Study the Effect of Rubbery Phase on Morphology and Rheology Development of PP/PA6/(EPDM: EPDM-g-MA) Ternary Blends

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Abstract—This study aimed to investigate the phase morphology of ternary blends comprising polypropylene (PP), polyamide 6 (PA6), and a blend of ethylene propylene diene monomer (EPDM) and maleic anhydride-grafted EPDM (EPDM-g-MA) in a 70/15/15 ratio. Varying ratios of EPDM to EPDM-g-MA were examined. As the proportion of EPDM-g-MA increased, an interlayer phase formed between the dispersed PA6 domains and the PP matrix. This resulted in the development of a core-shell encapsulation morphology within the blends. The concentration of the EPDM-g-MA component is inversely correlated with the average size of PA6 particles. Additionally, blends containing higher proportions of the EPDM-g-MA rubbery phase exhibited an aggregated structure of the modifier particles. Notably, as the concentration of EPDM-g-MA increased from 0% to 15% in the blend, there was a consistent monotonic reduction in the size of PA6 particles.

Keywords—Phase morphology, rheology, rubbery phase, rubber functionality, ternary blends.

I. INTRODUCTION

MELT blending of two or more polymers provides a common and effective solution for the production of commercial polymer materials [1]. Addition to mechanical properties such as modulus and tensile strength, the improvement of plastics and semi-crystalline polymers' toughness by using the elastomers have attracted the attention numerous researchers in recent years [2]-[5].

Nowadays, PP is highly valued for its easy processability and low price. Despite these benefits, PP is brittle under the conditions of a lower temperature, surface imperfection, and high speeds [6], [7]. To enhance its properties and reduce costs, PP is often combined with PA and rigid inorganic fillers such as glass fiber and calcium carbonate. PP/PA6 binary blends are immiscible and incompatible due to differing polarity structure of PA6 and PP blends. PP/PA6 binary blends have poor mechanical properties such as low strength and toughness. To improve the rheological properties and the mechanical, a coupling agent must be used between PP and PA6. It is well known that for polymer blends, the physical, mechanical, and the rheological properties greatly depend on the phase morphology [4], [8]-[10]. The morphology of immiscible polymer pairs (polymer blends) is greatly influenced by the proportions, interfacial interactions, and viscoelastic characteristics such as viscosity, elasticity ratios of the components, and the extent of deformation in the flow field of the blend constituents [11]-[16]. In essence, both kinetic and thermodynamic factors play a role in determining the morphology of binary and ternary blends. Furthermore, it is well-established that the rheological and mechanical properties of polymer blends are significantly affected by the resulting morphology during the mixing process [17].

In the binary polymer blends morphology can take on different forms, including droplets of one phase dispersed within the other, or the formation of co-continuous microstructures where both phases are continuous. In ternary blends comprising three immiscible polymeric components, various morphologies may arise. This includes the separate dispersion of minor phases within the major phase and the encapsulation of one minor component by another within the matrix phase, known as core-shell morphology [18]-[22]. In a previous study conducted within our research group, we investigated the impact of rubber functionality on fracture resistance and micromechanical deformations [23].

In the present work, we are further focused on studying the effect of the various ratios of EPDM: EPDM-g-MA in PP/PA6/ (EPDM+EPDM-g-MA) ternary blends to further clarify the relation between rheological properties and morphology.

II. EXPERIMENTAL SETUP

A. Materials

Polyamide 6 (PA6), with density of 1.13 g/cm^3 and melting temperature of 223 °C, used in this study was Tecomid NB40 NL E. The isotactic polypropylene (iPP), MFI = 5.0 g/10 min at 2.16 kg and 230 ° C, melting temperature of 165 °C, was obtained from Polynar Petrochemical Co., Tabriz, Iran. The EPDM used (KEP270) with mass density of 0.96 g/cm^3 and Mooney viscosity (ML(1+4), 125 °C) of 71, supplied from Kumho Polychem, Korea, was of medium ethylene grade (contents of ethylene, propylene and ethylidene norbornene: 57, 38.5, and 4.5 wt%, respectively). Ethylene-propylene-diene rubber grafted with maleic anhydride (EPDM-g-MA), with the trademark TRD-359EP, had a Mooney viscosity (ML (1+4), 100 °C) of 23, mass density of 0.875 g/cm^3, and a MAH content of 0.8-1.5wt%. It was purchased from Yangzhou Henghui

