

Journal-International Journal of Nanomaterials and Nanostructures
Title- Investigating the Impact of Silicate Modification on Polypropylene-Layered Silicate Nanocomposite

ISSN-2455-5584

RESEARCH

Volume:10

Issue:1

Year:2024

Article Received: 17 July, 2024

Article Accepted: 24 July, 2024

Article Published:

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Abstract

In this research, a co-rotating twin-screw extruder was used to create polypropylene/organo-layered silicate nanocomposites based on organo-muscovite. In the nanocomposite system, compatibilizers such as polypropylene grafted maleic anhydride and potassium succinate modified polypropylene grafted maleic anhydride were employed. The morphological, mechanical, thermal, and rheological characteristics of polypropylene/polypropylene grafted maleicanhydride/organo-muscovite and polypropylene/potassium succinate modified polypropylene grafted maleic anhydride/organo-muscovite nanocomposites were investigated in relation to the effects of layered silicate modification and compatibilizers. The availability of polypropylene grafted maleic anhydride or potassium succinate modified polypropylene grafted maleic anhydride allowed for the intercalation of organo-muscovite, which might partially exfoliate during mixing, according to TEM micrographs. Using potassium succinate modified polypropylene grafted maleic anhydride instead of polypropylene grafted maleic anhydride improved the exfoliation and distribution of organo-muscovite. It has been noted that compared to polypropylene/polypropylene grafted maleic anhydride/organo-muscovite nanocomposites, polypropylene/potassium succinate modified polypropylene grafted maleic anhydride/organo-muscovite nanocomposites exhibit superior overall mechanical properties. This was due in part to the fact that scanning electron micrographs (SEM) were expected to

show adhesion that was more favorable than that of polypropylene grafted maleic anhydride due to the compatibilization impact of potassium succinate modification. The study of differential scanning calorimetry suggests an increase in crystallinity, melting point, and crystallization temperature. Additionally, the rheological behaviors of nanocomposites are enhanced by the addition of potassium succinate modified polypropylene grafted maleic anhydride or polypropylene grafted maleicanhydride with organo-muscovite.

Keywords: Nanocomposites, polypropylene, organically modified layered silicate, compatibilizer, morphology, thermal properties

Introduction

Due to their superior tensile, thermal, and rheological characteristics over conventional nanocomposites, nanocomposites are held in high respect [1,2]. With layers of silicate inorganic polymer and inorganic clay minerals, the majority of nanocomposites appear to be hybrid materials [3,4]. When the Toyota research team tested polyamide-6/clay nanocomposites for the first time, they found that the clay filler's mechanical and thermal characteristics had developed at a far lower load stage than conventional composites [5]. Scientific publications have reported on polymer/clay nanocomposites [6-9]. According to López-Quintanilla et al. [10], three different kinds of polymer/clay nanocomposites were frequently intercalated like a traditional nanocomposite, allowing for the dispersion of some polymer components between exfoliated and layered silicate nanocomposites.

Polypropylene (PP) is a non-polar polymer that finds extensive application in a variety of fields, including automotive and packaging, due to its versatile nature, well-balanced properties, and intriguing property-price ratio. PP/organoclay nanocomposites have drawn a lot of scientific interest. However, because conventional PP has a low polarity, it is impossible to see the homogeneous dispersion of silicate layers in PP. This results from the incompatibility of PP, which lacks a polar group on its backbone, and biologically modified clay. On the other hand, with the use of compatibilizers such functional oligomers, PP/clay nanocomposites have grown increasingly feasible. For bulk PP to blend easily and to communicate with the silicate layer, these compatibilizers need to have sufficient polarity [11]. Researchers have typically utilized maleic anhydride (MA) [12,13], which can develop the polarity of polymer molecules, to promote the isolation of mineral clay in the PP matrix. Since PP-grafted MA provides the highest degree of strengthening effect of all PPs to date, it has been used in the majority of investigations utilizing PP/clay nanocomposites. nearly investigated in PP/clay nanocomposite as a compatibilizer using PP-grafted MA. The goal of

