

Effect of replacing EPDM with high molecular weight amorphous poly(1-hexene) on the mechanical behavior of iPP/iPP-g-MA/EPDM blends

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Received: 21 August 2021, Accepted: 6 July 2022

ABSTRACT

Varying amounts of a high molecular weight poly(1-hexene) (PH, $M_v=1.7\times 10^6$ Da) are substituted for EPDM in an iPP/iPP-g-MA/EPDM blend (weight ratio: 76:4:20) and mechanical properties as well as phase morphology of the blends are studied and compared. The results show that by substituting the entire EPDM with PH, the tensile strength-at-break increases from 18.7 to 21.1 MPa, elongation-at-break increases from 15.5% to 370.8%, and impact strength increases from 6.4 to 50.1 kJ.m⁻². Dynamic mechanical thermal analysis (DMTA) of the blends proved their immiscibility and SEM analysis confirmed these findings by showing droplet-matrix morphologies. Studying the creep behavior of the samples shows that the blends containing PH have more creep so that by substituting all EPDM in the blends with PH, the permanent deformation increases from 0.425% to 0.505%. According to the results, PH is introduced as a candidate for improving the impact properties of iPP/iPP-g-MA/EPDM blend. **Polyolefins J (2023) 10: 13-20**

Keywords: Rubber-toughened iPP; creep behavior; poly(1-hexene); two-phase morphology; DMTA, immiscible blends.

INTRODUCTION

Although being relatively cheap and easily processed, thermoplastic plastics cannot present all necessary mechanical properties especially impact properties. However, thermoplastic elastomers can be processed like thermoplastics and at the same time show elastic properties [1,2]. Isotactic polypropylene (iPP) is one of the most versatile low cost commodity thermoplastic polymers. Although this polymer has widespread applications, its limited impact strength, especially at low temperatures, is a problem which hinders its

utilization as an engineering plastic. Various strategies have been used to improve toughness and impact properties of iPP through changing its microstructure by designing new coordination catalysts and/or polymerization conditions [3-6], but the results were not satisfactory and as a result the blending strategy has become more popular [7].

The impact properties of iPP can be considerably improved by incorporation of another phase into it. The new phase which is usually rubbery is preferred

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to be incompatible with iPP matrix and therefore compatibilizers are used. Various impact modifiers that are studied by different research groups include ethylene-propylene rubber (EPR)[8], ethylene-propylene-diene monomer (EPDM)[9], ethylene vinyl acetate copolymer (EVA)[10], linear low density polyethylene (LLDPE)[11], low density polyethylene (LDPE) [12], high density polyethylene (HDPE)[13], natural rubber (NR) [14], poly *cis*-butadiene rubber (PcBR)[15], poly *iso*-butylene (PIB) [16], poly(1-butene) [17], styrene-butadiene-styrene (SBS)[18], styrene butadiene rubber (SBR) [19] and ethylene 1-octene copolymer [20]. The automotive industry is a major final target for this class of polymeric blends. The mechanical properties of these blends are generally dictated by the composition and level of dispersion of the phases [21].

Among the various strategies mentioned above, EPR and EPDM are the two common elastomers used for impact modification of iPP. Due to blending of iPP with EPDM, tensile strength and Young's modulus decrease while its impact strength and elongation-at-break increases [22]. Due to different degrees of crystallinity and molecular weight, iPP is not compatible with EPDM and EPR and therefore different types of compatibilizers may be used to guarantee homogeneous dispersion of the elastomeric phase in the plastic matrix which results in larger interface between the two phases and better damping abilities are achieved [23].

Poly(1-hexene) prepared via polymerization of 1-hexene by $MgCl_2 \cdot nEtOH/TiCl_4$ /donor Ziegler-Natta catalysts presents a highly stereoregular isotactic structure (high amounts of isotactic mm triads) in which butyl branches are repeated in an alternating manner. Although its microstructure is very close to that of LLDPE it represents completely different physical and mechanical properties, especially more tackiness, which is due to higher amounts of butyl branches [24, 25]. Due to the steric hindrance of the side groups on PH chains, crystallization of the polymer chains is prevented and therefore the polymer exhibits a completely amorphous structure [24].

