

RESULT OF THE PA6 CONTENT ON THE MECHANICAL, RHEOLOGICAL AND MORPHOLOGICAL PROPERTIES OF PP/PA6 BLENDS

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Abstract. *The mixture of polymers, known as polymer blends emerged as an alternative to the synthesis of new materials, combining the best properties of each polymer. The aim of this study is to evaluate the influence of polyamide 6 concentration and different compatibilizers on the mechanical properties, rheology and morphology of PP/PA6 blends. The blends were prepared in a twin-screw extruder and the samples for the tests were injection molded and characterized by mechanical properties (Tensile and impact strength), Scanning Electron Microscopy (SEM) and Rheology. To evaluate the influence of the PA6 concentration, the composition of PP/PA6 blend was 80/20, 70/30, 60/40 and 50/50 (wt%). The composition of 70/30 was chosen to evaluate the effect of compatibilizers PPgAA, PPgMA and E-GMA on this blend. The results showed that the impact strength considerably increased with the increase in the PA6 concentration. Fibrils were observed in the 60/40 and 50/50 PP/PA6 blends, which may have slowed the spread of cracks, while the tensile strength remained almost unchanged due to the immiscibility between the polymers that may have been reduced by the formation of a weak interface. There were significant improvements of mechanical properties with the addition of PP-g-MA and PP-g-AA (modulus, tensile strength) compared to 70/30 PP/PA6 blend. Rheological changes in viscosity of binary blends with respect to neat PP could be directly related to the morphology due to the formation of co-continuous phases for PA6 concentrations above 40% in the PP/PA6 blend.*

Keywords: *mechanical properties; polymer blends; polyamide 6*

1. INTRODUCTION

From the 70's there was a slowdown in the production of new polymers (homopolymers), accompanied by a dramatic increase in the number of techniques for modifying existing polymers. This is due to the fact that the production of new polymers has become a more expensive process, taking into account the long time required to develop the system of polymerization and processing equipment. Therefore, the reasons for the slowdown in production of new homopolymers were almost strictly economic (Ultracki et al, 1995).

From these reasons a new form of obtaining polymeric materials, ie by mixing one or more polymers through the formation of polymer blends. Soon, it became common practice to develop new polymeric materials by mixing polymers and / or different copolymers. (Zhang et al., 2007).

However, it is difficult to obtain good dispersibility and control of morphology in polymer blends whose components are insoluble in each other, particularly combinations of polar polymers with polar polymers (Tang et al., 2004, Agrawal et al., 2007, Lima et al ., 2010).

For immiscible polymer blends using compatibilizers is necessary to make the system compatible. The compatibilizers are block or graft copolymers, which exhibit intermolecular attraction or promote chemical reactions with components of the blend. (Dagli et al., 1994, Agrawal et al., 2007).

Blends of polyamide 6 (PA6) and polypropylene (PP) combine the thermo-mechanical and barrier PA6 with easy processability and low cost of the PP. However, these blends are immiscible due to chemical incompatibility between the polymers, since the PA6 is composed of polar groups and nonpolar groups of PP, which leads to an unstable morphology and consequently poor mechanical properties. Therefore, the addition of compatibilizers is an alternative to improve the interaction between the polymers.

The aim of this study is to investigate the influence of polyamide 6 and the performance of different compatibilized blends with the polypropylene matrix. Therefore, we used the following steps: in the first step, we evaluated the influence of the PA6 concentration in the PP/PA6 blend. In the second step of the study the influence of three types of compatibilizers with different functional groups in the performance of the PP/PA6(70/30) blend was evaluated.

2. EXPERIMENTAL

2.1. Materials

Polypropylene PP H503, MFI=3,5g/10min (2,16 kg/230°C – ASTM-D-1238-L), supplied by Braskem, was used as a matrix.

Polyamide 6 (PA6) Technil C216 natural (M= 10.500 g/mol), IV= 134ml/g, supplied by Rhodia/SP, was used as a dispersed phase.

Ethylene – Glycidyl Methacrylate copolymer (E-GMA), containing 8% of Glycidyl Methacrylate, Lotader AX 8840 (MFI= 5g/10min), density of 0.94 g/cm³ and Young Modulus of 104 MPa, was supplied by Arkema/SP.

Polypropylene grafted with 1% of maleic anhydride (PPgMA), Polybond 3200, MFI = 110g/10min was supplied by Crompton.