the current study was to create organoclay (OM) by organo-modifying muscovite utilizing cetyltrimethylammonium bromide (CTAB) as an alkyl ammonium. As compatibilizers of PP/OM nanocomposites, we investigated potassium succinate modified polypropylene grafted maleic anhydride (PPKS) and PP-grafted MA (PPMA). To the best of authors' knowledge, there is no literature available that discusses how specific compatibilizers affect the morphological, mechanical, thermal, and rheological properties of PP/OM nanocomposite when combined using the molten blending approach. Thus, the goal is to highlight this examination of mechanical and thermal properties employing two different compatibilizers and to clear this important information even.

Experimental

Ingredients

The thermoplastic polymer matrix PP, which has a specific gravity of 0.91-0.92 and a melting point of 160-170°C, was acquired from MTBE (Malaysia) Sdn. Bhd. as pellets. Bidor Minerals (M) Sdn. Bhd. was the source of unispensible muscovites, which have an average size of roughly 20 micrometers. Lithium nitrate (LiNO_3) and cetyltrimethylammonium bromide (CTAB), which were provided by Sigma Aldrich (M) Sdn. Bhd., were exchanged cations to create the modified muscovite, and also referred to as organo-muscovite (OM). PPMA, grade Polybond 3150, melt flow rate: 50 g/10 min at 230°C, 0.5 weight percent MA added, was purchased from Uniroyal Chemicals. At an oven with ventilation and a temperature of 80°C, the polymer and OM were gradually dried by weight. Table 1 contains the PP/OM nanocomposite compositions.

Table 1. PP/OM nanocomposite compositions

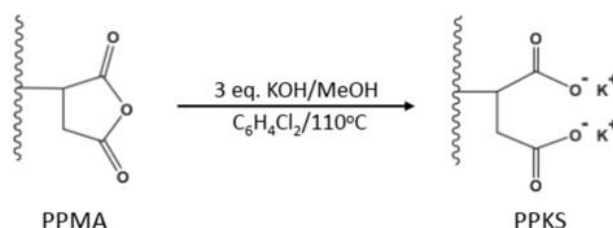
Samples	PP	OM	PPMA	PPKS
	wt%	wt%	wt%	wt%
PP	100	-	-	-
PPC5	95	5	-	-
PPC5M1	85	5	15	-
PPC5M2	85	5	-	15

PPMA: Maleated polypropylene; PPKS: potassium succinate grafted polypropylene

Methods

PPKS Arrangement

Using 1,2-dichlorobenzene (C₆H₄Cl₂), PPMA was diluted at 110°C. One drop solution contained the indicator (phenolphthalein). A 0.3 N methanolic KOH solution was used to integrate the drops until the solution's paint turned a light pink color. To verify the entire neutrality and visibility of the pink paint, it was heated for an additional half hour. PPKS was refined using hot MeOH after being exhausted in MeOH. To create a white paint, PPKS was filtered and dried at 80°C. According to Scheme 1, PPKS was produced by the immediate hydrolysis and mitigation of PPMA solution.



Scheme 1. KS-grafted-PP (PPKS) preparation.

Specimen Setting Up

Melt blending was used to create the nanocomposites in a co-rotating twin-screw extruder (Brabender Plasticorder, model: PLE-331) utilizing compatibilizers and a PP and OM combination. For every sample, the mixture was mixed for eight minutes at a fixed temperature of 190°C and a screw speed of 50 rpm. The nanocomposite samples were cooled to 25°C at the same pressure after being compacted into sheets with a 1 mm thickness for 5 minutes at 180°C and 10 MPa. The purpose of molded sheets was to be used for cutting and assessing various attributes.

Morphological Analysis

Transmission Electron Microscopy (TEM)

Using a 200 kV accelerating voltage, the transmission electron microscope (TEM; JEOL JEM-2010) was used to disperse OM in nanocomposite samples. Using a Leica Ultracut UCT diamond knife, extruded samples were microtomed into extremely thin pieces with a thickness of around 100 nm. These fragments were then photographed in a TEM.

