blend components were evaluated by means of dynamic mechanical analysis (DMA). The effect of EP composition on the mechanical relaxation profile (*G'*, *G''* and tan δ) of the heterophasic systems is demonstrated in Fig. 1. The effect of ethylene content on glass transition temperature of EP part of the studied heterophasic blends defined as a maximum in tan δ (see Fig. 1) is presented in Fig. 2a in comparison with the literature data for neat ethylene/propylene copolymers [5, 6]. As indicated, the two curves fit reasonably well, exhibiting a minimum value at intermediate EP compositions. For higher ethylene content an increase in glass transition temperature is observed. This result suggests that T_g of ethylene-rich copolymer seems to refer more likely to β transition of PE-LD or even to α transition of PE-HD.

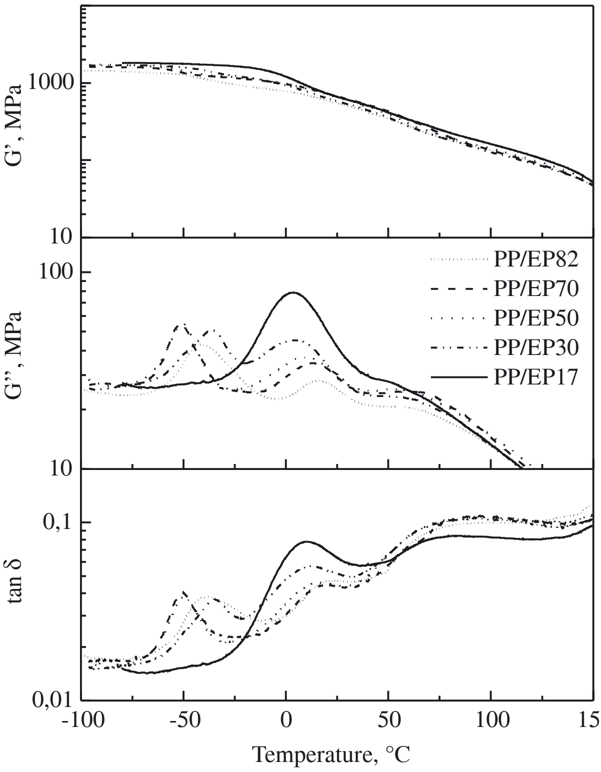


Fig. 1. Storage (G'), loss (G'') moduli and loss tangent (tan δ) of the blends as a function of EP composition (DMA)

Propylene-rich copolymer also shows a shift in its glass transition towards higher temperature, namely towards the glass transition temperature of neat polypropylene. In the materials being the subject of the present work, decreasing ethylene content in EP phase leads to