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III. BLEND PREPARATION

PA6 and EPDM-g-MA were dried for 24 h at 80 °C under vacuum oven prior to processing to minimize the degradation due to moisture. PP-base blends containing 30 wt% of the dispersed phase(s) were prepared. In the case of ternary blends, the content of PA6 and EPDM+EPDM-g-MA modifier phases was kept equal at 15 wt% and the weight ratio of EPDM: EPDM-g-MA was changed from 15:0 to 0:15. Melt blends were prepared using an internal mixer (Brabender W50EHT) with a 55-ml mixing chamber which was preheated at 210 °C and operated 60 rpm. The composition of the blends studied in this work is listed in Table I.

TABLE I
THE NOTION AND COMPOSITION OF THE TERNARY SYSTEMS STUDIED IN THIS WORK

Ternary Blends	Compositions (wt%)			
	iPP	PA6	EPDM	EPDM-g-MA
P-N6-R+mR 100%	70	15	15	0
P-N6-R+mR 75%	70	15	11.25	3.75
P-N6-R+mR 50%	70	15	7.5	7.5
P-N6-R+mR 25%	70	15	3.75	11.25
P-N6-R+mR 0%	70	15	0	15

A. Morphological Observation

The morphology of all blends was analyzed using field emission scanning electron microscopy (FESEM; Mira 3-XMU). The blend samples were cryogenically fractured in liquid nitrogen, and to gain a clearer understanding of the dispersion state of the dispersed phases, a selective extraction technique was employed on the elastomeric phase domains. The EPDM-g-MA and EPDM rubbery phase domains were etched using cyclohexane at 50 °C for 24 hours. Following this, the samples underwent drying overnight at 85 °C in a vacuum oven and were subsequently gold-sputtered to ensure effective conductivity of the electron beam. Microphotographs were then captured at various magnifications. Additionally, Transmission Electron Microscopy (TEM) was employed for the sample containing solely the functionalized rubber P-N6-R+mR 0%. TEM analysis was conducted using a Philips EM208 microscope (Netherlands) operating at 100 kV. The samples were microtomed at a temperature of -160 °C. Samples approximately 80 nm thick were prepared for TEM using a Reichert Ultracut ultramicrotome equipped with a diamond knife. Subsequently, the samples were stained by exposure to ruthenium tetroxide vapors generated from the oxidation of ruthenium dioxide by excess sodium periodate at room temperature for 30 minutes.

B. Rheological Studies

The viscoelastic properties of various samples were studied using a dynamic rheometer (MCR301, Anton Paar) with a parallel plate setup (diameter = 25 mm, gap = 1 mm). Dynamic frequency sweep tests were conducted over the range of 0.04–625 rad/s at 230 °C, with a 1.0% strain amplitude to ensure the materials remained within the linear viscoelastic range.

