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Investigation of effects of MoEpPOSS nanoparticle on the morphological and rheological properties of PA6/TPE blends

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ABSTRACT

Polyamide 6 (PA6) is one of the used engineering thermoplastics with the advantages of high resistance to chemicals and abrasion, high fatigue resistance and toughness. However, it has some disadvantages such as low impact strength and notch sensitivity. The blend of PA6 with elastomers can mitigate these shortcomings. Lately, thermoplastic elastomers (TPE) have been frequently used to toughen notch-sensitive polymers such as PA6 due to their outstanding properties such as high elasticity, recyclability, and easy processing. As it is known, obtaining superior properties in polymer blends relies on the interfacial interaction between the components of the blend. Additionally, by using compatibilizers, blends with the required properties can be created by enhancing interaction between phases, or interfacial adhesion. Recently, polyhedral oligomeric silsesquioxane (POSS) nanoparticles, organic/inorganic hybrid nanoparticles, are preferred as an alternative compatibilizer to conventional types. In this study, PA6/TPE blends were compatibilized with POSS nanoparticle with single epoxy group (MoEpPOSS). The morphological and rheological properties of PA6/TPE blends compatibilized with MoEpPOSS nanoparticle were investigated. Also, possible chemical interactions between PA6 and/or TPE and MoEpPOSS nanoparticle were determined via Fourier transform infrared spectroscopy (FTIR) analyses.

I. INTRODUCTION

Polyamide 6 (PA6) stands as a widely recognized engineering thermoplastic material with a wide range of uses due to its exceptional mechanical and thermal properties, including fibers, films, textiles, and different molding products. However, its high moisture-absorbing ability, poor dimensional stability, low impact strength, and notch sensitivity limit its application areas. Therefore, studies on modifying polyamide to impart new properties to PA6 and eliminate such disadvantages by improving its physical properties have been frequently studied by both industry and academia [1, 2]. In recent years, PA6/elastomer blends have been prepared to remove these negative properties of PA6.

Recently, thermoplastic elastomers (TPE) have become one of the most frequently used materials in the field of polymer technology in both industry and academia due to their rubbery properties, such as low permanent deformation, high elasticity, high fatigue resistance, and thermoplastic properties for instance easy processing and recyclability. Thanks to their superior properties, such as durability, low density, and low production costs, they

*Corresponding author. Tel.: +90-262-303-3540; e-mail: yildirimmrumeysa@gmail.com have many applications, such as automotive, packaging, and electrical industries [3]. In addition to such applications, TPEs are frequently used in toughening PA.

Many studies have been conducted in the literature on the preparation of blends of PAs with elastomers to improve the impact resistance of PAs [4, 5]. Yu et al. investigated the effect of ethylene vinyl acetate rubber (EVM) on the impact strength enhancement of PA1010. The results showed that EVM significantly improved the notched impact strength of PA1010 [6]. Xu et al. examined the effects of ethylene-propylene elastomer (EPM) with or without maleic anhydride on the mechanical and morphological properties of PA6. The studies showed that the Izod impact strength values were not improved with the addition of EPM in PA6; however, the impact strength was increased significantly with the addition of maleic anhydride grafted EPM [7].

However, PA6/TPE blends are thermodynamically immiscible, as with many polymer blends. Therefore, compatibilization is necessary to achieve the desired properties. Lately, polyhedral oligomeric silsesquioxane (POSS) nanoparticles have emerged prominently as effective compatibilizers, owing to their pliable physical and chemical characteristics and cost-effectiveness when applied on an industrial scale. POSSs exhibit a distinctive structural configuration characterized by cage-shaped molecules, akin to polyhedral skeletons comprised of silicon and oxygen, denoted by the closed formula $(RSiO_{1.5})_n$. The R group in the molecular structure can encompass a wide variety of functional groups [8].

