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ORIGINAL RESEARCH

Polypropylene toughened with ethylene-*n*-butyl acrylate-carbon monoxide terpolymer: structure–property relationship

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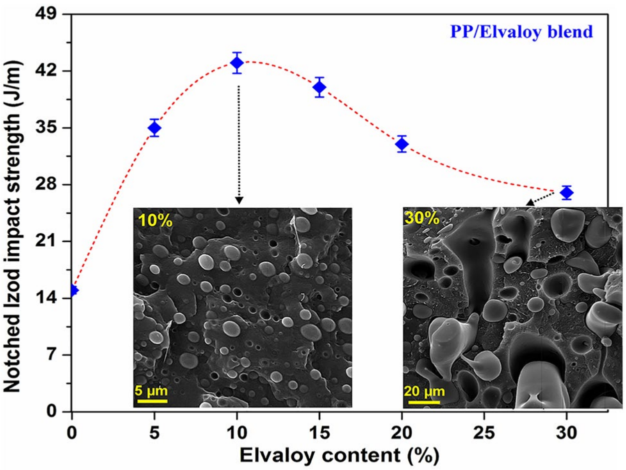
Abstract

Phase morphology, mechanical properties, melt rheology, and failure mechanisms of polypropylene (PP) blended with 0–30% (by weight) of ethylene-*n*-butyl acrylate-carbon monoxide (E-*n*BA-CO) were studied. A typical matrix/dispersed-droplet morphology was observed for all blends together with a relatively coarse dispersion of modifier domains in the blends having more than 20% (by weight) of E-*n*BA-CO. Binary blends showed tremendous improvements in tensile ductility compared with neat PP. The elastic modulus, yield stress, and tensile strength decreased steadily with E-*n*BA-CO loading in the blend, but the degree of reductions was insignificant and the blends exhibited a good balance of tensile properties. The impact strength on notched samples increased sharply with E-*n*BA-CO content up to 10% (by weight) and then decreased at higher modifier contents. E-*n*BA-CO did not influence the crystallization and melting characteristics of PP matrix. E-*n*BA-CO changed the rheological behavior of PP, and melt viscosity and elasticity for the blends increased in direct proportion to the E-*n*BA-CO fraction. A transition from a liquid-like response to a nearly solid-like one at low-frequency regions was detected with the progressive incorporation of E-*n*BA-CO into the PP matrix. Fractography analysis of impact-fractured samples revealed some localized, small-scale plastic deformations along with a relatively poor interfacial adhesion across the phase boundaries between the dispersed domains and the surrounding PP matrix. Extensive interfacial debonding–cavitation and pull out of dispersed domains were responsible for the low impact toughness for the blends containing more than 15% (by weight) of E-*n*BA-CO.

Graphical abstract



Keywords Blending · Phase morphology · Mechanical properties · Impact resistance · Phase adhesion

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Introduction

The melt blending of two or more polymers provides an easy and efficient way to generate new polymeric materials with novel and targeted properties at a relatively low cost compared to developing a new polymer [1–3]. The great majority of useful polymer blends are immiscible, and their outstanding performance stems from their multiphase morphologies [3–5]. In these heterogeneous polymeric systems, macroscopic performance and mechanical behavior are strongly dependent on the microstructure and phase morphology of the blend.Indeed, the phase morphology and dispersion state of modifier components play a key role in the overall properties of the resulting multi-phase material [6–8]. Hence, the control and the prediction of morphologies for optimizing desired properties have always been a research focus [9–11]. In multiphase polymer systems, the phase morphology is generally determined by the following factors: blend composition, material characteristics (surface energies as well as rheological properties of the blend constituents), and processing conditions (mixing time, temperature, and the type and the extent of deformation flow field) [12–14].

Polypropylene (PP) is one of the most important commodity thermoplastics, which is widely used in automobile, household appliances, construction, and packaging applications due to its balanced mechanical and chemical properties as well as excellent processability [14–16]. However, PP homopolymer, especially its isotactic grade, exhibits a ductile-to-brittle transition at both low temperatures as well as room temperature under triaxial and/or impact loadings. This change in behavior is problematic as it exposes structural parts to serious risks of failure in service, especially in the presence of notches or under complex loading conditions. Blending of PP with various elastomeric or plastomeric copolymers, such as ethylene–propylene copolymers (EPR or EPDM), ethylene vinyl acetate (EVA), styrene–butadiene–styrene (SBS), styrene–ethylene–butylene–styrene (SEBS), and other thermoplastic polyolefin elastomers (TPE-O), is the most common practice to improve the impact resistance of PP [17–19]. Toughened PP resins have been developed successfully by the incorporation of the above-mentioned impact modifiers into the PP matrix during melt blending. The toughened PP resins have gained widespread applications in various sectors, most notably in automotive industry, pipes and construction industry, and household appliances [20]. The obtained results for toughened-PP binary blends further indicate that the level of increase in the impact resistance of resulting blends is controlled by the following factors: the type and chemical structure of the rubbery phase, the content of rubbery phase in the blend, interfacial interactions (interfacial tension) between the rubbery phase and PP matrix, rheology or melt viscosity of both PP and the impact modifier, and processing conditions [20–22].

Ethylene/*n*-butyl acrylate (E/*n*BA) functionalized with different chemically reactive groups is an ethylene terpolymer which has been used as modifiers (plasticizer and impact modifier) for a wide variety of polymers, most commonly in acrylonitrile–butadiene–styrene (ABS)and poly(vinyl chloride) (PVC) [23–25]. E-*n*BA-based terpolymers have also been widely used as a compatibilizer as well as an impact modifier for antagonistically incompatible blends of polyolefins and polar thermoplastics, such as polyamides and polyesters [26–28]. Improved phase morphology, increased phase adhesion between the components of the blends, followed by enhanced mechanical properties have been observed in the blends modified by E-BA-based terpolymers [29–31]. For example, in the work conducted by Kaci et al. [25] the addition of the E-*n*BA-based terpolymer to a binary blend of low density polyethylene (LDPE) and poly(ethylene terephthalate) (PET) reduced the size of the PET inclusions, improved the interfacial adhesion strength between LDPE and PET, and increased the tensile properties and impact strength [25]. Yang et al. [26] found a remarkable increase in impact strength, a small reduction in tensile strength, and a finer morphology for poly(butylene terephthalate) (PBT)/polyolefin elastomer (POE) blends upon the addition of E-BA-CO. You et al. [27] observed that an E-BA-based toughener provided a significant increase in impact strength at a cost of a 25% fall in modulus for poly(ethylene terephthalate)/polylactide (PET/PLA) blend as compared with the unmodified blend. An increase in melt viscosity, phase compatibility, impact strength and elongation-at-break of polyoxymethylene (POM)/poly(lactic acid) (PLA) blend was also reported by Andrzejewski et al. [28] as a result of the incorporation of an E-BA-based terpolymer [28].

While E-*n*BA-based terpolymers have gained widespread applications in both thermoplastics as well as polymer blends, their potential as modifiers for PP polymers has not been explored. To the best of the authors' knowledge, there is no scientific report in open literature focusing on the influence of E-*n*BA-based tougheners on the different properties of PP homopolymer. In this regard, the present was carried out with the aim of investigating the morphology and different properties (especially ductility and impact toughness) of binary blends of PP and E-*n*BA-CO terpolymer containing 0–30% (by weight) of E-*n*BA-CO. Phase morphology, mechanical properties, impact toughness, melting and crystallization behavior, melt rheology, and failure mechanisms under the impact test of the blends were examined systematically. A structure–property correlation was established for the blends under investigation.