IV. RESULTS AND DISCUSSION

A. Morphological Characterization of Blends

The SEM micrographs taken from the cryo-fracture surfaces of PP/PA6/(EPDM: EPDM-g-MA) (70/15/15) ternary blends of different EPDM: EPDM-g-MA weight ratios are shown in Fig. 1. The dark cavities visible on the surfaces of samples in the micrographs are related to the etched rubbery phases in these blends. A substantial change in the morphology and dispersion state of modifier particles can be seen in the micrographs in Fig. 1 as the fraction of EPDM-g-MA of the rubbery component in the blend was increased. For ternary blend with EPDM: EPDM-g-MA weight ratio of 15:0, a separately dispersed morphology is apparent in Fig. 1 (a). The course particle size distribution of dispersed PA6 phase, coupled with a seamlessly smooth interface lacking visible roughness between the phases, suggests a significant interfacial tension between the components. Upon the introduction of EPDM-g-MA into the blend, as shown in Fig. 1 (b), a decrease in PA6 domains can be observed. In the sample containing an equal percentage of both EPDM and EPDM-g-MA, these components are evenly spread throughout the PP matrix, with a notable decrease in their size (Fig. 1 (c)). By increasing the percentage of functionalized rubber to 11.25%, as it can be seen in Fig. 1 (d), the PA6 particles, coated with a rubber layer, approach each other in a uniformly distributed manner. Ultimately, the blends comprising only EPDM-g-MA show the development of aggregated/agglomerated tiny PA6 structures covered in a thick rubbery shell distributed in the matrix phase. The number of relatively isolated large PA6 domains is lowered as the EPDM:EPDM-g-MA weight ratio was changed from 15:0 to 0:15 in the blends. The SEM images in Figs. 1 (d) and (e) clearly reveal that the dispersed clusters of PA6 particles are surrounded by cavities left by the extraction of rubbery phases. Fig. 1 (f) confirms that the morphology in the ternary blends is of the core-shell type, with PA6 as the core and the rubbery phase(s) forming the shell. These phases are joined together, resulting in sea-island morphology in the blend. In the blends containing EPDM-g-MA, the maleic anhydride (MA) groups on the EPDM-g-MA phase chemically react with amine end groups of PA6 chains, leading to the in–situ formation of EPDM-g-PA6 copolymer which locates at the interface between the PA6 and PP matrix. The graft copolymer formed reduces the interfacial tension between the PA6 particles and the PP matrix, leading to a notable increase in interfacial adhesion through a compatibilization mechanism at the interface. Higher concentrations of EPDM-g-MA in the ternary blend result in greater compatibilization, leading to a more uniform distribution of PA6 particle sizes. Therefore, it can be claimed that the morphology in ternary blends in Figs. 1 (e) and (f) is mainly in the form of agglomerated structures of core-shell particles in the matrix.

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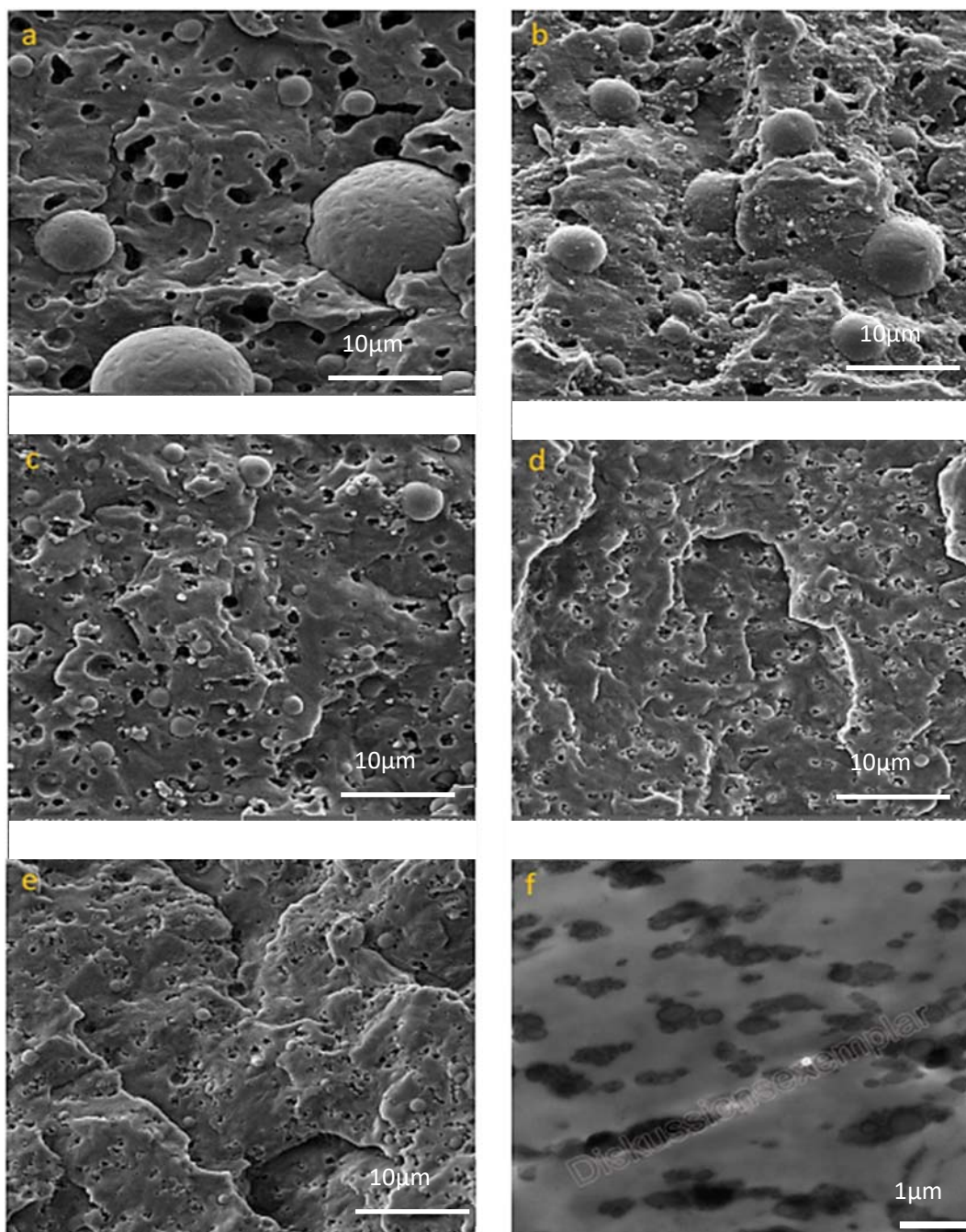Vol:18, No:12, 2024