In this research, the compatibilization effectiveness of hybrid POSS nanoparticles with a single reactive epoxy group (MoEpPOSS) in PA6/TPE blends at varying ratios was investigated for the first time in the literature. The morphological and rheological properties of PA6/TPE blends were examined in relation to the MoEpPOSS loading ratio. Moreover, the possible interactions between the components in the presence of MoEpPOSS were evaluated via Fourier transform infrared spectroscopy (FTIR) analyses.

II. MATERIALS AND METHODS

2.1 Materials and Preparation Techniques

Polyamide 6 (PA6; trade name; Tecomid NB60 NL) and polyester-based thermoplastic elastomer (TPE; trade name; Arnitel UM552 TPC-ES) were purchased from Eurotec (Türkiye) and DSM (The Netherlands), respectively. Glycidylisobutyl-POSS (MoEpPOSS) with a single reactive epoxy group was obtained from Hybrid Plastics Company (USA).

2.2 Sample Preparation

Pure polymers, PA6 and TPE, were kept in a vacuum oven at 80 °C for 12 h to eliminate moisture prior to blending. The samples were prepared with a laboratory-scale twin screw co-rotating micro-compounder (Xplore Instruments 15 cc micro-compounder) with barrel temperature, screw speed, and residence time of 230 °C, 100 rpm, and 2 min, respectively. The compounding procedure was carried out by continuously purging the barrel with nitrogen gas to prevent thermo-oxidative degradation. At the end of the residence time, the blends were molded with a laboratory-scale micro-injection device (Xplore Instruments 12 cc Injection Molder) with a melt temperature of

230 °C, mold temperature of 25 °C and pressure of 10 bar to obtain standard test samples. Two different PA6/TPE ratios, 50 and 70 wt% TPE, and two MoEpPOSS ratios, 0.5 and 1 wt%, were considered.

2.3 Characterization of materials

2.3.1 Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) analyses were carried out to identify possible interactions between PA6, TPE and MoEpPOSS nanoparticles. Tests were performed with a PerkinElmer spectrum 100 FTIR instrument. The samples were analyzed in the 4000-650 cm^{-1} wavenumber range.

2.3.2 Scanning electron microscope (SEM)

The phase morphologies of the samples were examined with a QUANTA FEG 450 model scanning electron microscope (SEM). The SEM images were taken from the surfaces of the cryogenically fractured samples, and the samples were coated with gold before analysis.

2.3.3 Rheological analyses

The rheological properties of the samples were detected with Anton Paar MCR 102 with parallel plate geometry. Frequency scanning was performed at a constant temperature of 230 °C under a constant nitrogen atmosphere. The measurements were performed in an angular frequency range of 0.1-600 rad/s at a shear strain of 0.1%.

III. RESULTS AND DISCUSSIONS

3.1 Fourier transform infrared spectroscopy (FTIR)

The chemical structures of pure PA6, pure TPE, compatibilized and uncompatibilized PA6/TPE blends and the chemical interactions between them were examined with FTIR analyses.

The spectra of pure polymers and PA6/TPE blends were given in Figure 1. The results showed that the intensities of the N-H and C=O peaks of PA6 decreased and the intensity of the C=O peak of TPE increased with the decrease in the amount of PA6 in PA6/TPE blends, as expected [9].

It was observed that the peak located at 908 cm^{-1}, representing the epoxy group of MoEpPOSS, disappeared in PA6/TPE/MoEpPOSS blends with the addition of MoEpPOSS nanoparticle with a single epoxy group to PA6/TPE blends (Figure 2). This is evidence that the reactive epoxy group in MoEpPOSS was opened by ring opening reaction and interacted with reactive functional groups of PA6 and/or TPE as represented in Figure 3.