Experimental

Materials

The isotactic PP homopolymer (PP: SF 060, MFI 6.0 g/10 min at 230 °C and 2.16 kg) was purchased from Polynar Petrochemical Co., Tabriz, Iran. Ethylene/*n*-butyl acrylate/carbon monoxide (E/*n*BA/CO) terpolymer, with the trademark of Elvaloy HP4051, the density of 1 g/cm^3, melt flow rate of 12 g/10 min, and melting point of 59 °C was supplied from DuPont. Irganox 1010 and Irgafos 168 antioxidants were used for minimizing thermo-oxidative degradation during melt mixing.

Blend preparation

PP and E-BA-CO (hereafter referred to as Elvaloy HP4051) were dried in a vacuum oven at 80 °C for 24 h before melt processing. All the PP/Elvaloy HP4051 compositions having 0–30% (by weight) of Elvaloy HP4051 were prepared using a lab mixer of HAAKE PolyLab OS System Torque (Thermo Fisher Scientific-50EHT) with a rotor speed of 70 rpm operating at 200 °C. In the case of the blend samples, a small amount of the prepared mixtures was rapidly quenched in liquid nitrogen for morphological studies. The prepared blend samples were then compression-molded at 200 °C into desirable specimens for different analyses.

Morphological observations

The morphological texture of the cryo-fractured samples was analyzed using a TESCAN FEG scanning electron microscopy (SEM) instrument operating in high vacuum mode. Cryo-fractured surfaces in liquid nitrogen were gold-sputtered for good conductivity of electron beam and microphotographs were taken at different magnifications. For the purpose of particle size analysis, at least 400 particles from independent SEM micrographs were analyzed using the image processing software (ImageJ, NIH, USA). The cross-sectional area (A_i) of each individual particle (i) was measured and converted into an equivalent diameter of a sphere using Eq. 1 as follows:

$$d_i = 2\sqrt{A_i/\pi}. \tag{1}$$

The number-average particle diameter, d_n, was determined using Eq. 2 as follows:

$$d_n = \frac{\sum n_i d_i}{\sum n_i}, \tag{2}$$

where n_i is the number of particles having the diameter d_i.

Mechanical tests

Tensile tests were conducted on an Instron Universal Tensile Testing Machine (model 3382) at a fixed crosshead speed of 5 mm/min at room temperature (23 °C) according to ISO527. At least five tensile specimens were tested for each composition and the resulting tensile properties were averaged. The impact fracture energy of the samples was determined by a notched Izod impact tester (Zwick/Roell B5102 pendulum impact tester) according to ASTM D256. The results of the impact strength are the average of at least six repetitions performed at 25 °C.

Differential scanning calorimetry (DSC)

Melting and crystallization behaviors of the samples were studied by a Netzsch-DSC 20 0F3 (Germany) instrument under nitrogen atmosphere. Each sample of 10 ± 0.2 mg was taken from a molded sheet and encapsulated in an aluminum closed pan. Samples were first heated from 40 to 210 °C at a heating rate of 20 °C min^{-1}, held at 210 °C for 5 min to erase any previous thermal history and then cooled to 40 °C at the cooling rate of 10 °C min^{-1}and heated again to 210 °C with the 10 °C min^{-1} heating rate. The results of the cooling and the second heating run are presented in this work. The crystalline phase percentage of PP matrix (X_c) was estimated using the following equation:

$$X_\mathrm{c}(\%) = \frac{\Delta H_m}{w_f \Delta H_m^\circ} \times 100, \tag{3}$$

where ΔH_m is the enthalpy of melting for analyzed sample, w_f is the mass fraction of PP in the sample and $\Delta H_\mathrm{m}^\circ$ is the enthalpy of fusion for 100% crystalline PP, taking the value of 209 J g^{-1} from the literature [12, 14].

Fractographic analysis

To elucidate the role of phase morphology on the fracture behavior of the samples, and also to understand the underlying micromechanisms of deformation operating in different systems under the Izod impact loading, FESEM micrographs were also prepared from the surface of impact-fractured specimens of different samples. The impact-fractured surfaces were gold-coated before SEM analysis and then the micrographs were prepared at different magnifications.

Rheological studies

The linear viscoelastic properties of different samples in molten state were investigated using a dynamic rheometer

(MCR301, Anton Paar) equipped with parallel plate geometry (25 mm diameter, and 1 mm gap). The strain sweep tests were performed in the range of 0.01–100% to determine the linear viscoelastic range at 220 °C. Then, the frequency sweep tests were carried out in the range of 0.04–625 rad/s at the same temperature under dry nitrogen atmosphere with an amplitude of 1% to maintain the response of materials in the linear viscoelastic region.

Results and discussion

Phase morphology

The SEM micrographs taken from the cryo-fractured surfaces of the PP/Elvaloy HP4051 blends of different Elvaloy contents are shown in Figs. 1 and 2. Typically, a matrix/dispersed-droplet morphology is clearly visible in these micrographs for all the binary blends prepared and the Elvaloy rubber domains are homogeneously distributed in the PP matrix. There are also some signs of Elvaloy rubber domains pulled out from the surrounding matrix in the micrographs, as evidenced by holes left on the fractured surfaces. Nonetheless, a close examination of micrographs reveals some degrees of interfacial adhesion between the Elvaloy droplets and the surrounding PP matrix. As it is apparent in the SEM micrographs, the number and the size of dispersed rubbery domains increase gradually with the increase of the Elvaloy content in the blends from 5 to 30% (by weights).

The change in the size of dispersed Elvaloy droplets as a function of Elvaloy weight fraction in the binary blends is depicted in Fig. 3. According to Fig. 3, the number-average diameter of the dispersed domains in the binary blends containing 5% and 30% (by weights) of the Elvaloy component is about 2 and 15.5 µm, respectively. The microscopy observations presented above indicate the development of coarse phase morphology in binary blends containing more than15% (by weight) of Elvaloy terpolymer.

Tensile properties

The typical tensile stress–strain curves for neat PP and binary PP/Elvaloy HP4051 blends of different compositions are shown in Fig. 4. Neat PP exhibited a semi-ductile behavior under the tensile test which is in line with other reports [14–16]. Interestingly, all the binary PP/Elvaloy blends displayed a fully ductile tensile failure mode. As can be seen in Fig. 4, the tensile ductility, reflected in strain-at-break, gradually increased with Elvaloy content by 20% (by weight), and then decreased when the Elvaloy content was further increased to 30% (by weight). Nonetheless, the tensile ductility of the blend with 30% (by weight) of Elvaloy is still much higher than that of neat PP and the blends having 5% to 15% (by weights) of Elvaloy. The blend having 20% (by weight) of Elvaloy showed the most stable cold-drawing and neck propagation response among the different binary blends studied, so that this sample exhibited a strain hardening behavior during the tensile test. The results obtained clearly indicate that Elvaloy HP4051can function as an effective toughener for isotactic PP under the quasi-static tensile test.

The change in tensile parameters of PP/Elvaloy HP4051 blends with weight fraction of Elvaloy is illustrated in Fig. 5. The elastic modulus of the PP/Elvaloy blend showed a gradual decline as the Elvaloy content increased to 30% (by weight), similar to the effect observed with other rubbery polymers used to modify PP [16, 17, 20]. Compared with a neat PP, the modulus of the blend with 30% (by weight) of Elvaloy is reduced by 25%. The yield stress of the blends was also lower than that of neat PP, and the trend of this parameter with Elvaloy content was similar to that with Young's modulus. The yield stress of neat PP was about 32 MPa, which was reduced to 29.5 MPa for the binary blend containing 30% of Elvaloy. For strain-at-break, the data in Fig. 5b demonstrate that the elongation rose markedly with the Elvaloy concentration to 20% (by weight) and then dropped at higher loading of Elvaloy (i.e., 30% (by weight)). The highest elongation-at-break, ~ 800%, was obtained for the blend containing 20% (by weight) of Elvaloy, which was about 40 times as large as that of neat PP (~ 20%). In the case of tensile strength parameter, it can be seen in Fig. 5b that, with the exception of the blend comprised 20% of Elvaloy, all the blends have lower tensile strength values compared to neat PP polymer. For the 80/20 binary blend, the ultimate tensile strength was close to the yield stress of neat PP because of the occurrence of strain hardening phenomenon during tensile deformation for the former blend system, which did not take place for the other blend systems studied. Overall, the tensile results clearly imply that there is a tremendous improvement in the tensile ductility as a result of modification with Elvaloy HP4051. In addition, the level of drop in stiffness, yield stress, and ultimate tensile strength for the blends studied, as compared with neat PP resin, is not significant. The tensile findings in this work are of paramount importance for the use of such blend systems in structural applications that require a good balance of tensile properties.