Polypropylene grafted with 6% of acrylic acid (PPgAA), Polybond 1001, MFI = 40g/10min, was supplied by Crompton (Chemtura). E-GMA, PPgMA and PPgAA were used as compatibilizers.

2.2. Blends Preparation

Before mixing with polypropylene (PP), polyamide 6 (PA6) and the compatibilizers were dried under vacuum at 80 °C for. The PP/PA6 binary blends and PP/PA6/compatibilizers (PP-g-MA, PP-g-AA and E-GMA) ternary blends were prepared in a conical counter-rotating twin screw extruder, coupled to a Haake Buchler System 90 torque rheometer at screw speed of 50 rpm. The thermal profile from hopper to die was 160:240:240:240:240°C.

Neat PP was processed under the same conditions. The obtained material was granulated and dried under vacuum at 80°C for 24h.

For PP/PA6 blends, the influence of the PA6 concentration (20, 30, 40 and 50 wt%) on PP/PA6 blend was evaluated. PP/PA6 (70/30) composition was chosen to study the influence of the compatibilizers on the properties of this blend.

2.3. Samples Preparation

Samples for tensile and impact strength tests were prepared in a FLUIDMEC H30/40 injector at 240°C. The mold temperature was kept in 20 ± 2° C.

3. Mechanical Properties

Tensile tests were carried out in a Shimadzu Universal Testing Machine at crosshead speed of 50mm/min according to ASTM D 638. The results reported are an average of 10 samples.

IZOD impact strength tests were performed in notched samples at room temperature using a CEAST RESIL 5.5 equipped with a 2.75J hammer according to ASTM D 256. The results reported are the average of 10 samples.

3.1 Scanning Electron Microscopy (SEM)

Fracture surfaces of the samples subjected to impact strength tests were coated with gold and the morphology was analyzed using a Shimadzu SSX-550 Superscan Scanning Electron Microscope. The voltage used in the filament was 15 kV.

3.2. Linear Viscoelasticity Regime Oscillatory Rheometry

An Aton Par MCR301 oscillatory rheometer was used to study the rheological behavior of the blends at 240 °C with frequencies varying from 0.1 to 100 rad/s. The limit of linear viscoelasticity was determined at 10% strain and frequency of 10 rad/s. Analyses were performed in samples taken from injected specimens.

4. RESULTS AND DISCUSSION

4.1. Influence of the PA6 content on the PP/PA6 blends

Figures 1 and 2 show the tensile properties results for the neat PP and PP/PA6 blends containing 20, 30, 40 and 50 wt% of PA6. It is observed in Fig. 1 that compared to pure polypropylene, the values of modulus of the blends showed a tendency of reduction in stiffness when PA6 concentration was increased from 0 to 30 wt%. On the other hand when the PA6 concentration was increased from 30 to 50 %wt, an increase in the modulus was observed. This behavior can be explained by the following hypothesis: the polymers PP and PA6 are immiscible and form a biphasic system with a weak interface between the phases, as seen through the morphology presented in the following item on the research and other work (Agrawal et al., 2007).

Concentrations up to 30% polyamide by weight, the rigidity of the systems was affected by poor adhesion between the phases, i.e., there is no physical or chemical interaction at the interface. However, when the concentration exceeded a threshold value, in this case 30% of PA6, there was a gradual increase in stiffness due to the higher concentration of polyamide which is stiffer than the polypropylene. Therefore, this suggests that the rigidity of immiscible blends could be related to the competitive effect between interface quality and content of the polymer which has a higher stiffness (modulus).

In Figure 2, it may be observed that the neat PP showed higher tensile strength than that of PP/PA6 blends. This is may be due to the pure polymer provide greater continuity in its structure than with the addition of PA6 polymer that is immiscible in PP. As discussed earlier, the immiscibility caused by the presence of PA6 favors the appearance of areas with poor interfacial adhesion, which enables the reduction the tensile strength in immiscible systems. PP/PA6 (50/50) composition shows a recovery tendency in this property due to higher PA6 content.