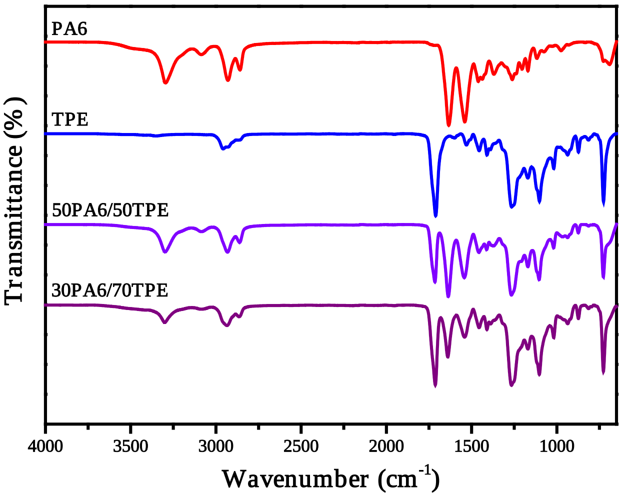

Figure 1. ATR-FTIR spectra of neat polymers and PA6/TPE blends

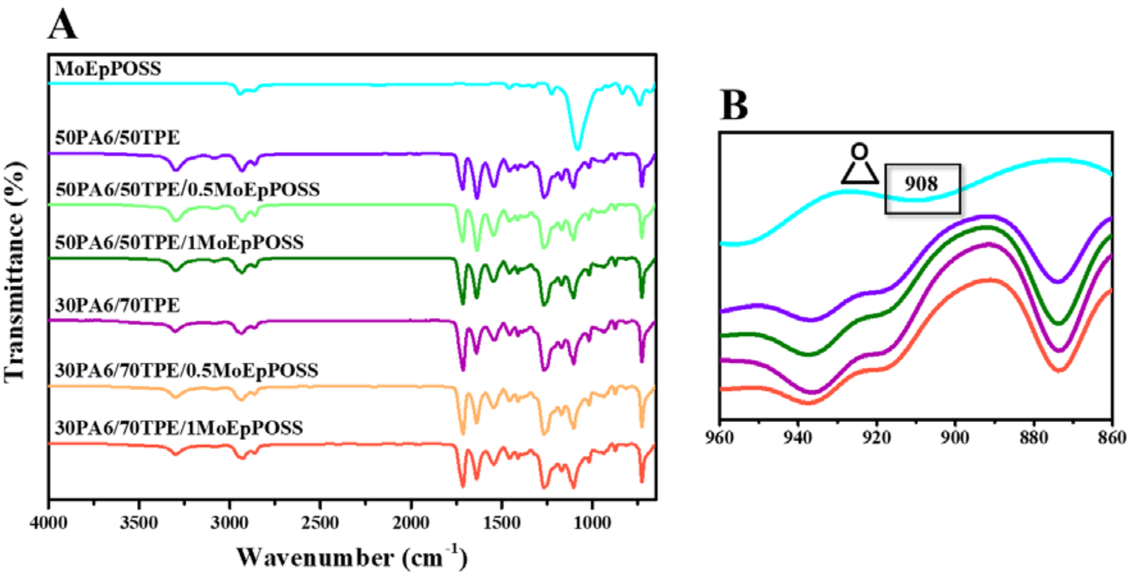

Figure 2. ATR-FTIR spectra of **A)** MoEpPOSS, PA6/TPE, and PA6/TPE/MoEpPOSS blends, **B)** the disappearance of epoxy peaks of pure MoEpPOSS in 50PA6/50TPE/1MoEpPOSS and 30PA6/70TPE/1MoEpPOSS blends