Impact strength

As mentioned earlier, PP and its blends are widely used in the automobile and construction industry due to their balanced mechanical properties [13–15]. However, PP usage is usually restricted in applications requiring acceptable levels of toughness, for example, under triaxial and/or impact loadings as well as at low temperatures. Therefore,

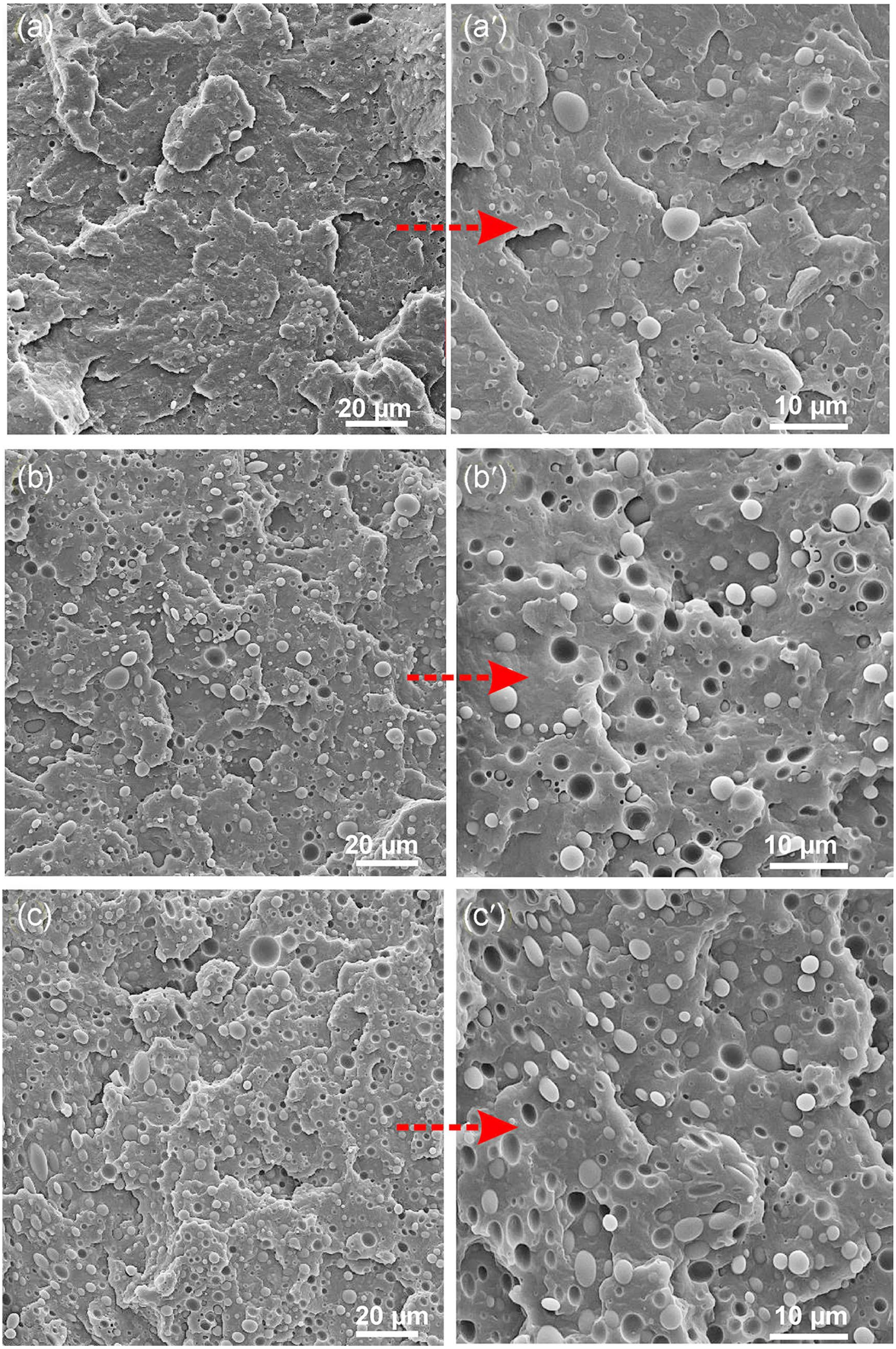

Fig. 1 SEM micrographs taken from the cryo-fractured surfaces of PP/Elvaloy HP4051 blends with different compositions: **a**, **a′** 95/5, **b**, **b′** 90/10, and **c**, **c′** 85/15