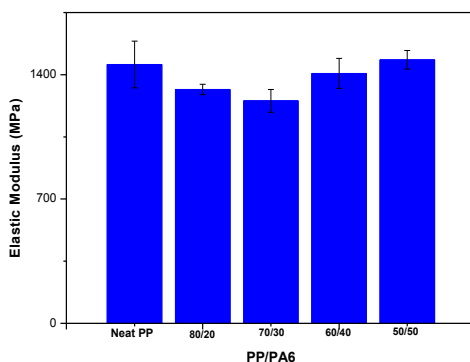


Figure 1. Elastic modulus of neat PP and PP/PA6 blends.

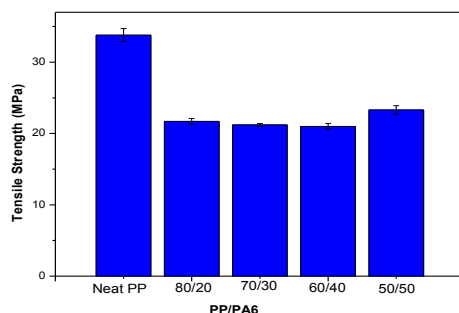


Figure 2. Tensile Strength of neat PP and PP/PA6 blends.

Figure 3 shows the results of the Izod impact strength tests of neat PP and PP/PA6 blends containing 20, 30, 40 and 50 wt% of PA6. It may be observed that there is a significant increase in the impact strength of the blends with the increase in the PA6 content, nearly triple compared to pure PP when 50% of PA6 is used. This increase might be related to the morphology developed in systems with high concentrations of PA6, showing that the presence of "fibrils or ribbons" possibly from the formation of co-continuous phase.

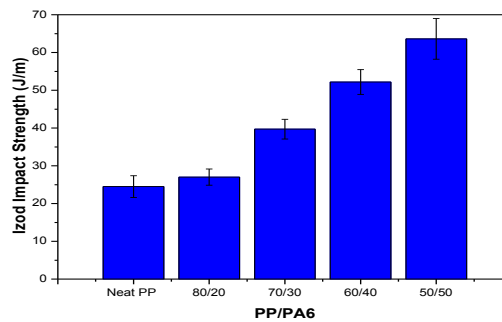
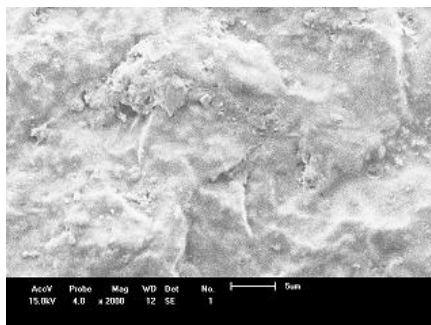


Figure 3. Impact Strength of neat PP and PP/PA6 blends.

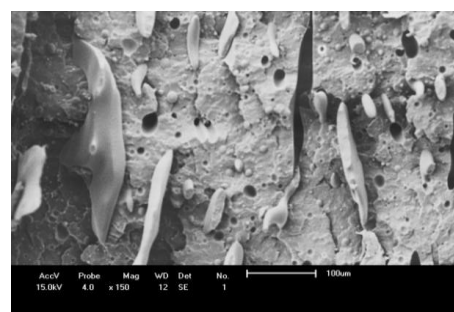
Figures 4 (a) to 4 (e) show the SEM micrographs (X150) of the neat PP blends containing an PP/PA6 20, 30, 40 and 50 wt% of PA6. In Fig. 4 (a), it was expected, in the neat PP an aspect of ductile fracture is observed. In Fig. 4 (b) is the PP/PA6 (80/20) blend, there are PA6 dispersed particles of various sizes and some holes that represent the absence of particles that have been pulled out from the surface during the impact test. This morphology shows the immiscibility between the polymers characterized by poor adhesion between the phases, which helped in reducing the mechanical properties observed in the previous item.

In Figure 4 (c) for the PP/PA6 (70/30) blend, besides PA6 particles, PA6 fibrils or ribbons are observed. These fibrillar structures may be responsible for the increase in the impact strength of the blends despite poor adhesion with PP matrix. As seen in Fig. 4 (d) and 4 (e) where the concentration of PA6 increased further to 40 and 50 wt%, respectively, the number of dispersed particles was reduced the number of "fibrils" increased, indicating the predominant formation of co-continuous phases of the polymers in the blend and consequently leading to an increase in the impact strength when compared to neat PP.