In the present article, different amounts of a high molecular weight poly(1-hexene) (PH) [24] are substituted for EPDM in an iPP/iPP-g-MA/EPDM blend with the weight ratio of 76:4:20 and the mechanical properties, especially impact properties, are studied and compared. At last the phase morphologies of the blends are studied and the obtained mechanical properties are analyzed on the basis of the recorded morphologies.

EXPERIMENTAL

Materials

iPP (HP525J, bulk density 0.9 g/cm^3 , MFR 3 g/10min (2.16 kg, 230°C)) was obtained from Jam Petrochemical Company (JPC, Asalouyeh, Iran). EPDM (KEP270, Moony viscosity 71(ML 1+4, 125°C)) containing 57 wt% ethylene and 4.5 wt% ethylene norbornene was purchased from Kumho Polychem (South Korea). Maleic anhydride-grafted polypropylene (PP-g-MA) was acquired from Solvay with the trade name of Addcomp Priex 20070 (MFI 64 g/min, grafted maleic anhydride 0.1 wt%) and was used as coupling agent. PH ($M_v 1.7 \times 10^6$ Da) was donated by Iran Polymer and Petrochemical Institute (IPPI) [24].

Blending

According to formulations given in Table 1, at first EPDM and PH were weighed and introduced in a Brabender internal mixer (Model W50 (2002), Germany). After complete melting and mixing the two components for 2 minutes, iPP and iPP-g-MA were introduced. The mixing process was continued for 8 minutes. The initial mixing temperature was set at 185°C . The compounded materials were then hot pressed using a hot press instrument.

Characterization and measurements

Tensile properties

The tensile properties of the samples including tensile strength and percentage elongation-at-break were measured according to ASTM D638 using a Gotech Instrument (Model: AI-7000-LA). The test was done at a speed of $50 \text{ mm} \cdot \text{min}^{-1}$ and constant temperature (25°C). The samples were prepared in the form of sheets with a thickness of 1 mm using a hot press (Toyoseiki Mini Test Press, Japan) and they were punched according to ASTM D638 Type IV. The prepared samples were free from any bubbles, cracks

Table 1. Weight percentage of each component in iPP/EPDM/PH blends*.

Entry	iPP	iPP-g-MA	EPDM	PH
PH0	76	4	20	0
PH5	76	4	15	5
PH10	76	4	10	10
PH15	76	4	5	15
PH20	76	4	0	20

*The total weight of the components in the mixer was equal to 50 g.

or defects. For each treatment level, three replications were tested.

Impact properties

The notched Izod impact strength analysis of samples was carried out on a Gotech Impact Tester (GT-7045-MDH) at 25°C according to ASTM D256. The analysis was repeated three times on replicate samples. The dimensions of prepared specimen were 63.5×12.7×3.2 mm. The results are reported in energy lost per unit cross-sectional area in the notch (kJ/m²).

Creep properties

The creep behavior of the prepared samples was determined by loading the specimens with a constant stress (2.5 MPa). The test was done at 25°C. The specimens were prepared as flat sheets with 20×5×0.5 mm dimensions. The test was performed in a DMA1 instrument (Model: Stare System, Mettler-Toledo). The primary region, which is the early stage of loading when the creep rate decreases rapidly with time, the secondary region, which is the steady state region, and finally, the permanent deformation of the samples are reported and compared.

Dynamic mechanical thermal properties

To better analyze the damping ability of the samples, their DMTA was performed on a DMA1 thermal analysis system (Model: Stare System, Mettler-Toledo) in bending mode at 1 Hz from -80 to 100°C. The samples were prepared in 30×10×1 mm dimensions. Furthermore, the results were also used to investigate the compatibility of the phases.