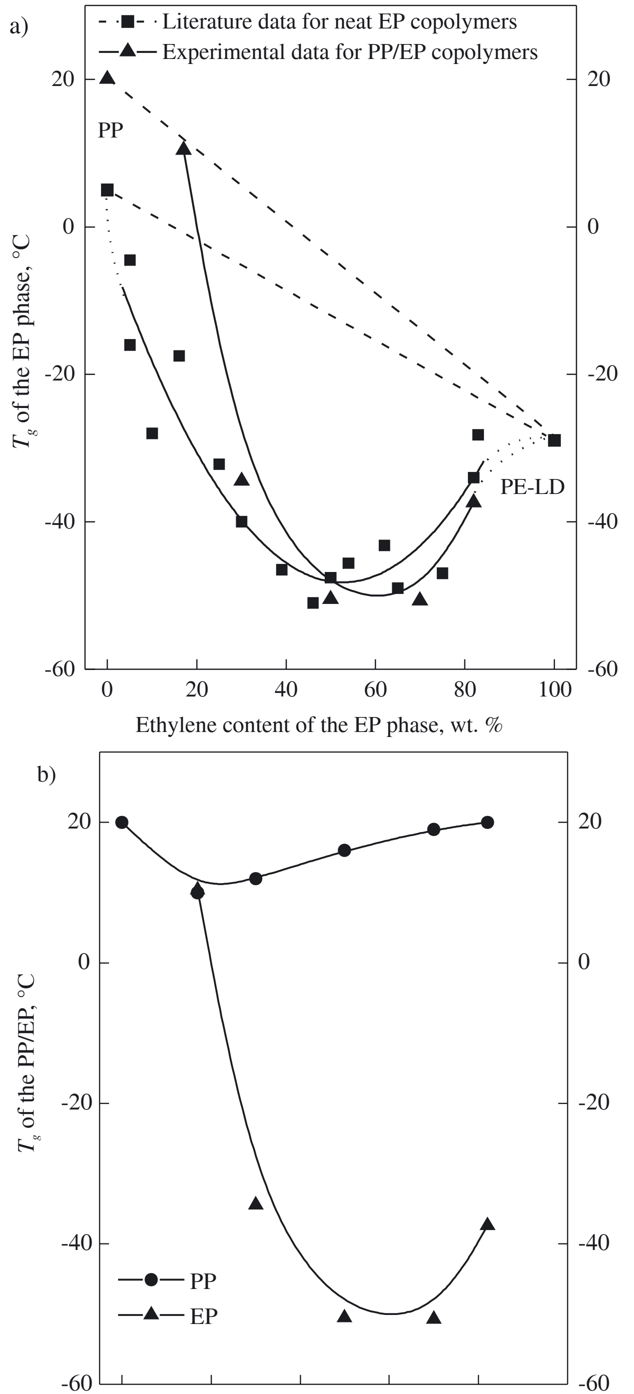


Fig. 2. Effect of EP composition on: a) T_g of EP phase as compared to the literature data of neat ethylene/propylene copolymers [5, 6], b) T_g of PP and EP phases in PP/EP systems

a simultaneous shifting of glass transition temperature of both the dispersed phase and the matrix towards each other (Fig. 2b).

The extent of shifting was used in order to evaluate the compatibility between the polypropylene matrix and ethylene/propylene copolymer dispersed phase. According to the results, the increase of propylene content in EP leads to better chemical affinity between PP matrix and propylene-rich dispersed phase and subsequently to better interaction between the components resulting in higher compatibility of the blends.

It has been detected that the intensity of PP glass transition peak, which is associated with the relaxation