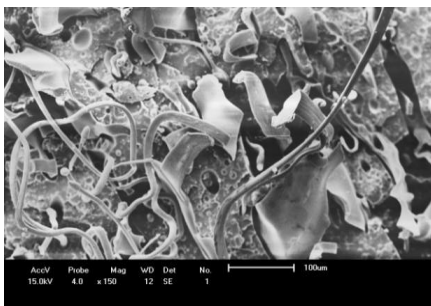
The increase in the impact strength of these blends may be related to a complex combination of several toughening mechanisms, including slowing the spread of the crack (notch) in the presence of these "fibrils" that are oriented perpendicular to the direction of propagation.



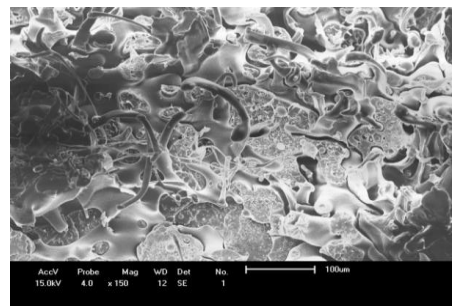
(a)



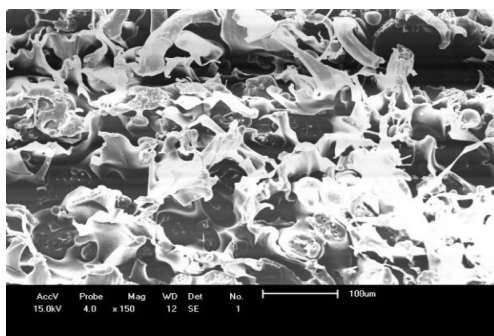
(b)



(c)



(d)



(e)

Figure 4. Sem Micrographs of: (a) neat PP; (b) PP/PA6 (80/20); (c) PP/PA6 (70/30); (d) PP/PA6 (60/40) e (e) PP/PA6 (50/50).

Figure 5 shows the results of oscillatory rheometry tests of neat PP and for PP/PA6 blends containing 20, 30, 40 and 50 wt% of PA6. It is observed that at low frequencies the viscosity of the PP/PA6 (80/20) and PP/PA6 (70/30) blends are superior to that of neat PP, whereas for PP/PA6 (60/40) and PP/PA6 (50/50) blends, the opposite happens. This behavior may be related to changes in morphology, i.e., PP and PA6 form co-continuous morphology for the PA6 concentration above 40%. When increasing the angular frequency all the compositions tend to have approximate values of viscosity.

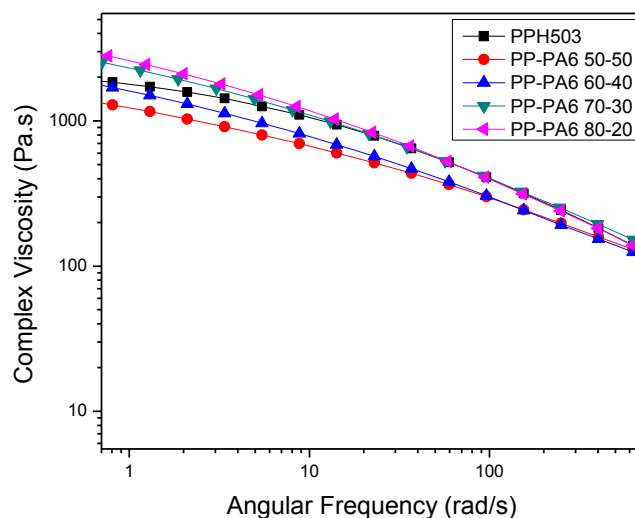


Figure 5. Complex viscosity of neat PP and PP/PA6 blends containing 20, 30, 40 and 50% wt of PA6.

5. Influence of the compatibilizers on the performance of PP/PA6 blends.

Figures 6 and 7 presented the results of the mechanical properties obtained from tensile tests of the ternary blends. It is observed in Figs. 6 and 7 that the elastic modulus and the tensile strength of PP/PA6/PPgAA and PP/PA6/PPgMA blends were higher than those of PP/PA6 (70/30) and PP/PA6/EGMA blends indicating that the reaction occurred in the mixing process, was more effective, i.e., the compatibilization in these two compositions favored a synergistic effect in these two properties. The reduction in these properties for the PP/PA6/EGMA system may be related to EGMA copolymer which is flexible. The impact strength results are shown in Figure 8. It may be observed that the best result was obtained by the PP/PA6/PPgMA blend, indicating better performance with the PPgMA compatibilizer.