Fig. 1 The FE-SEM micrograph of the cryo-fractured surface, the proportions indicating the blend of EPDM and EPDM-g-MA: (a) iPP/PA6/EPDM+EPDM-g-MA 100%+0%; (b) iPP/PA6/EPDM+EPDM-g-MA 75%+25%; (c) iPP/PA6/EPDM+EPDM-g-MA 50%+50%; (d) iPP/PA6/EPDM+EPDM-g-MA 25%+75%; (e) iPP/PA6/EPDM+EPDM-g-MA 0%+100%; (f) TEM of microtome surface of iPP-PA6-EPDM+EPDM-g-MA 0%+100%

B. Rheological Properties of Blends

Fig. 2 displays the frequency sweep test conducted to examine how the storage modulus of the ternary blends is affected by varying the ratio of EPDM to EPDM-g-MA. Based on the loss modulus versus frequency plot, the blend lacking functionalized rubber exhibits a liquid-like behavior in the low-frequency region. This is attributed to the separate distribution of the PA6 and EPDM inclusion phases within the matrix, with

minimal adhesion between them. However, with the incorporation of EPDM-g-MA into the blends, there is a significant shift in behavior at low frequencies. A second plateau emerges, indicating enhanced compatibility between PP and PA6 phases. With a further increase in the proportion of the functionalized rubbery phase, as evident from the sample morphology, the PA6 droplets diminish in size and become more uniform. A sudden rise in the loss modulus is observed in

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the sample containing a 7.5/7.5 (w/w) ratio of both rubbers, indicating the completion of the rubbery shell encasing the PA6 cores within this composition. A similar upward trend in the loss modulus is noted with higher concentrations of EPDM-g-MA. This increase is attributed to the fusion of the core-shell inclusions, forming aggregated regions within the matrix phase.