Surface morphology

Surfaces morphologies of the samples before and after etching with toluene were recorded on a WEGA (TESCAN) scanning electron microscope after coating with gold. An accelerating voltage of 20.00 kV was used with a mean working distance of 14 mm. All images were captured as TIFF files at the highest possible resolution with the same SEM magnitude of 2.00 kX. The samples were cold fractured after immersing in liquid nitrogen (causing brittle fracture) for investigating the phase morphology of the components in the bulk of the samples. The new surfaces emerged after fracture were also etched with toluene before analyzing. Toluene dissolves the elastomeric phase, leaving holes and cracks instead,

and simplifies the detection and differentiation of the dispersion pattern of the dispersed phase.

RESULTS AND DISCUSSION

Mechanical properties of polymeric blends depend on characteristics of the phases as well as the interfacial region. In the present study, PP-g-MA is used to provide a good adhesion between the plastic (iPP) and elastomeric (EPDM and PH) phases at the interfacial regions. Table 2 depicts the measured mechanical properties of the prepared samples. It is clear that upon substituting PH for all or some parts of EPDM, the ductility of the blend has increased considerably. This is manifested by the 700% and 12% and 2300% increase in impact strength, stress-at-yield and elongation-at-break (EB) of the samples, respectively.

This increase in ductility could be explained by enhanced toughening or plastification in the presence of high molecular weight PH [26, 27]. When PH is absent in the blends, the mechanical properties are weakened due to the high interfacial tension and weak adhesive forces between the elastomeric and plastic phases (incompatible phases). Upon substituting PH for EPDM, the mechanical properties enhance, which can be due to the high tackiness of PH. This PH property, along with its higher amount of entanglement (high M_n and longer chains) may cause EPDM chains to move more sluggishly and better dispersions of the phases, which can result in more tensile strength. Also, as seen in the SEM micrographs of the samples, many rubber microspheres can be found in the crystalline region. Existing amorphous microspheres can facilitate relative sliding among lamellas under external force, which can lead to increased elongation-at-break [28]. To better justify the results obtained in the present work, the obtained impact strength results were compared with impact strength

Table 2. Mechanical properties of iPP/EPDM/PH blends.

Entry	Impact strength (kJ.m ⁻²)	Stress-at-yield (MPa)	EB%	Young's modulus (MPa)
Neat iPP	5.4	32.0	9.0	1450
PH0	6.4	18.8	15.5	N.O.
PH5	18.4	19.9	51.3	708
PH10	9.8	20.3	41.1	611
PH15	24.0	20.5	189.0	670
PH20	50.1	21.1	370.9	N.O.

N.O.: Not Obtained

data of several other toughened iPP published in the literature. The obtained data confirm that PH can be a good candidate for impact modification of iPP [12, 15, 27].

Dynamic mechanical thermal analysis (DMTA) of the samples confirmed the incompatibility of the phases. As can be seen from Figure 1, the loss tangent curves of entries PH5 to PH15 show three separate peaks. Since the positions of the peaks did not show a shift towards each other compared to entries PH0 and PH20, the incompatibility of the three phases was confirmed (Approx. $T_g(\text{PP})=15^\circ\text{C}$, $T_g(\text{PH})=-30^\circ\text{C}$ and $T_g(\text{EPDM})=-45^\circ\text{C}$). The maximum loss tangent value for the polypropylene phase was seen for entry PH10, in which the weight percentage of EPDM and PH was equal. This means that the molecular mobility and therefore the energy dissipation potential of iPP matrix is maximum in this entry. When the morphologies of the phases were investigated by SEM, it was observed that the entry PH10 has a droplet-like morphology with the most homogenous dispersion compared to the other prepared samples. The area under the PP $\text{Tan } \delta$ peaks of the entries is also compared in Figure 2. As it is clear from the figure, the maximum area is observed for the entry PH10, which shows that the maximum damping ability and impact absorbance are obtained from this entry.