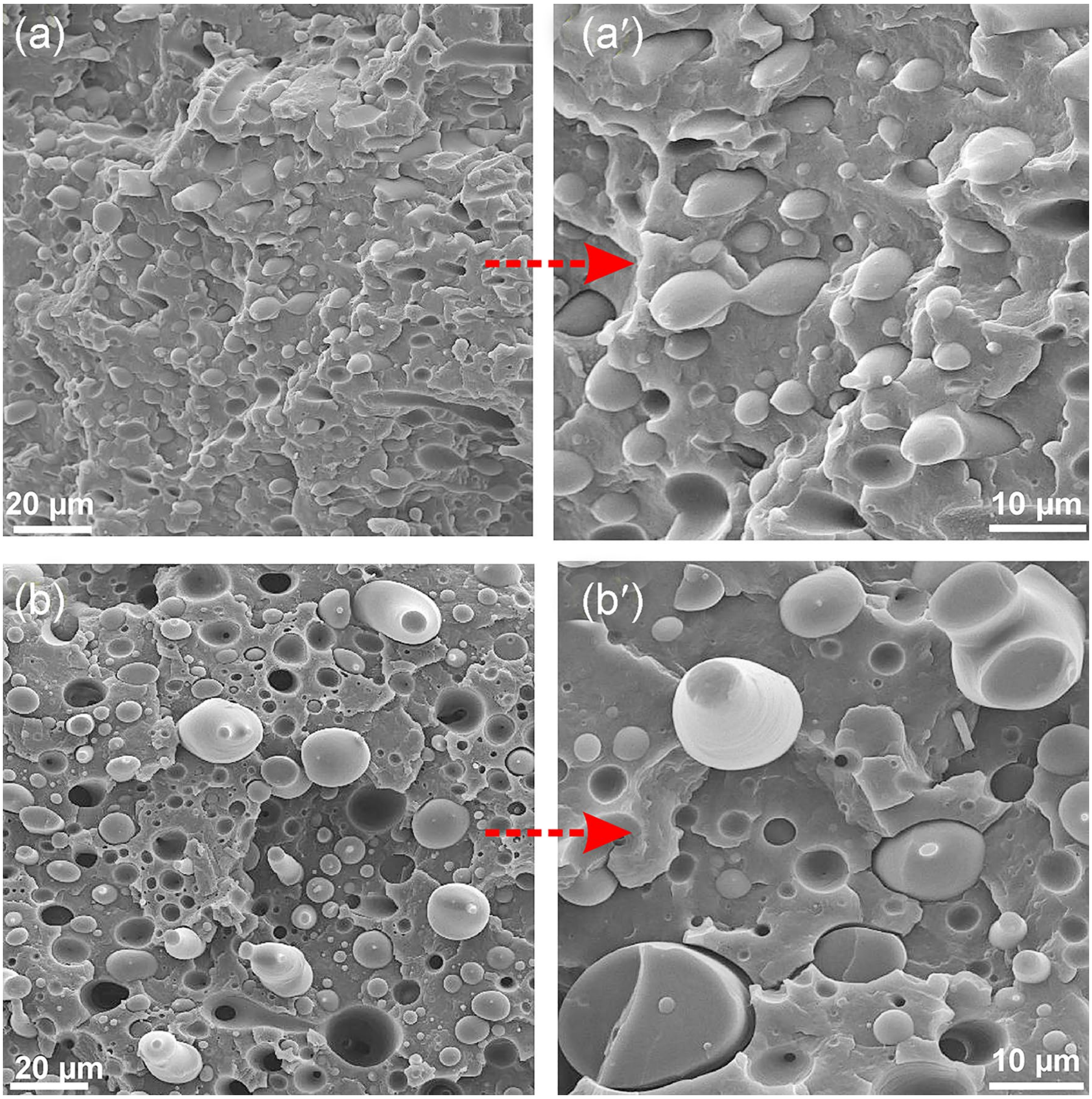

Fig. 2 SEM micrographs taken from the cryo-fractured surfaces of PP/Elvaloy HP4051 blends with different compositions: **a**, **a′** 80/20, and **b**, **b′** 70/30

an improvement in PP impact resistance is of great importance [13–15]. The notched Izod impact strength of neat PP and binary blends with different Elvaloy HP4051 loadings are shown in Fig. 6. All the blends showed improvements in impact toughness over neat PP polymer, as the blends revealed higher impact strength values than the PP sample. However, the amount of increase in impact toughness of the blends was strongly dependent on the Elvaloy content.

According to Fig. 6, the impact energy steadily increased with Elvaloy proportion up to 10% (by weight) and then gradually decreased at higher percentages of the rubbery component up to 30%. Nonetheless, the impact fracture energy of the blend with 30% rubbery phase was still approximately twice that of neat PP. The most noticeable rise in impact strength was observed for the blends containing 5% and 10% (by weight) of Elvaloy, which showed between two and three times enhancement in impact strength compared to neat PP.

While the tensile results revealed a substantial improvement in the tensile ductility of PP upon blending with the Elvaloy, the extent of the rise in impact fracture energy for the blends was not very significant. Different factors may be responsible for a limited improvement in the Izod impact energy for PP/Elvaloy blends, even at 20–30% of the rubbery component. Obviously, phase morphology and microstructure of the blends play a vital role in the impact strength of a multi-phase system [12, 14, 15]. In this respect, the interfacial interactions, the size of dispersed particles, and

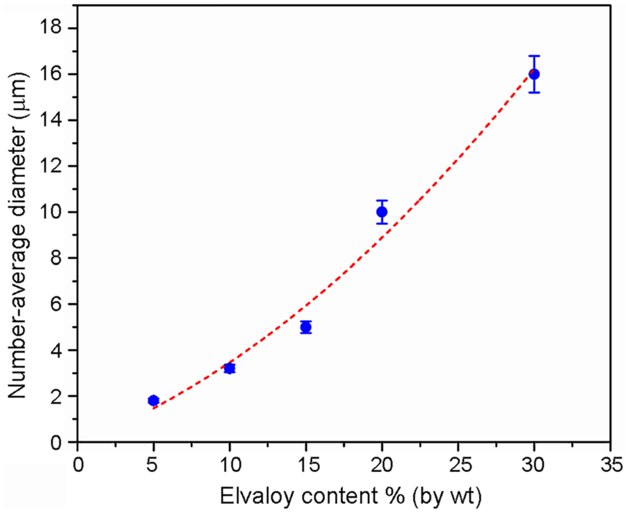

Fig. 3 Number-average diameter (d_n) of Elvaloy HP4051 dispersed domains as a function of blend composition for PP/Elvaloy HP4051 blends. The error bars indicate the standard deviation

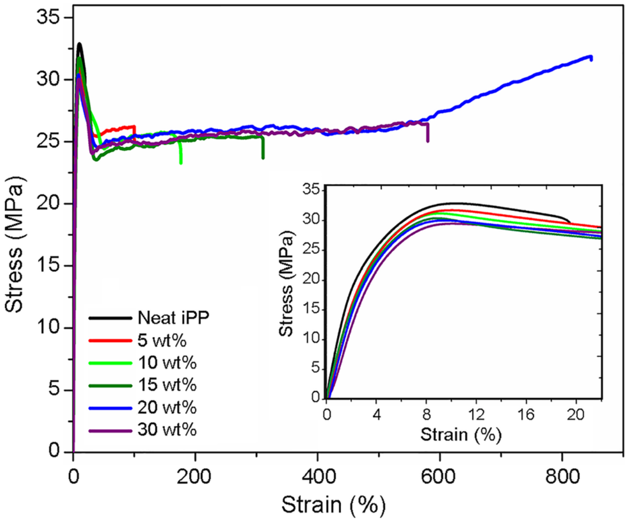

Fig. 4 Typical tensile stress–strain curves for neat PP and binary PP/Elvaloy HP4051 blends with different contents of Elvaloy

dispersion state are the most important and mutually interconnected micro-structural characteristics that directly affect the impact resistance of toughened binary blends [17, 18, 31]. It is well-documented that the optimum particle size to achieve the highest toughening effect under notched impact tests for semi-crystalline polymers, such as PP, is on the order of 0.2–0.8 μm [17, 18, 31]. It is also well-known that any deviation from this optimum particle size range to higher or lower values would probably give rise to a fall in the impact toughness of the resulting blends [17, 18, 31]. The average diameter of the dispersed domains in binary blends prepared in this work was 2.2 μm for the blend having 5% (by weight) of Elvaloy, which then gradually rose to about 15 μm for the blend containing 30% (by weight) of Elvaloy. Thus, it is clear that, even at the lowest Elvaloy content of 5% (by weight), the average size of the dispersed rubbery domains is greater than the optimal value, and therefore the highest impact toughness is not obtained. Therefore, this can severely restrict the effectiveness of dispersed rubbery Elvaloy particles as efficient impact modifier for PP matrix in this work. A literature survey [32–34] on the successfully toughened PP-based binary blends clearly showed that the average diameter of dispersed impact modifiers lies in the range from 0.8 to 1.5 μm for the blends containing 20–30% of the impact modifier. These reports further demonstrate the importance of the size and dispersion state of the modifiers to achieve an effective toughening effect, as well as the large deviation of the average size of the dispersed domains for the PP/Elvaloy blends prepared in this work compared to the successfully toughened blends in the literature [14, 35, 36]. It is worth mentioning that the Elvaloy terpolymer used in this work has a higher polarity than a polar PP homopolymer, because of the presence of polar *n*-butyl acrylate monomer as well as epoxide functional group in the backbone of the Elvaloy macromolecular chains. Thus, there is an imbalance between the surface energies of PP and Elvaloy, which gives rise to a lack of sufficient compatibility of these polymers with the consequence of relatively coarse dispersion of Elvaloy phase domains in the blends studied in this work. Consequently, the impact resistance would be adversely affected by the coarse dispersion state and insufficient compatibility of the components in the PP/Elvaloy blends, especially when the modifier content in the blend is higher than 15% (by weight).