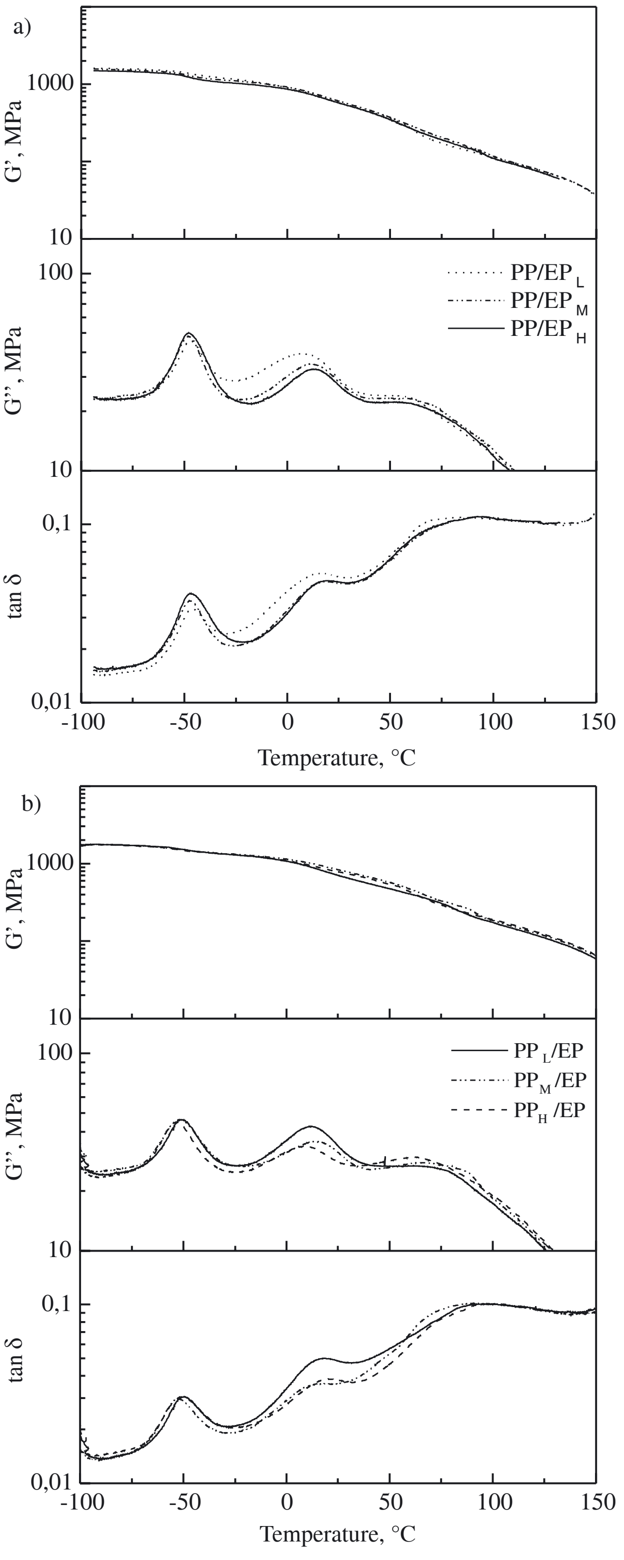


Fig. 3. Storage (G'), loss (G") moduli and loss tangent (tan δ) of the blends as a function of: a) EP molecular weight level, b) PP molecular weight level

occurring in the amorphous regions of the polypropylene, increases with increasing propylene content in EP (tan δ in Fig. 1). Taking into account that the magnitude of each peak is characteristic for the relative concentration of the respective phase in the blend it could be concluded that a certain amount of propylene/rich EP copolymer is partially dissolved in the amorphous region between polypropylene lamellae. Further on, the material PP/EP17, showing the highest propylene content, exhibits single glass transition at temperature intermediate to the glass transition temperatures of PP and EP phases, respectively. The result suggests a high degree of compatibility of the blend components. However, despite the apparent homogeneity of this material, a nanoscale dispersion of EP is still visible at SEM micrographs as will be discussed below.

The effects of the molecular weights of the matrix and the dispersed phase on the mechanical relaxation behavior of the reactor blends have been studied as well. Glass transition temperatures (mechanical relaxation profile) of both the blend components, in spite of the slight fluctuations, remained generally independent on the variation of the molecular weights either of the matrix or of the dispersed phase of the heterophasic systems (Fig. 3). However, a clear trend of increasing area under the peak of tan δ at glass transition *i.e.* increasing strength of molecular relaxations is observed for EP (Fig. 3a) and PP (Fig. 3b) phases with increasing of their molecular weights (*i.e.* with increasing *IV* of XS and lowering MFR_{matrix}). This is an indication of high energy absorption capacity and could be attributed either to the higher amount of molecular entanglements in the mostly amorphous, at this ethylene content, EP or to an increase in the tie molecule density in the semi-crystalline matrix with increasing molecular weight, respectively. Moreover, the strength of the molecular relaxations was found to correlate with the mechanical performance, especially with the fracture toughness of a given material [7, 8] as will be confirmed also in this study.

Morphology

The studied blends reveal typical heterophasic morphology consisting of EP domains embedded in polypropylene matrix. The crystallizable fragments of ethylene/propylene copolymer, when present, were found to be incorporated as inclusions into the amorphous EP domains, because of interfacial energy considerations (Fig.4b—c). However, the overall blend morphology as well as the internal morphology of the composite dispersed phase particles showed to be highly influenced by the ethylene/propylene copolymer composition. According to the results, the size of the dispersed domains decreases strongly with decreasing ethylene content in EP (Table 1, D_w values).