Investigating the creep behavior of the samples showed higher creep for the samples containing PH. By increasing the weight percentage of PH in the samples, their permanent deformation increased. Solid-state creep resistance of polymeric materials depends on their various microstructural properties including molecular weight (chain length), MWD, crystallinity, etc., [29]. Among the aforementioned factors, crystallinity plays a more important role. In the present work,

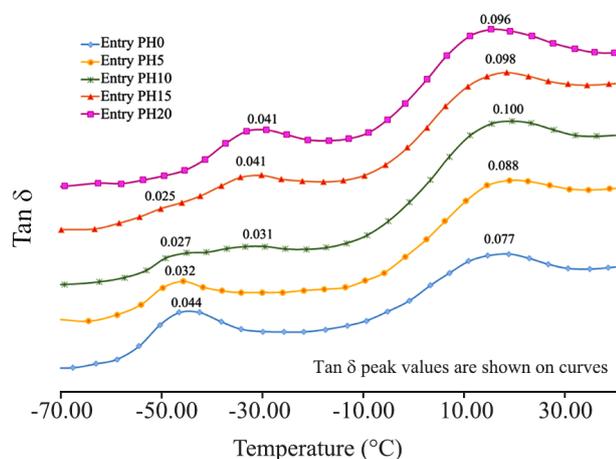


Figure 1. Dynamic mechanical thermal analysis of prepared iPP/EPDM/PH blends.

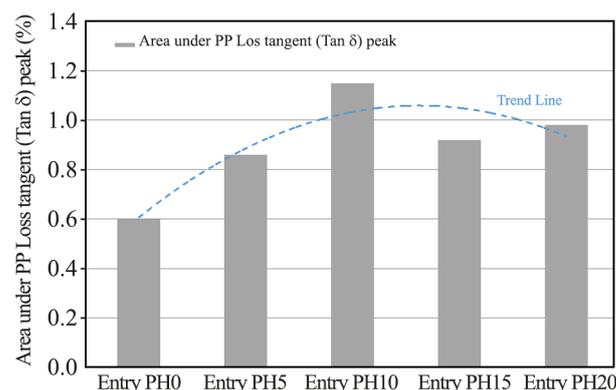


Figure 2. Comparison of the area under PP $\text{Tan } \delta$ peaks of prepared iPP/EPDM/PH blends.

it can be said that with the increase of amorphous PH in the blends, the creep resistance decreases considerably due to lower amount of crystallinity. Table 3 and Figure 3 show the creep behavior of selected samples.

SEM micrographs of the etched samples confirmed the presence of two distinct phases in them. Figure 4 shows the SEM micrographs of fractured surfaces of selected samples before and after etching with toluene. The elastomeric phase (EPDM and PH) is dispersed in the plastic matrix in droplet-matrix morphology, where the elastomeric phase is dispersed in the PP matrix. By comparing the micrographs, it seems that in the absence of PH, the interfacial adhesion is very poor and a high rate of coalescence of EPDM droplets can be observed (Figure 4a). [23] When some of the EPDM is replaced

Table 3. Creep results for selected iPP/EPDM/PH blends.