Melting and crystallization behavior

It is well documented that the mechanical properties of the blends are strongly dependent on the crystalline microstructure of the matrix phase [12, 15, 16]. Since PP is a semicrystalline polymer, therefore, the change in the mechanical properties of PP/Elvaloy blends prepared in this work may be partly due to the change in matrix crystallinity as a result of the blending process. Thus, the study of the crystalline structure of the PP/Elvaloy blend systems is essential to determine the possible alteration in the matrix crystallinity in the blends and its subsequent effect on the mechanical properties, especially material toughness. The DSC thermograms for neat PP and PP/Elvaloy blends with different Elvaloy contents are shown in Fig. 7. The main transition peaks visible in these thermograms are related to the PP component of the blends. A weak and relatively broad melting peak around 60 °C is also visible in the heating curves, which is believed to be due to the melting of the Elvaloy component in the blends. This finding is in good agreement

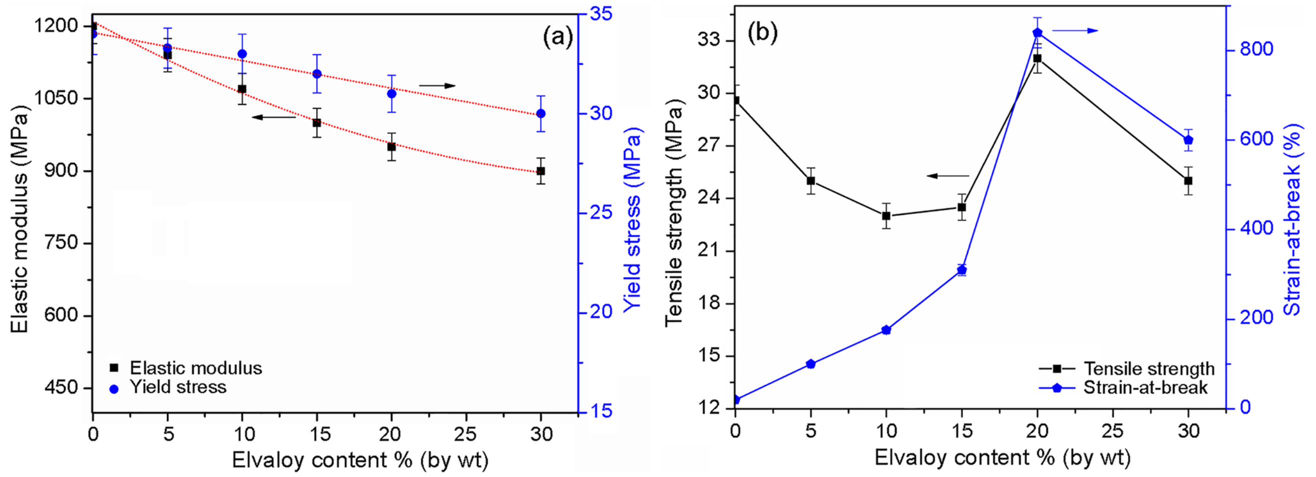

Fig. 5 Tensile parameters of binary PLA/Elvaloy HP4051 blends as a function of Elvaloy content: **a** elastic modulus and yield stress, and **b** tensile strength and strain-at-break. The error bars indicate the standard deviation

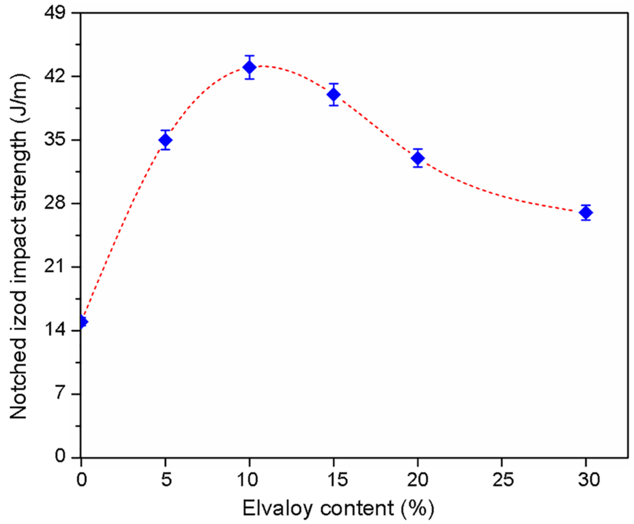

Fig. 6 Notched Izod impact strength of PP/Elvaloy HP4051 blends as a function of Elvaloy content. The error bars indicate the standard deviation

with the melting point value provided by the supplier for this rubbery modifier. The Elvaloy melting peak in the heating curves becomes more intense as its content in the blend gradually increases. In contrast, the intensity of the melting peak of the PP component in the blends steadily drops with Elvaloy loading in the blend. The melting and crystallization results obtained from DSC thermal scans for the neat PP and the PP/Elvaloy blends with different compositions are summarized in Table 1.

According to the data in Table 1, the addition of Elvaloy, up to 30% (by weight), into PP did not influence the crystallization temperature (T_c) of the PP matrix, while the melting temperature (T_m) of PP crystalline phase in the blends was higher than that of unmodified PP sample. Thus, no nucleation effect was seen for the dispersed Elvaloy droplets in the PP matrix for the binary blends except for the blend with 20% (by weight) of Elvaloy. Both the melting and crystallization enthalpies of the PP matrix phase showed a steady fall for the blend samples with a gradual increase in Elvaloy content up to 30% (by weight). These drops are due to the fact that the crystalline PP component in the blend is progressively replaced by Elvaloy, and thereby, the overall fraction of PP in the resulting blend is reduced up to 30% (by weight). In the case of the degree of crystallinity of the PP matrix phase, the DSC data show that the degree of crystallinity of the PP phase in the binary blends is close to that of neat PP sample. The difference in the degree of crystallinity is greater for the blend having 20% (by weight) of Elvaloy, but not significantly. Considering the DSC data in Table 1, it can be concluded that the effect of Elvaloy on the mechanical properties of PP/Elvaloy blends is not contributed by its possible influence on the crystalline structure of the PP matrix upon the blend formation. Instead, the mechanical results obtained are a direct consequence of the presence of Elvaloy droplets in the PP matrix and the type of phase morphology developed in this blend as well.

Melt rheology

The frequency dependence of complex viscosity (η^*) and storage modulus (G') for the neat PP and the PP/Elvaloy blends with different compositions is shown in Fig. 8. Compared to neat PP, the blends represented higher melt viscosity and elasticity values over the entire range of frequency, especially at low frequencies. In fact, the viscosity and elasticity of the resulting blend are directly proportional to the weight fraction of Elvaloy component in the blend. The slope