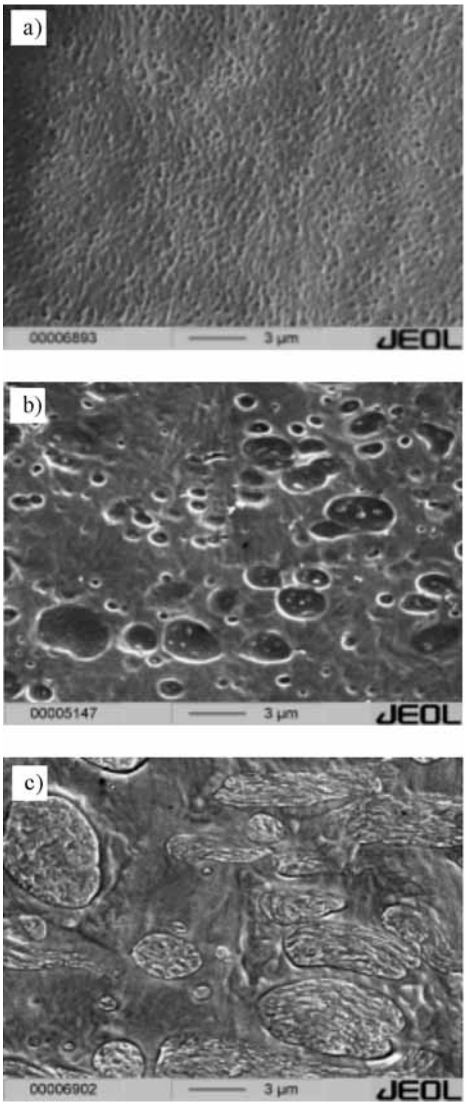


Fig. 4. SEM micrographs of: a) PP/EP17, b) PP/EP50, c) PP/EP82

The effect is ascribed from one side to the high degree of solubility of the propylene-rich EP in the amorphous region between PP lamellae as it was suggested by the dynamic mechanical investigations and from the other side to the decreased interfacial tension between the matrix and the high propylene containing ethylene/propylene copolymer [9]. Furthermore, it should be emphasized that several orders of magnitude reduction of the size of dispersed EP particles took place. The material PP/EP82 (Fig. 4c) exhibits a very coarse texture with average domain size of 3 µm and its morphology appears like a co-continuous. At the other concentration edge, ethylene/propylene copolymer with the highest propylene content (Fig. 4a) organizes itself in nanoscale dispersion with average particle size of 0.20 µm. The domains are regularly distributed both by shape and size. The phenomenon is ascribed to the very high degree of compatibility between the matrix and the propylene-rich dispersed phase as estimated by the single glass transition temperature that this material exhibit at DMA investigations. Parallelly with the variation of the dispersed domain size, the microstructure of EP do-

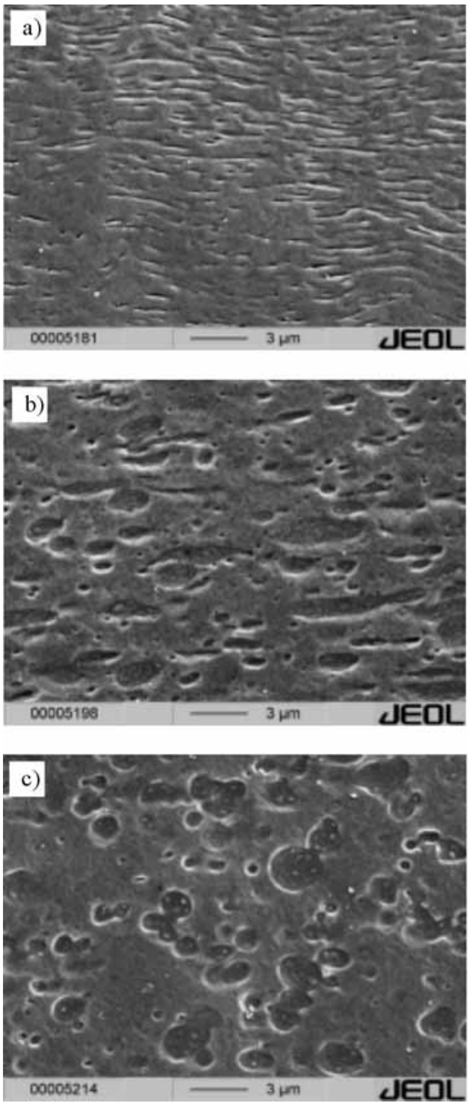


Fig. 5. SEM micrographs of: a) PP/EP$_L$, b) PP/EP$_M$, c) PP/EP$_H$

mains varies with the ethylene/propylene copolymer composition as well. The heterophasic materials with ethylene content above 50 wt. % demonstrate composite EP particles comprising an amorphous shell with incorporated polyethylene-like semi-crystalline inclusions. For the materials PP/EP50 and PP/EP70 mainly two types of structure could be discerned (Fig. 4b—c). Smaller particles exhibit core-shell structures with single inclusions while "salami-like" structures with multiple inclusions are observed for larger particles. It is suggested that some of the larger particles are formed as a result of the coalescence of smaller particles. The number and size of the inclusions were found to correlate with ethylene content in EP. The material showing the highest ethylene content (Fig. 4c) exhibits completely different internal structure of the dispersed particles. Both the small and the large EP domains manifest a core-shell structure, with a large core of semi-crystalline ethylene/propylene copolymer surrounded by a very thin layer of amorphous ethylene/propylene copolymer shell. The core itself appears to be composed of crystalline lamellae with amorphous material entrapped between them.