Entry	Permanent deformation (%)
PH0	0.425
PH10	0.505
PH20	0.536

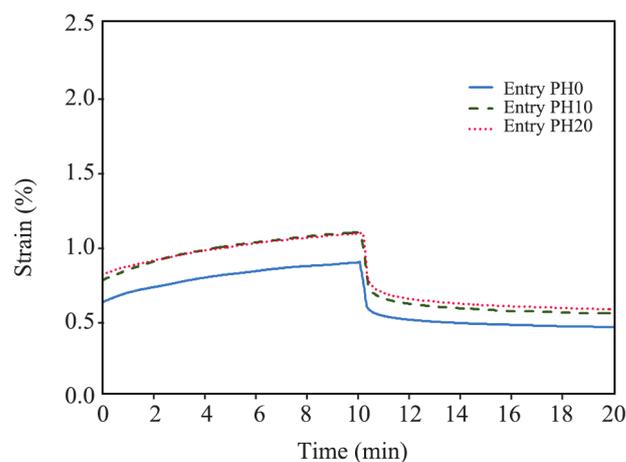
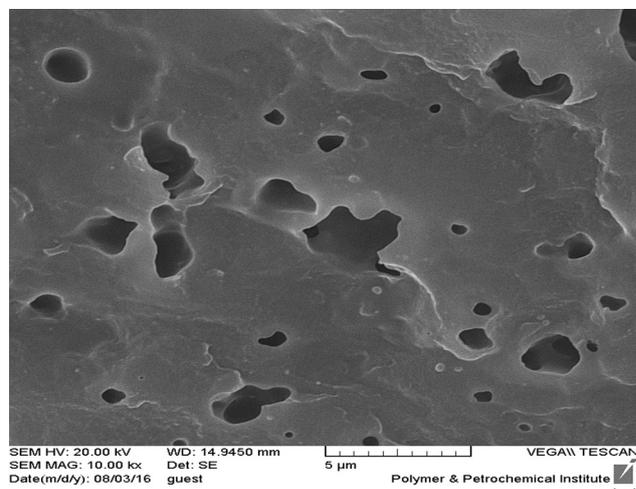
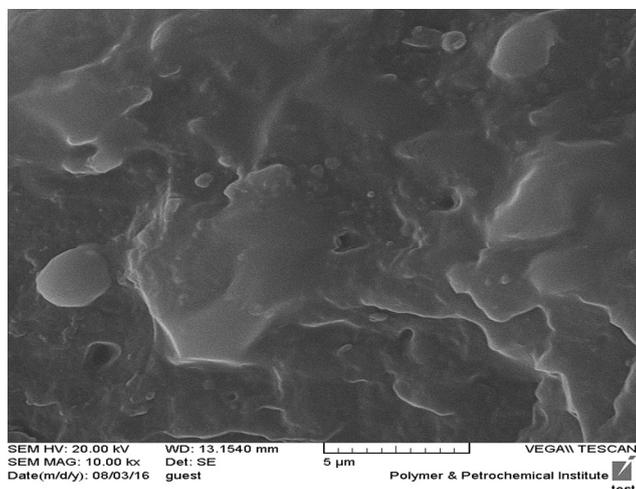


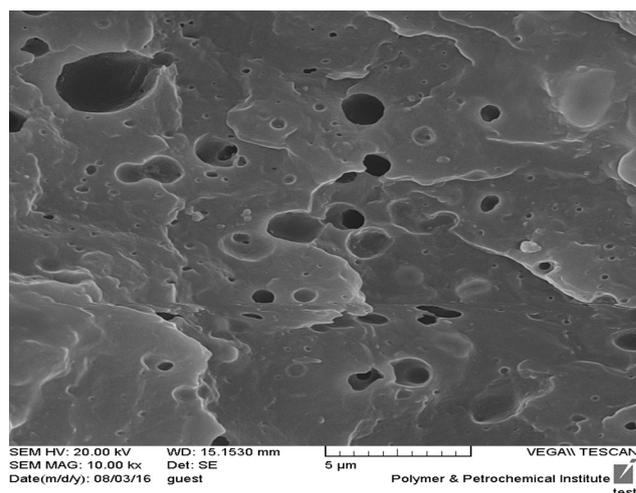
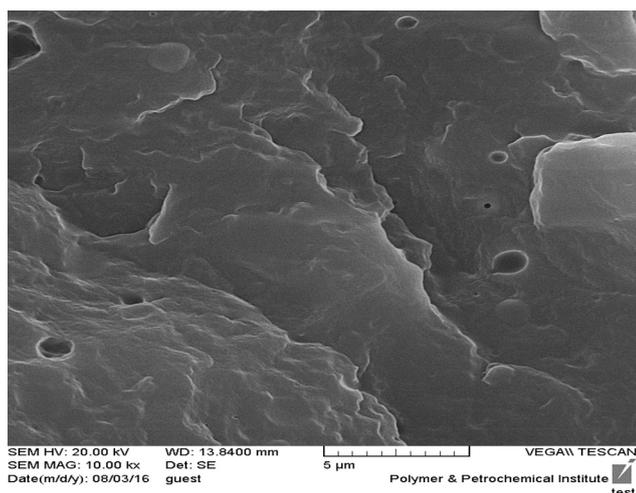
Figure 3. Creep behavior of selected samples.