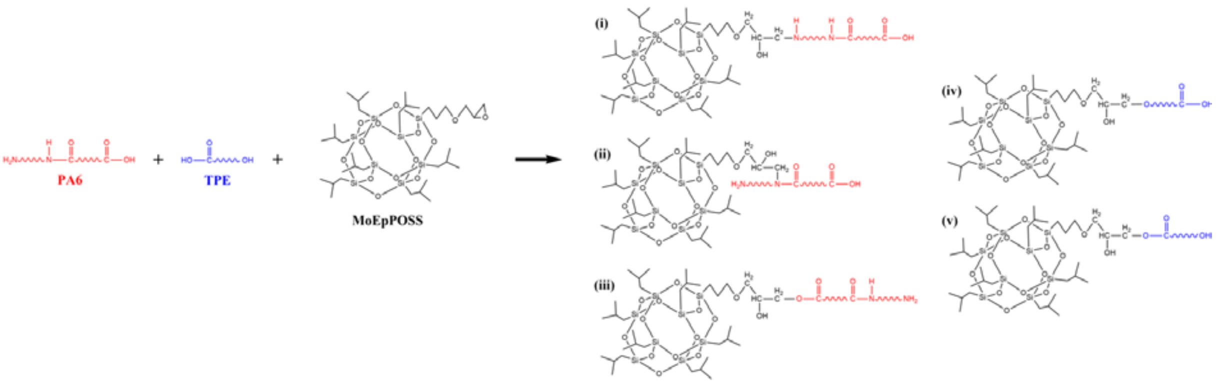

Figure 3. Possible reactions between PA6, TPE, and MoEpPOSS nanoparticle

3.2 Scanning electron microscope (SEM)

SEM analyses were performed to investigate the phase morphology of the samples. As is known, immiscible polymer blends often exhibit poor properties as a result of their unstable phase morphology. Therefore, in order to produce a material that exhibits the desired properties, it is essential that the dispersed phase particle size is reduced and uniformly distributed in the matrix [10, 11].

From the SEM images of PA6/TPE blends (Figure 4), a consistent morphological structure characterized by two distinct phases was observed, regardless of the blend ratio. Introducing 50 wt% TPE to PA6 resulted in a co-continuous phase morphology, wherein TPE particles with an average particle size (dAVG) of 1.52±0.32 µm were discerned at the dispersed phase location. Subsequently, elevating the TPE content to 70 wt% led to an increase in the dAVG value to 3.11±0.68 µm, concomitant with a heightened instability in the phase morphology, as documented in Table 1. These outcomes emanate from the inherent thermodynamic immiscibility between PA6 and TPE, coupled with a weakened interfacial interaction attributed to the lower average molecular mass of the TPE utilized in this study as compared to that of PA6.

Upon analysis of SEM images, a discernible reduction in the particle size of the dispersed phase in PA6/TPE blends was noted with the incorporation of MoEpPOSS nanoparticles with single reactive epoxy group, irrespective of the blend ratio (refer to Table 1). This trend was particularly pronounced with escalating MoEpPOSS loading ratios. For instance, in the 30PA6/70TPE blend, d_{AVG} of the dispersed phase, initially measured at 3.11±0.68 µm, experienced a decrement from 1.09±0.23 µm to 0.71±0.13 µm as the MoEpPOSS loading ratio increased from 0.5% to 1 wt%. This shift towards a diminished particle size coincided with the attainment of a more homogeneous surface morphology. These observations indicate that the epoxy reactive group in the MoEpPOSS nanoparticle structure reacts with the amide (-NHCO-), amine ($-NH_2$) and carboxylic acid (-COOH) groups in PA6 as well as the hydroxyl (-OH) or -COOH groups at the chain end of TPE. This interaction facilitated the creation of new molecules by an elevated molecular weight within the interphase. Consequently, the MoEpPOSS nanoparticle augmented interfacial compatibility, inducing a more uniform structure in the dispersed phase within the polymer matrix [12, 13].