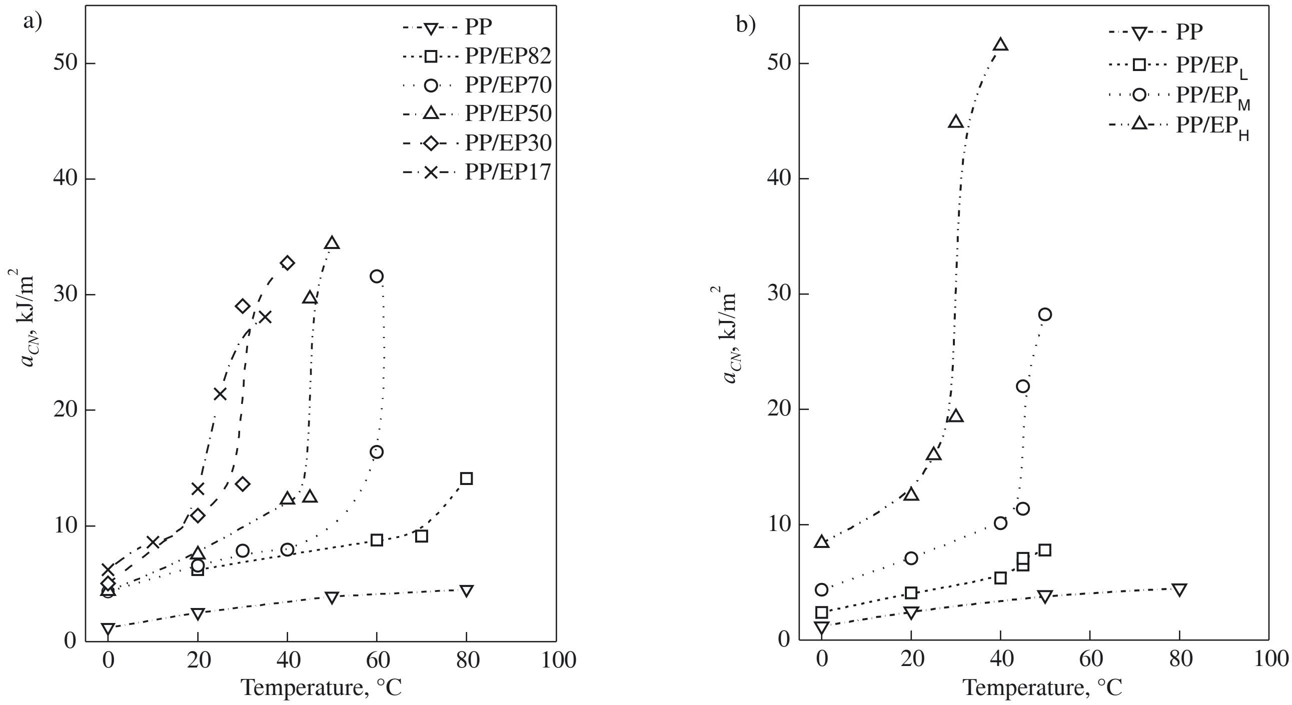
The molecular weights of the dispersed phase and the matrix were considered playing a very important role in determining the structure as well as the mode and state of dispersion of the minor component in the polymer blends (Fig. 5). Most of the studies reported a steady increase in the dispersion coarseness with increasing molecular weight of the minor phase. However, the advantage of the blends discussed is that mixing between the components could be obtained relatively independently on their molecular weights. For the studied materials it was observed that despite the continuous increase in *IV* (increasing molecular weight) of EP, at constant composition and PP molecular weight only an initial increase in the dispersed particle size followed by a plateau was noticeable (Fig. 5 and D_w in Table 1). Nevertheless, a systematic reduction of the aspect ratio of ethylene/propylene copolymer domains with increasing molecular weight was observed.

Varying molecular weight of the matrix at constant composition and molecular weight of EP also produces a variation in the viscosity ratio and thus in the size of the dispersed domains. Decrease in the molecular weight of the matrix gives a raise to a slight but continuous increase in the size of the dispersed phase domains (Table 1) in accordance with the increased viscosity ratio of the blend. However, it should be indicated for the materials studied that the changes in the sizes of the dispersed EP domains caused by variation of the molecular weights either of the matrix or of the dispersed phase are taking place in a much smaller scale than those produced by variation of the ethylene/propylene composition.