In the two compositions containing 11.25% and 15% of EPDM-g-MA, the curves closely align with each other. Consistent with the FE-SEM images, there's minimal disparity between these two blends. The convergence of these curves indicates that the optimal percentage for observing agglomerations is 11.25%, and further increasing the percentage to 15% does not affect the size of the inclusions. FESEM analysis similarly indicates a lack of significant difference between these two blends. The elevated loss modulus at terminal frequencies in both samples is attributed to the presence of numerous agglomerated inclusions encapsulated by a substantial rubbery shell.
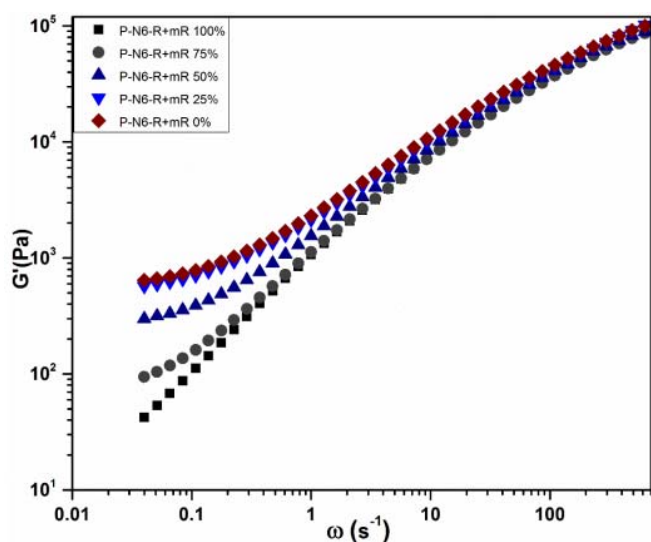

Fig. 2 Alteration of the storage modulus of PP/PA6/ (EPDM: EPDM-g-MA) ternary blends by changing the EPDM: EPDM-g-MA ratio (70/15/15) w/w

V. Conclusion

In the present study, the correlation between the phase morphology and the viscoelastic properties of ternary blends PP/PA6/(EPDM: EPDM-g-MA) containing different ratios of the EPDM: EPDM-g-MA is studied. As the ratio of EPDM-g-MA to EPDM increases, an interlayer phase develops between the dispersed PA6 domains and the iPP matrix. This interlayer facilitates the formation of a core-shell encapsulation morphology within the blends. With a higher concentration of the EPDM-g-MA component, there is a noticeable reduction in the average size of the PA6 particles. Furthermore, in blends containing a significant proportion of the EPDM-g-MA rubbery phase, there is an emergence of a clustered structure among the modifier particles. This phenomenon becomes more pronounced as the concentration of EPDM-g-MA gradually increases from 0% to 15% in the blend. Consequently, there is a consistent decrease in the size of the PA6 particles. The

frequency sweep test yielded significant understanding regarding the storage modulus characteristics of ternary blends as the ratio of EPDM to EPDM-g-MA was adjusted. Increasing the presence of functionalized rubber in the blends led to a shift in the storage modulus behavior, transitioning from a liquid-like state due to the individual distribution of PA6 and EPDM inclusions to exhibiting a second plateau, characteristic of solid-like materials. This shift indicates the formation of agglomerations comprising core-shell particles enveloped by a thick rubber layer. These findings underscore the influence of morphological alterations on the rheological properties of the blends.