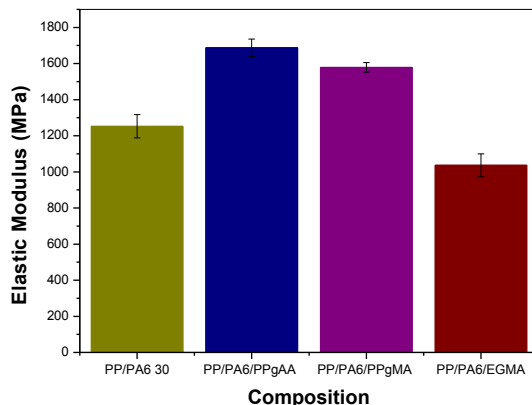


Figure 6. Elastic modulus of uncompatibilized and compatibilized PP/PA6 (70/30) blends.

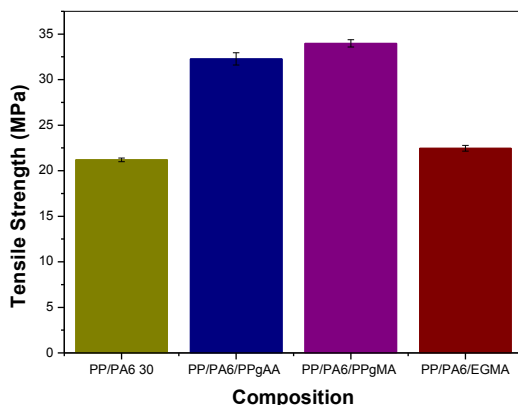


Figure 7. Tensile strength of uncompatibilized and compatibilized PP/PA6 (70/30) blends.

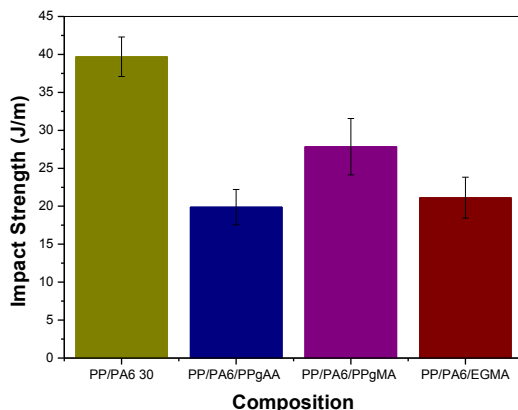


Figure 8. Impact strength of uncompatibilized and compatibilized PP/PA6 (70/30) blends.

Figures 9 to 11 show the SEM micrographs (2000X) of PP/PA6/PPgMA, PP/PA6/PPgAA and PP/PA6/EGMA the ternary blends. It is observed in Fig. 9, that the PP/PA6/PPgMA ternary blend that presented, in general, better mechanical properties. A surface with the presence of tiny particles (less than 3 μm) but without "fibrils" is observed in comparison to the morphology of the PP/PA6 (70/30) composition. This suggests that the change in morphology affect the mechanical properties of the blends in this composition. Fig. 10 show the SEM micrograph of PP/PA6/PPgAA blend. Comparing to the morphology presented by the PP/PA6 (70/30) blend, this blend presents a different structure on its surface.. There are some PA6 particles dispersed in the PP matrix and there is a good adhesion

between PA6 and PP phases.. The presence of PP-g-AA increased the stiffness of the blend. Fig. 11 shows the SEM micrograph of the PP/PA6/EGMA blend. A “rough” surface is observed for this blend.