by PH, droplet coalescence is suppressed and a finer dispersion of elastomeric particles is found in the PP matrix. These observations can show that PH can increase interfacial adhesion and decrease interfacial

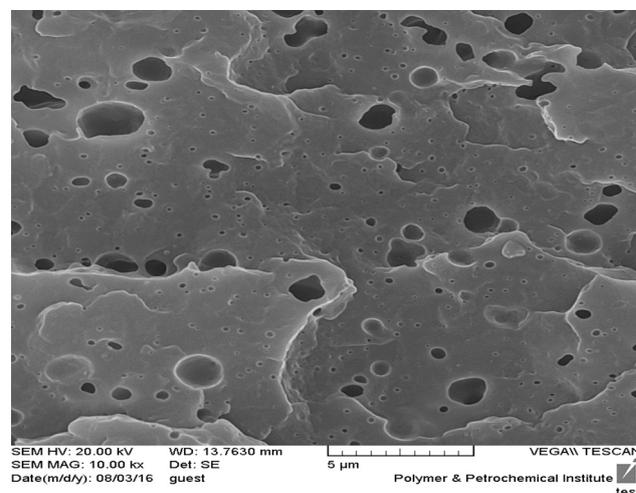
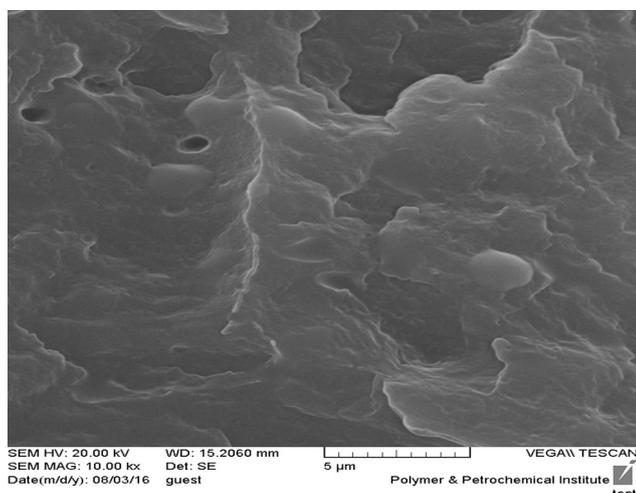
tension between iPP and EPDM (perhaps due to the highly branched structure of PH). However, when EPDM was totally replaced by PH, the coalescence returned (entry PH20, Figure 4e) but at a much lower



(a)



(b)



(c)