References

[1] Han, C., Multiphase flow in polymer processing. 2012: Elsevier.
[2] Wang, B. B., L. X. Wei, and G. S. Hu, Synergetic toughness, and morphology of poly (propylene)/nylon 11/maleated ethylene-propylene diene copolymer blends. Journal of applied polymer science, 2008. 110(3): p. 1344-1350.
[3] Wilkinson, A., et al., Phase structure in polypropylene/PA6/SEBS blends. Polymer, 1999. 40(17): p. 4971-4975.
[4] Mazidi, M. M., et al., Structure–property relationships in super-toughened polypropylene-based ternary blends of core–shell morphology. Rsc Advances, 2016. 6(2): p. 1508-1526.
[5] Li, L.-p., et al., Characterization of PA6/EPDM-g-MA/HDPE ternary blends: The role of core-shell structure. Polymer, 2012. 53(14): p. 3043-3051.
[6] Cartier, H. and G. H. Hu, Morphology development of in situ compatibilized semicrystalline polymer blends in a co-rotating twin-screw extruder. Polymer Engineering & Science, 1999. 39(6): p. 996-1013.
[7] Hu, G.-H., H. Cartier, and C. Plummer, Reactive extrusion: toward nanoblends. Macromolecules, 1999. 32(14): p. 4713-4718.
[8] Mazidi, M. M. and M. K. R. Aghjeh, Synergistic toughening effects of dispersed components in PP/PA6/EPDM ternary blends; quantitative analysis of the fracture toughness via the essential work of fracture (EWF) methodology. RSC Advances, 2015. 5(58): p. 47183-47198.
[9] Wilkinson, A., M. Clemens, and V. Harding, The effects of SEBS-g-maleic anhydride reaction on the morphology and properties of polypropylene/PA6/SEBS ternary blends. Polymer, 2004. 45(15): p. 5239-5249.
[10] Afsari, B., Razavi Aghjeh, M. K. and Hasanpour, M., 2020. Evolution of morphology and morphology stability in PP/PA6/EPDM-g-MA reactive ternary blends using viscoelastic measurements. Rheologica Acta, 59, pp.399-414.
[11] Vanoene, H., 1972. Modes of dispersion of viscoelastic fluids in flow. Journal of Colloid and Interface Science, 40(3), pp.448-467.
[12] Wu, S., 1987. Formation of dispersed phase in incompatible polymer blends: Interfacial and rheological effects. Polymer Engineering & Science, 27(5), pp.335-343.
[13] Hemmati, M., Nazokdast, H. and Shariat Panahi, H., 2001. Study on morphology of ternary polymer blends. I. Effects of melt viscosity and interfacial interaction. Journal of applied polymer science, 82(5), pp.1129-1137.
[14] Hemmati, M., Nazokdast, H. and Shariat Panahi, H., 2001. Study on morphology of ternary polymer blends. II. Effect of composition. Journal of applied polymer science, 82(5), pp.1138-1146.
[15] Tchomakov, K. P., Favis, B. D., Huneault, M. A., Champagne, M. F. and Tofan, F., 2004. Composite droplets with core/shell morphologies prepared from HDPE/PS/PMMA ternary blends by twin-screw extrusion. Polymer Engineering & Science, 44(4), pp.749-759.
[16] Paul, D. R., 2012. Polymer Blends Volume 1 (Vol. 1). Elsevier.
[17] Salehiyan, R. and Sinha Ray, S., 2018. Processing of polymer blends,

emphasizing melt compounding; influence of nanoparticles on blend morphology and rheology; reactive processing in ternary systems; morphology–property relationships; performance and application challenges; and opportunities and future trends. In *Processing of Polymer-based Nanocomposites: Processing-structure-property-performance relationships* (pp. 167-197). Cham: Springer International Publishing.

[18] Horiuchi, S., Matchariyakul, N., Yase, K. and Kitano, T., 1997. Morphology development through an interfacial reaction in ternary immiscible polymer blends. *Macromolecules*, *30*(12), pp.3664-3670.

[19] Horiuchi, S. and Nakayama, K., 1999. Morphology Development during Melt Processing of Immiscible Polymer Blends. *Macromolecular Science and Engineering: New Aspects*, pp.301-318.

[20] Reignier, J., Favis, B. D. and Heuzey, M. C., 2003. Factors influencing encapsulation behavior in composite droplet-type polymer blends. *Polymer*, *44*(1), pp.49-59.

[21] Valera, T. S., Morita, A. T. and Demarquette, N. R., 2006. Study of morphologies of PMMA/PP/PS ternary blends. *Macromolecules*, *39*(7), pp.2663-2675.

[22] Ravati, S. and Favis, B. D., 2010. Morphological states for a ternary polymer blend demonstrating complete wetting. *Polymer*, *51*(20), pp.4547-4561.

[23] Mazidi, M. M., Aghjeh, M. K. R. and Hasanpour, M., 2018. Fracture resistance and micromechanical deformations in PP/PA6/EPDM ternary blends: effect of rubber functionality, dispersion state and loading conditions. Engineering Fracture Mechanics, 191, pp.65-81.