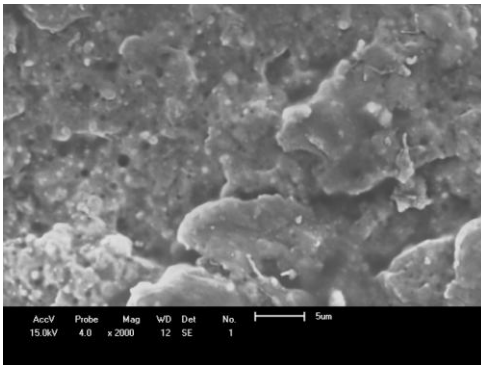


Figure 9. SEM PP/PA6/PPgMA blend

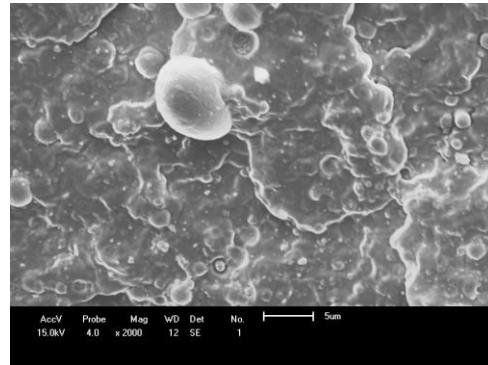


Figure 10. SEM PP/PA6/PPgAA blend

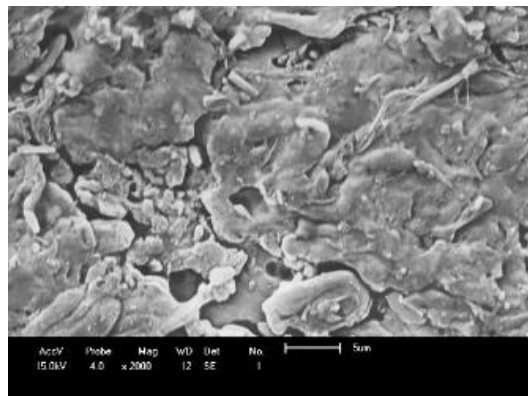


Figure 11. SEM PP/PA6/E-GMA blend

Figure 12 shows the results of oscillatory of rheometry tests for the PP/PA6 (70/30), PP/PA6/PPgMA, PP/PA6/PPgAA and PP/PA6/E-GMA blends. It is observed that at low angular frequencies, the viscosity of the PP/PA6/PPgAA and PP/PA6 (70/30) blends is lower than that of PP/PA6/PPgMA and PP/PA6/E-GMA blends. At high angular frequencies, the viscosities of PP/PA6/PPgAA and PP/PA6/E-GMA blends were lower those of the others. It is also observed that at low frequencies the viscosity all the ternary blends were higher than that of the PP/PA6 (70/30) binary blend indicating the compatibilization of the blends.

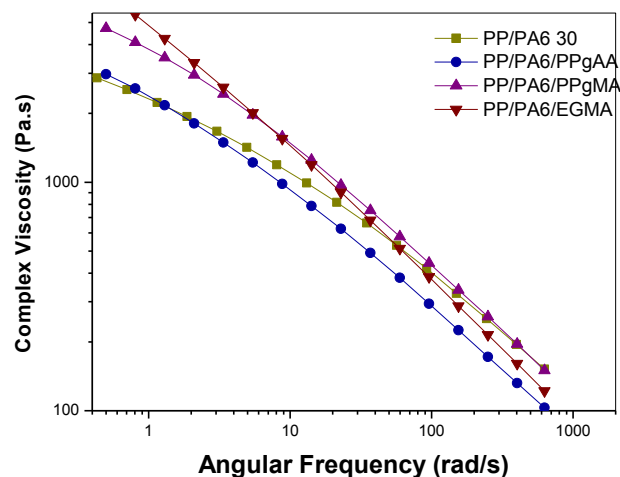


Figura 12. Complex viscosity of uncompatibilized and compatibilized PP/PA6 (70/30) blends

6. CONCLUSIONS

It was found that due to the immiscibility between the polymers, the tensile strength of the blends without the addition of compatibilizers may be reduced due to the formation of a weak interface. The impact strength of the binary blends increased significantly with the increase in the PA6 concentration due to the formation of a "fibrillar" morphology which may have slowed the crack propagation.

There were significant improvements on the mechanical properties (modulus, tensile strength) with the addition of PP-g-MA and PP-g-AA compatibilizers to the PP/PA6 (70/30) blend. The use of compatibilizers, with chemical affinity between the polymers is essential to mitigate the incompatibility.

SEM results revealed that significant changes in the morphology of the ternary blends, which present an structure with smaller dispersed particles when the compatibilizers are added.

The changes in the viscosity of binary blends with respect to pure PP could be directly related to changes in morphology, i.e., PP and PA6 form co-continuous morphology for the PA6 concentration above 40%. The increase of the viscosity at low frequencies for the ternary blends, indicates that the compatibilization between the copolymer and PA6 has occurred.

7. ACKNOWLEDGEMENTS

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