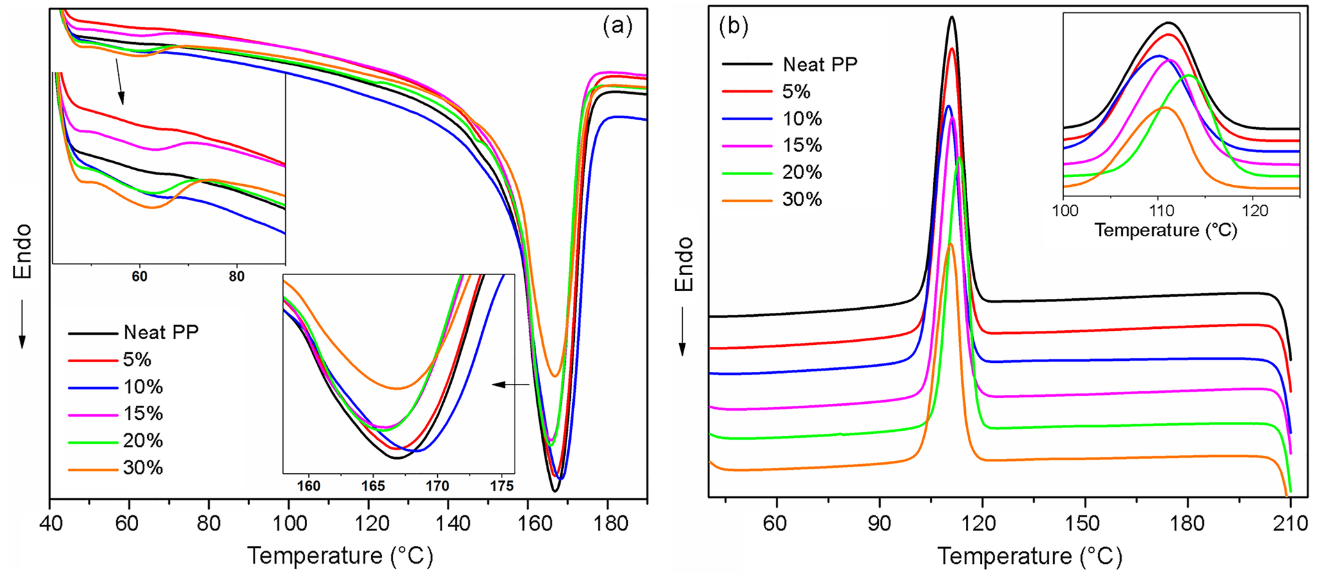

Fig. 7 DSC thermograms for neat PP and binary PP/Elvaloy HP4051 blends with different compositions: **a** heating curves, and **b** cooling curves

Table 1 Melting and crystallization parameters for neat PP and PP/Elvaloy blends with different compositions obtained from DSC curves

Sample (PP/Elvaloy)	T_c (°C)	T_m (°C)	ΔH_c (J g^{-1})	ΔH_m (J g^{-1})	X_c (%)
100/00	110.10	166.70	96.88	94.93	45.20
95/05	111.70	166.80	92.74	89.13	44.87
90/10	110.10	168.15	88.38	86.10	45.70
85/15	111.24	165.87	81.39	78.30	44.07
80/20	113.21	165.70	76.44	70.53	42.20
70/30	110.75	166.93	66.09	64.58	44.20

of $G'-\omega$ curves for the blends with different compositions at low frequencies gradually decreases with the increase of the Elvaloy content, indicating a progressive deviation from the liquid-like behavior with the rubbery phase content in the blend [39, 40]. In the case of the viscosity curves of the samples, it can be seen that the viscosity behavior at low frequencies gradually shifts toward non-Newtonian behavior and, at the same time, the blends undergo an earlier and more intense shear thinning response in the intermediate- and high-frequency regions as the Elvaloy content in the blends is increased up to 30% (by weight).

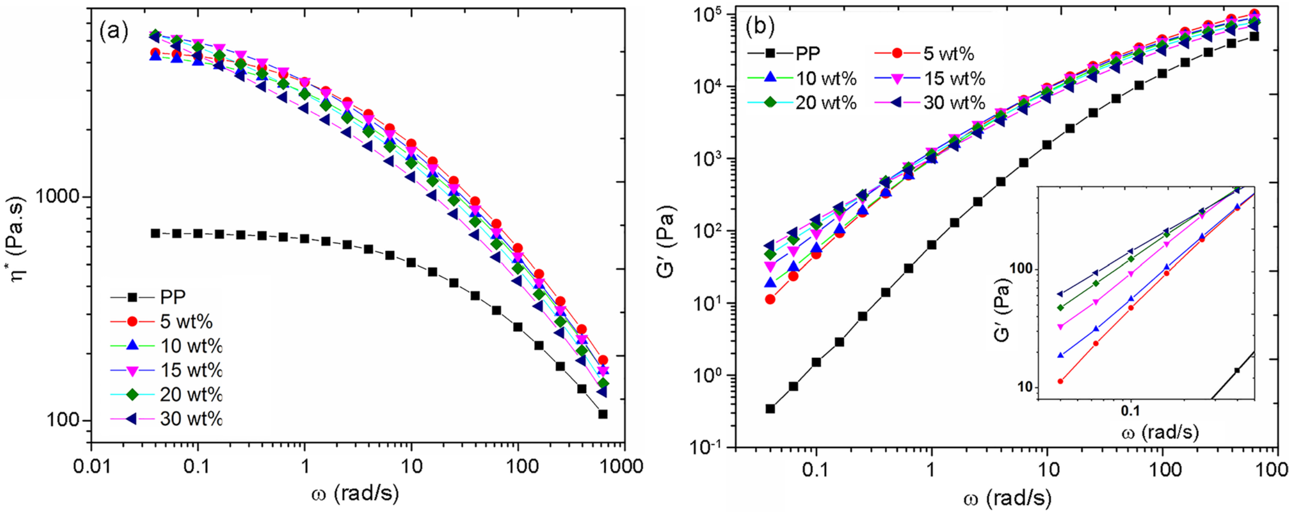

Fig. 8 Angular frequency dependence of complex viscosity and storage modulus of PP/Elvaloy HP4051 blends with different compositions

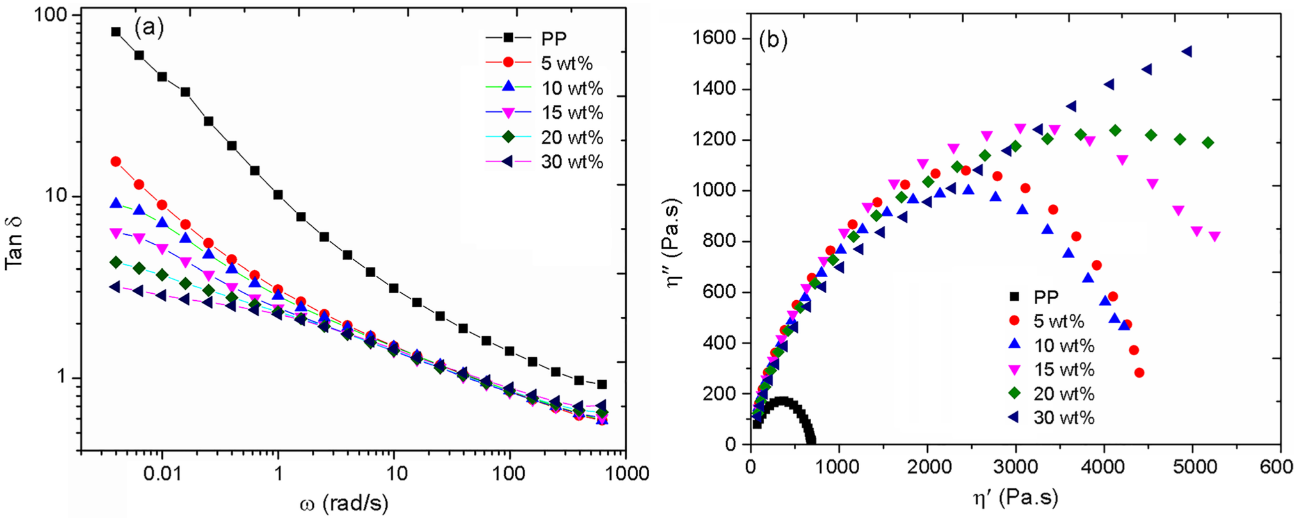

Fig. 9 **a** Angular frequency dependence of loss tangent, and **b** Cole–Cole plots for PP/Elvaloy HP4051 blends with different compositions

The loss tangent (Tan δ, or damping factor) and Cole–Cole plots for different blends are represented in Fig. 9. All the blends exhibited lower damping factor values than the neat PP, which is significant at lower frequencies. The damping factor at this region gradually shifts toward lower values as the Elvaloy content in the blend was increased up to 30% (by weight). In addition, a tendency toward a solid-like behavior can be detected at low frequencies for blends having 20–30% (by weight) rubbery phase as evidenced by some changes in the shape of curves at low to medium frequencies at higher loadings of Elvaloy component [37–39]. In the case of Cole–Cole plots in Fig. 9b, an arc-shaped curve is visible for neat PP and blends with 5% and 10% (by weight) of Elvaloy. For blends with higher Elvaloy content, a deviation from arc shape toward linear curves is apparent. Moreover, the Cole–Cole curves clearly reveal that the relaxation behavior of blends gradually shifted toward longer relaxation times as the Elvaloy fraction in the blends was increased. Similar changes in the melt rheological properties of the blends, especially at low-frequency regions, upon the incorporation of rubbery components in other polymeric materials have been reported in the literature [37–39].