Table 1. The average particle size (d_{AVG}) of the dispersed phase in PA6/TPE blends

Sample	**d_{AVG} (µm)**
50PA6/50TPE	1.52±0.32
30PA6/70TPE	3.11±0.68
50PA6/50TPE/0.5MoEpPOSS	0.98±0.17
50PA6/50TPE/1MoEpPOSS	0.95±0.13
30PA6/70TPE/0.5MoEpPOSS	1.09±0.23
30PA6/70TPE/1MoEpPOSS	0.71±0.13

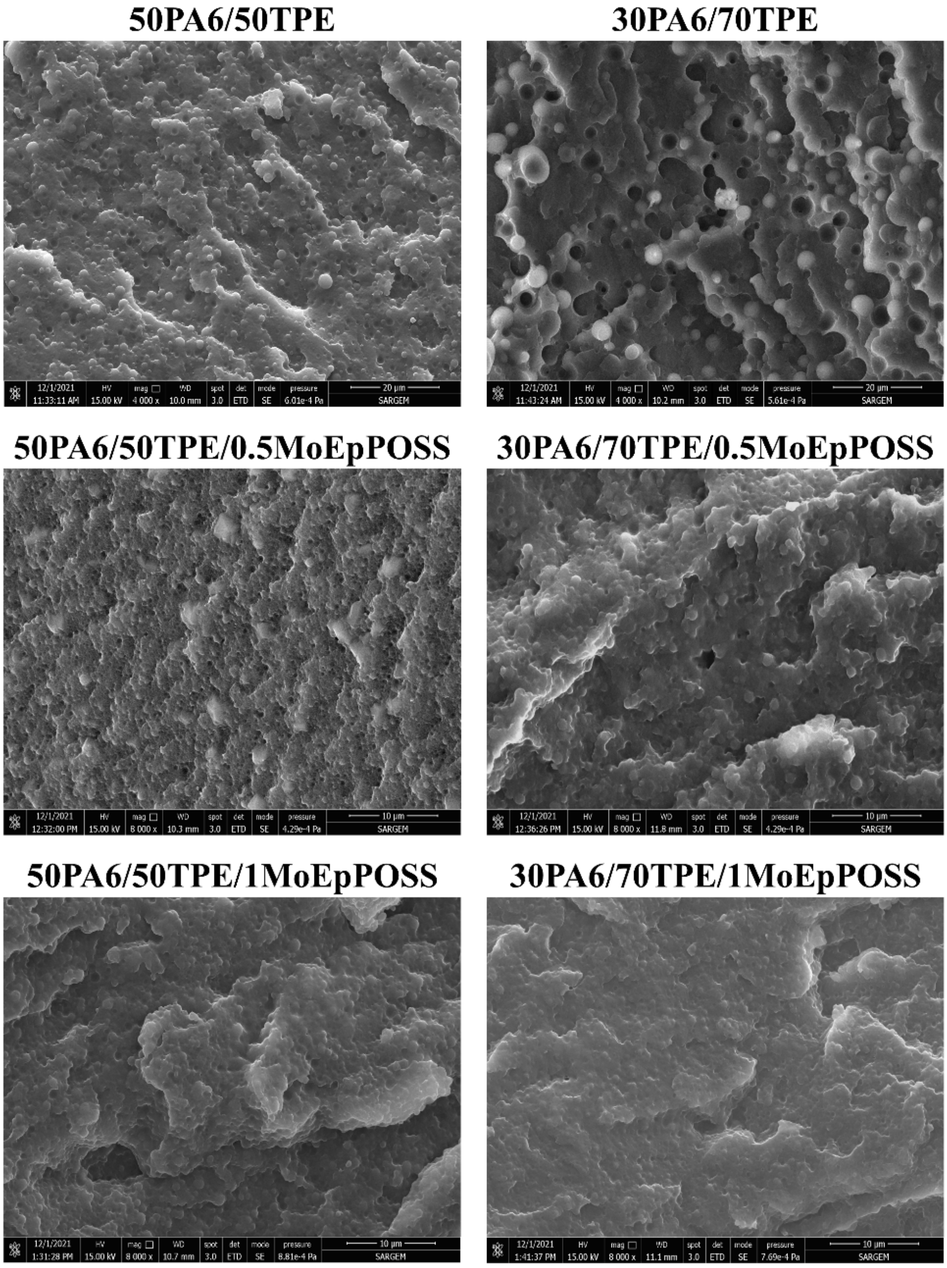

Figure 4. SEM images of PA6/TPE and PA6/TPE/MoEpPOSS blends (Magnification: 4000x and 8000x)