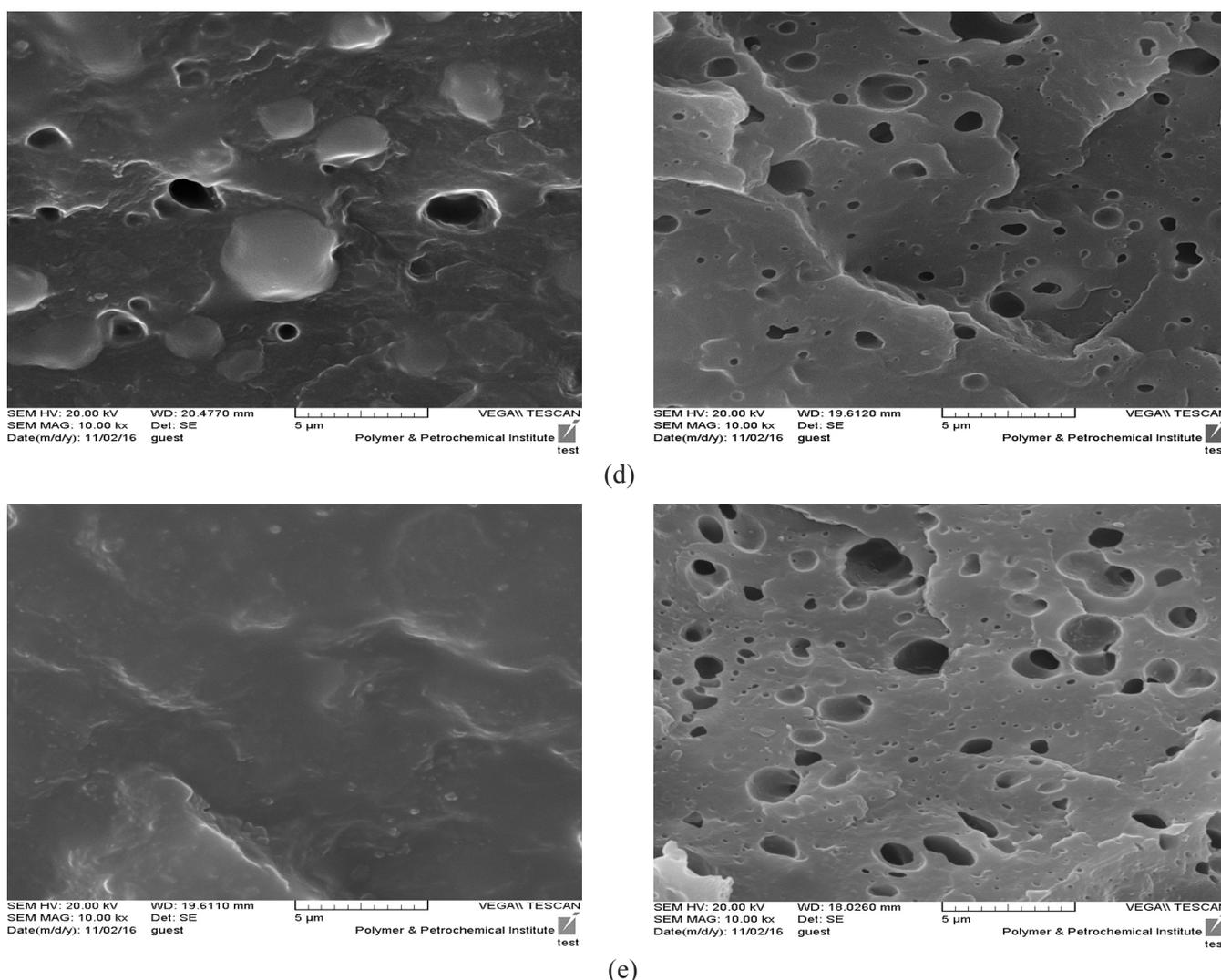


Figure 4. SEM micrographs of prepared iPP/EPDM/PH blends before (left) and after (right) extraction in boiling toluene: (a) entry PH0; (b) entry PH5; (c) entry PH10; (d) entry PH15; (e) entry PH20.

rate of occurrence compared to entry PH0, which could indicate a better compatibility of PH with the matrix compared to EPDM. The best dispersion of the elastomeric phase in the matrix was seen for entry PH10, in which the weight percentage of the two elastomers was equal.

According to the results, it can be said that by using PH and EPDM with the same weight ratios, better dispersions and phase morphologies are obtained for the blend.

CONCLUSION

In this study, the effect of replacement of EPDM with PH on the mechanical properties of iPP/PP-g-MA/EPDM blend was investigated and the obtained results

were justified according to their phase morphology. Impact strength, stress-at-yield and elongation-at-break improved with increasing pH content in the blend, while permanent deformation worsened. DMTA results showed that the highest $\tan \delta$ value for the plastic phase was obtained when the weight ratio of the two elastomers was the same. SEM results showed that the best dispersion of EPDM and PH droplets in the iPP matrix was obtained when the weight ratio of the two elastomers was the same. It might be concluded that each of the two elastomers act as a compatibilizer for the other elastomer.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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