Microscopic deformations under impact test

The SEM micrographs taken from the impact-fractured surfaces of PP/Elvaloy blends with different compositions are shown in Figs. 10 and 11. The SEM micrographs were prepared from the crack initiation zone, just after the pre-notch region. The neat PP showed a smooth and featureless fracture surface with no signs of excessive deformation, indicating a typical brittle mode of failure, in line with other reports in the literature [13–15].

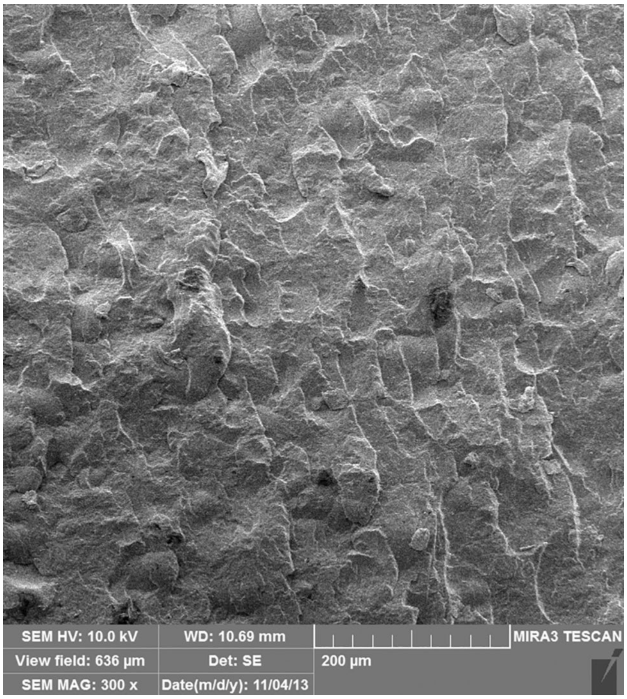

Fig. 10 SEM micrograph taken from the impact-fractured surface of neat PP

A relatively smooth fractured surface was observed for the blend having 5% (by weight) of Elvaloy. Some of the dispersed Elvaloy particles are pulled out during the impact fracture test, leaving holes on the surface. Nonetheless, there is some evidence of good adhesion between the dispersed particles and the surrounding matrix. Consequently, the dispersed domains can dissipate the impact energy as a result

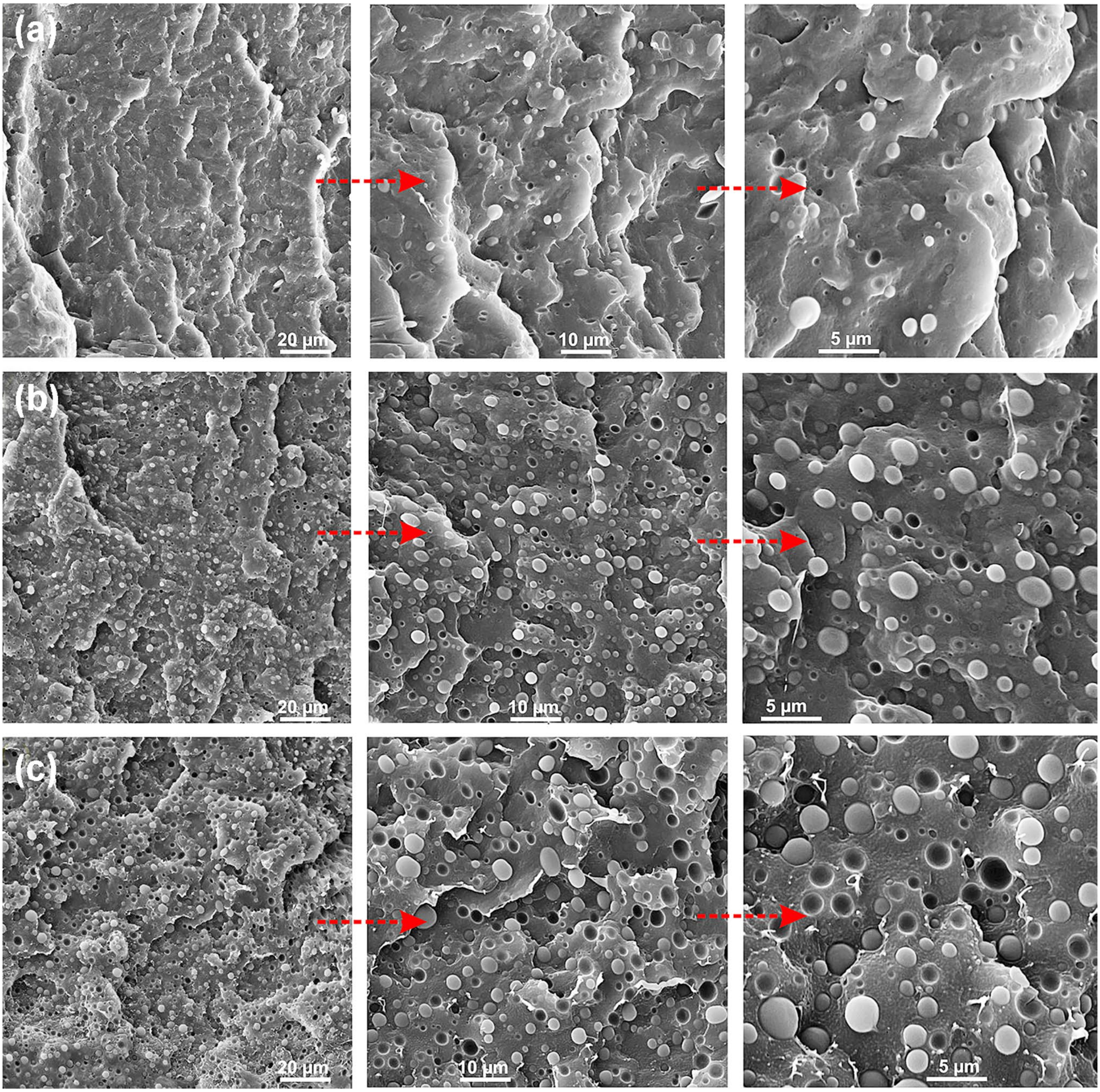

Fig. 11 SEM micrographs taken fromthe impact-fractured surfaces of binary PP/Elvaloy HP4051 blends: **a** 95/5; **b** 90/10; and **c** 85/15

of efficient stress transfer from the matrix to the dispersed rubbery particles [13–15]. The same features are also clearly visible on the fracture surface of the blend having 10% (by weight) of Elvaloy. The level of rubber debonding and/or pull out is not significant on the fractured surface, further corroborating effective energy absorption and/or dissipation during the impact test, which in turn, resulted in further improvement in impact strength compared with the blend with 5% (by weight) of Elvaloy. In the blend with 15% (by weight) of Elvaloy, vast debonding of rubbery domains from the surrounding matrix was observed. In addition, some localized and insignificant matrix plastic deformations just around the Elvaloy particles are also visible on the fractured surface. These micrographs clearly indicate that the extent of interfacial strength between the dispersed domains and the surrounding PP matrix is not sufficient which, in turn, leads to intensive pullout of rubbery particles and interfacial fracture process [13–15].