3.3 Rheological analyses

The possible interactions between PA6/TPE blends and MoEpPOSS nanoparticle were investigated by rheological analyses and the variations of complex viscosity, storage and loss modulus values with angular frequency were investigated in order to determine the differences in the rheological properties of the samples. The rheological properties of the blends are shown in Figure 5 and Figure 6.

When the complex viscosity values of PA6/TPE blends versus angular frequency were analyzed, the complex viscosity values shifted to lower values over the entire angular frequency with increasing amounts (from 50% to 70 wt%) of TPE added to PA6. This might be seen as an indicator that the thermodynamic incompatibility between the components grows as the TPE content of the blend increases.

As seen in Figure 5, it was observed that the complex viscosity values increased to higher values with the addition of MoEpPOSS to the PA6/TPE blend. Additionally, it was observed that this enhancement in complex viscosity was greater when the loading ratio of MoEpPOSS was 1 wt%. This indicates that the single reactive epoxy group in the structure of MoEpPOSS reacts with the reactive groups in the structure of PA6 and/or TPE by ring-opening reaction, resulting in increased molecular weight [14]. The increased molecular weight resulted in the droplet particle break-up of dispersed PA6 phase. This contributed to the enhanced interfacial interaction between PA6 and TPE and improved rheological properties, such as complex viscosity.

When the variations of storage and loss modulus values of pure polymers and polymer blends with angular frequency are examined, it is seen that the loss modulus values are higher than the storage modulus values for both pure polymers and PA6/TPE blends in the entire frequency range because of the predominant viscous character of the samples.

As can be seen from the variations of the storage and loss modulus of PA6/TPE/MoEpPOSS blends versus angular frequency in Figure 6, the blends exhibited higher values in the presence of MoEpPOSS than the blends without MoEpPOSS. It is also observed that the loss modulus is greater than the storage modulus in the whole frequency range. In other words, the viscous character is dominant. In the presence of MoEpPOSS, the molecular weight of the 30PA6/70TPE blends increased substantially less than that of the co-continuous phase 50PA6/50TPE blends. This is thought to be due to the higher potential of the epoxy group in the MoEpPOSS structure to react with PA6 compared to TPE.

The cross-over point provides a qualitative comparison of the molecular weight of polymer melts and is also a measure of the relaxation time of the melts. Polymers exhibit a viscous (liquid-like) character with the relaxation of chains after a certain frequency depending on the structure of the polymer. The relaxation time of the chains gives a chance to have an idea in terms of comparing the molecular weight of the polymers [15]. It was observed that, no cross-over transition point was determined for 30PA6/70TPE blend, indicating that relaxation behavior occurs in very short times and the interaction between MoEpPOSS and PA6 and/or TPE is very weak. In the presence of MoEpPOSS, the increase in molecular weight in the systems with continuous phase TPE was much smaller compared to the systems with continuous phase PA6.