Mechanical properties

For a comprehensive characterization of the structure-property relationship in the investigated materials, the impact performance of the blends is discussed in relation on to the observed phase behavior and morphology. Fig. 6 demonstrates the notched impact strength (a_{CN}) as a function of the temperature and compositions of the materials studied.

The decrease in ethylene content in EP leads to a significant enhancement of a_{CN} of the studied blends (Fig. 6a). The effect is in accordance with the demonstrated improvement of the compatibility between components forming the matrix and the dispersed phase, respectively. The systematic decrease in the brittle to ductile transition temperature (T_{BDT}) with decreasing ethylene content in EP in conjunction with the observed reduction of the sizes of the dispersed domains (D_w), complies with the predictions of the critical interparticle distance theory [10]. Despite the dimension, ethylene content in ethylene/propylene copolymer was found to control also the microstructure (Fig. 4) and subsequently the stress distribution around the dispersed particles [11,



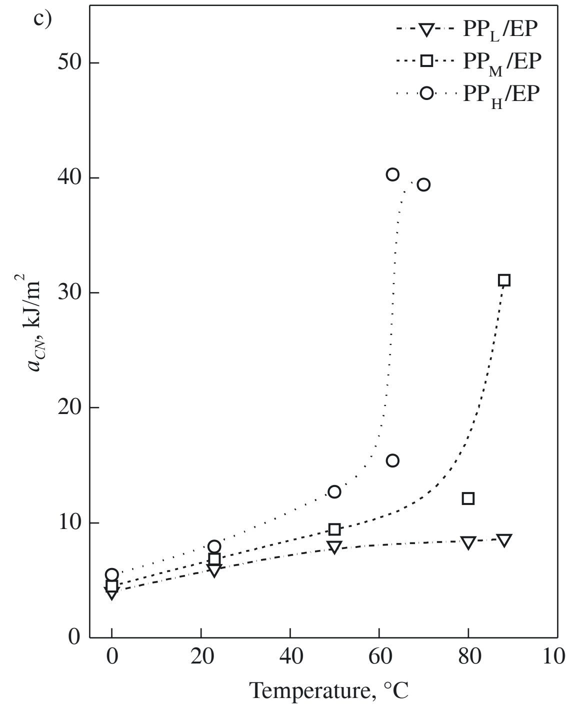


Fig. 6. Notched impact strength (a_{CN}) as a function of the temperature and: a) EP composition, b) EP molecular weight, c) PP molecular weight

12]. For the studied materials, the role of the composite EP particles with ethylene content above 70 wt. % as stress concentrators and impact modifiers is highly impaired because of the existence of a very large semi-crystalline polyethylene-like core.

The overall impact energy level of the investigated materials was found to be governed mainly by the molecular weights of the dispersed phase (Fig. 6b) and the matrix (Fig. 6c), respectively. An increase in both the molecular weights of ethylene/propylene copolymer and polypropylene produces a pronounced improvement of a_{CN} and a decrease in T_{BDT} (Fig. 6a—b). The results are attributed to the high deformation and energy absorption capacity of the high molecular EP and PP, respectively, and are correlating with the strength of the molecular relaxations, namely the areas under the glass transition peaks of the both blend components determined by DMA.

CONCLUSIONS

The phase interactions, structure evolution and the resulted impact properties of heterophasic PP/EP systems as influenced by ethylene/propylene copolymer composition as well as by the matrix and dispersed phase molecular weights have been investigated. It was demonstrated that ethylene/propylene ratio of EP is the main parameter governing the phase compatibility of the investigated materials, as estimated by dynamic mechanical analysis. Further on, ethylene content in ethylene/propylene copolymer was found to dominate the interfacial tension between the matrix and the dispersed phase and respectively the size as well as the internal morphology of EP domains. A reduction of the particle size with several orders of magnitude down to the nanoscale with increasing propylene content in EP has been observed. Accordingly, increasing propylene content in ethylene/propylene copolymer was found to exert also a beneficial effect on the impact strength and the brittle to ductile transition temperature of the materials. The influence of the molecular weights of the matrix and ethylene/propylene copolymer on the phase structure and the impact performance of the heterophasic materials were demonstrated as well. The results suggest that the dominant role in determining of EP domain size or at least the range of its variation is played by ethylene/propylene copolymer composition. Nevertheless, a systematic increase in the impact strength of the blends with increasing both molecular weights of the matrix and of the dispersed phase was observed. The results could be qualitatively correlated to the strength of the molecular relaxations at glass transition for PP or EP respectively.

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