For the blend with 20% and 30% (by weight) of Elvaloy, the debonding and/or pull out of rubbery domains during

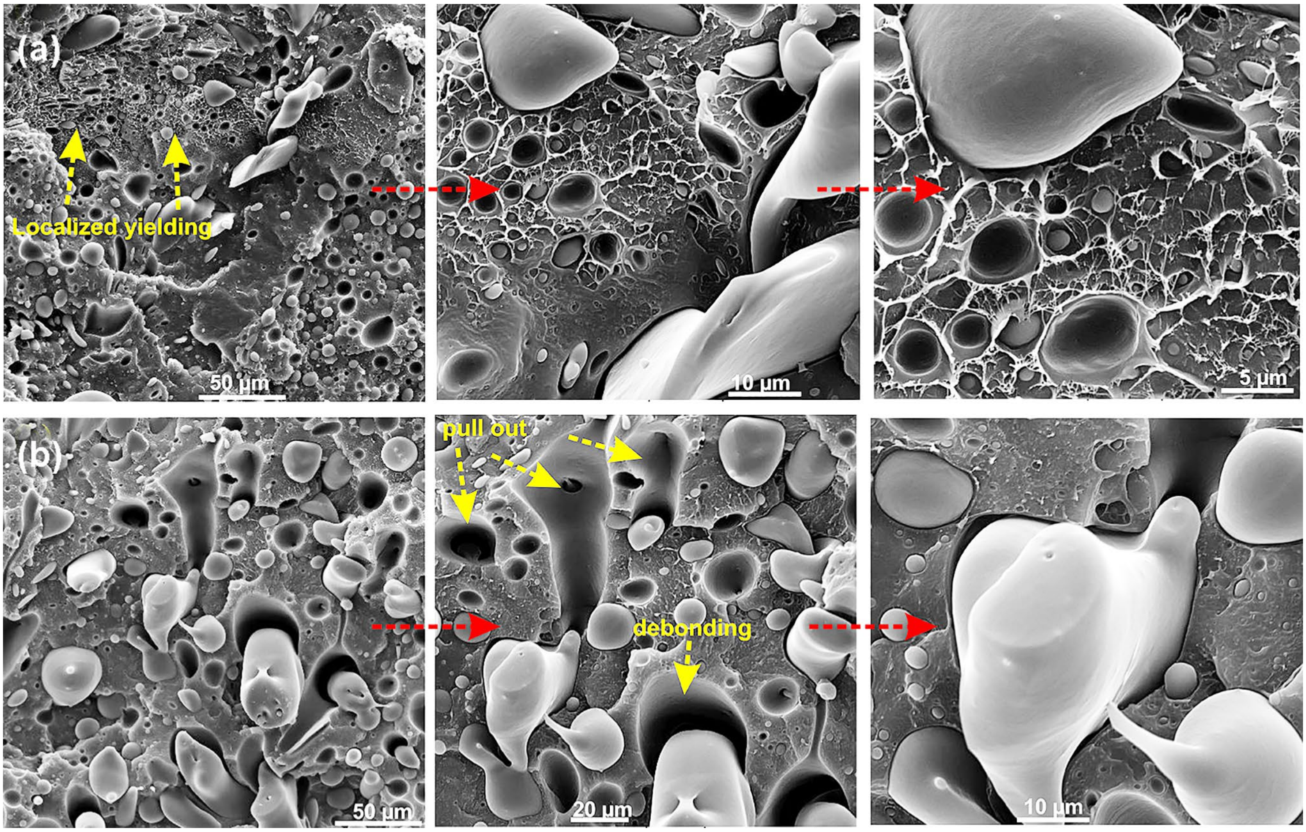

Fig. 12 SEM micrographs taken from the impact-fractured surfaces of binary PP/Elvaloy HP4051 blends: **a** 80/20; and **b** 70/30

the impact loading seems to be the dominant mode of deformation as is apparent in the SEM micrographs (Fig. 12). Some small-scale and highly localized matrix yielding and plastic drawing were observed for the blend having 20% (by weight) of Elvaloy, while such dissipative deformation was not detected for the blend comprised 30% (by weight) of Elvaloy. These findings suggest that the extensive debonding and/or pull out of most of dispersed domains control the impact energy of these blends.

It is well established that the dispersed domains act as stress concentrating sites in the matrix [13–15]. With an increase in the weight fraction of rubbery component up to 30% (by weight), the number as well as the size of localized stress fields in the matrix of PP would increase because of an increase in the number and the size of dispersed Elvaloy domains. The interfacial debonding as well as pulling out of dispersed domains under impact test produces extensive interfacial voids and/or isolated cavities in the matrix [13–15]. Obviously, the lack of suitable phase compatibility between the PP and the Elvaloy modifier is responsible for poor phase adhesion across the interface between these two components in the resulting blends [13–15]. The size and the frequency of these micro-structural defects gradually increase as the Elvaloy content in the blend was increased to 30% (by weight). For the blend containing 20–30% (by weight) of Elvaloy, the aforementioned micro-deformations (interfacial voids and separately dispersed cavities) are large enough to serve as critical-sized deformation zones for facile micro-crack nucleation as well as weak micro-structural regions for subsequent micro-crack propagation through the blend under the impact test [13–15]. In other words, the resistance of the blends against micro-crack nucleation and propagation under impact tests tends to decrease at Elvaloy loadings greater than 15% (by weight). Consequently, the impact fracture energy falls significantly for the blends composed of 20–30% (by weight) of Elvaloy.

Conclusion

Structure–property correlations were examined for binary blends of isotactic PP with an ethylene/*n*-butylacrylate/carbon monoxide (E/nBA/CO) rubbery terpolymer commercially available as Elvaloy HP4051. The objective was to evaluate the efficacy of E/*n*BA/CO as a toughener for PP resin. Morphological observations revealed a phase-separated microstructure with a coarse dispersion state of E/*n*BA/CO in the blends prepared. While the tensile ductility of the blends showed substantial increase compared with that of neat PP resin, a limited improvement in impact resistance on notched samples was obtained. Binary blends exhibited a fully ductile mode of failure under tensile test, whereas a completely brittle fracture was detected for the same blends under impact loading. Among the blends containing up to 30% (by weight) E/nBA/CO, the highest tensile strain-at-break was obtained for the blend composed of 20% (by weight) rubbery modifier, while the greatest impact fracture energy was achieved for the blend comprised 10% (by weight) E/*n*BA/CO. These findings indicate the importance of the dispersion state of rubbery modifier in achieving a high impact resistance toughened PP resin. A gradual reduction in the stiffness and strength of the blends was observed as the E/nBA/CO content in the blend was increased, as expected. Elvaloy increased the melt viscosity and elasticity of PP resin, and promoted the non-Newtonian behavior of the resulting blends. Large phase domains of Elvaloy along with insufficient phase adhesion with their surrounding PP matrix caused extensive void formation through debonding and pull out of the dispersed domains, which were found to be responsible for low impact resistance of the blends containing more than 15% (by weight) Elvaloy. According to the data obtained, it can be concluded that the Elvaloy HP4051 is not a good candidate for improving the impact strength of PP resins to a satisfactory level. This is due to the fact that Elvaloy HP4051 is polar in nature, while the PP is almost apolar. Therefore, a relatively high interfacial tension is expected for the PP/Elvaloy HP4051 blend system, which results in a poor compatibility followed by a weak phase adhesion between PP and Elvaloy in their blends. As a result, a coarse phase morphology would develop in PP/Elvaloy binary blends with the consequence of an insignificant increase in the impact toughness compared to neat PP resins.

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Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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