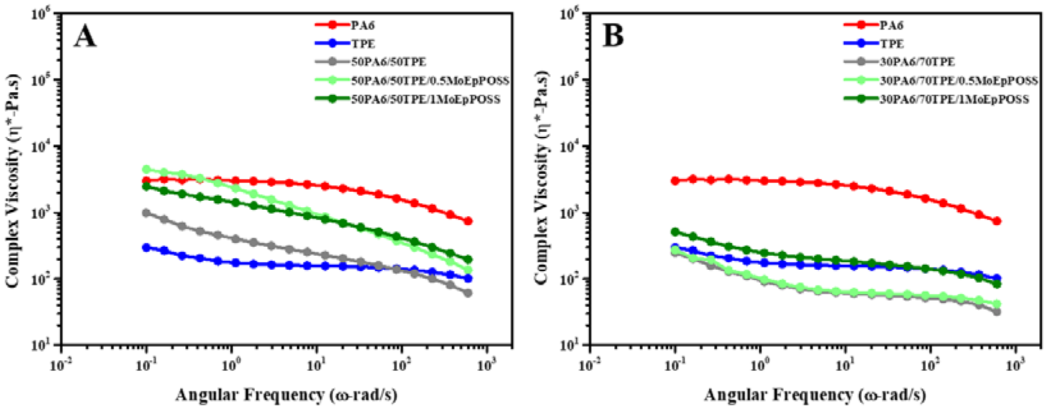

Figure 5. Complex viscosity versus angular frequency of **A)** 50PA6/50TPE and 50PA6/50TPE/MoEpPOSS blends, **B)** 30PA6/70TPE and 30PA6/70TPE/MoEpPOSS blends

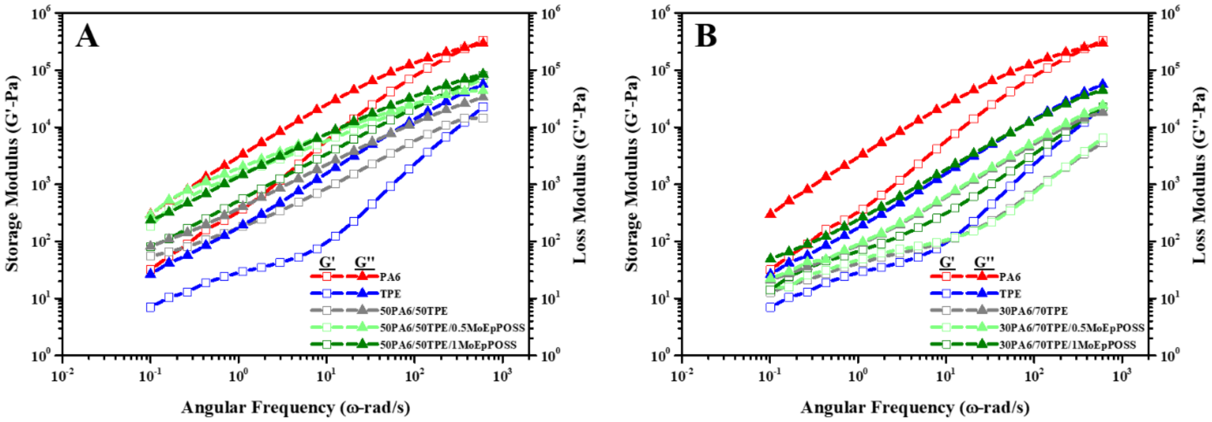

Figure 6. Storage and loss versus angular frequency of **A)** 50PA6/50TPE and 50PA6/50TPE/MoEpPOSS blends, **B)** 30PA6/70TPE and 30PA6/70TPE/MoEpPOSS blends

IV. CONCLUSIONS

This study aimed to investigate the compatibilizing efficiency of MoEpPOSS nanoparticles with a single epoxy group for thermodynamically immiscible PA6/TPE blend. Then, the morphological and rheological properties of the blends were determined. Moreover, possible reactions between PA6, TPE and MoEpPOSS were investigated via FTIR analyses. As a result of the SEM analyses, it was found that the addition of MoEpPOSS decreased the d_{AVG} and improved the interfacial interaction. Rheology analyses showed that higher complex viscosity values were achieved in the presence of POSS, and high molecular weight chains were formed as a result of possible reactions between components and POSS. Also, FTIR analyses proved that the epoxy group in the structure of POSS opened and reacted with PA6 and/or TPE. In the light of all these results, it can be concluded that the MoEpPOSS nanoparticle is an effective compatibilizer for the PA6/TPE polymer blends.

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