Scanning Electron Microscopy (SEM)

Extruded samples were fractured in liquid nitrogen and the fracture surface of the samples was observed using Scanning Electron Microscope (SEM; JEOL, Japan JSM-6360LV) at an

accelerating voltage of 15 kV. The fracture surfaces of the sample were coated with a thin layer (10–20 nm) of gold before analysis.

Mechanical Properties

Tensile Features

A screw-driven universal testing machine (model: Instron 4466) was used to assess the tensile properties of the composite samples in accordance with ASTM standard procedure. The gauge length was 10 mm, and the crosshead speed was 20 mm/min. The conditions for all the samples were set at 25°C and 55% relative humidity.

Thermal Properties

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (Perkin Elmer DSC-7, Wellesley, MA, USA) was used to determine the melting and crystallization temperatures as well as the crystallinity of the samples. The heating rate was set to 10°C/min in a N₂ atmosphere. The sample weighed between five and eight milligrams.

Heat Distortion Temperature (HDT)

By applying the ASTM D 648 technique, samples of 125 × 12.50 × 3.0 mm³ were used to calculate the HDT of PP and nanocomposites. Using Advanced HDT/Vicat softening point apparatus (Ray Ryan Test Equipment, Ltd.), the test was conducted at a heating rate of 2°C/min.

Measurements of Rheology

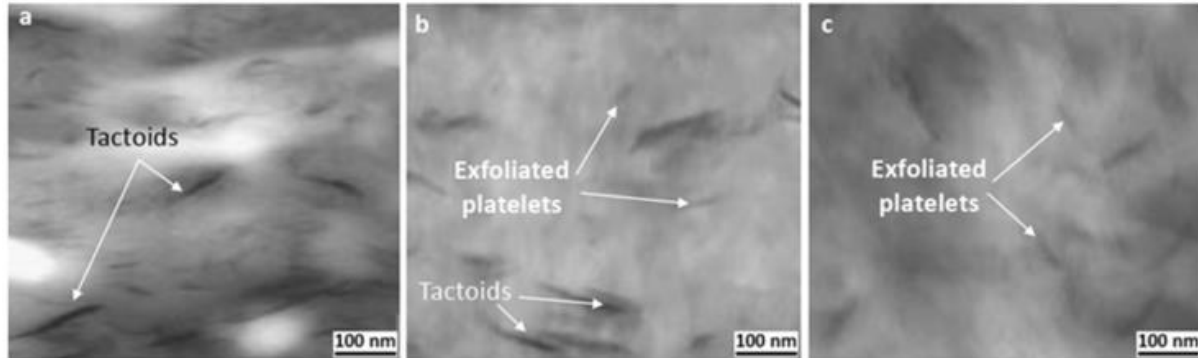
The advanced rheometric expansion system (ARES) was used to test the rheological parameters of the nanocomposite disc samples, including elastic modulus (G'), loss modulus, (G''), and complex viscosity (η^*). Nanocomposites were compression molded in a hot press set at 200°C to create a disc sample. Every test was conducted with a frequency range of 0.1-200 rad/s and at 200°C.

Results and Discussion

TEM Examination

Three photomicrographs are shown in Figure 1, which correspond to the nanocomposites of PP/5% OM (identified as PPC5), PP/15% PPMA/5% OM (marked as PPC5M1), and PP/15% PPKS/5% OM (designated as PPC5M2). A significant number of OM particles are seen in Figure 1(a). These particles are not intercalated and most likely form a "micro composite" structure because compatibilizers are not present. The section in black (piled silicate platelets)

displays the clay tactoids, while the remaining area shows an unbroken PP. Yet, certain dark patterns might represent a few clay granules that are unevenly distributed. Figure 1(b) illustrates the much smaller clay particles in contrast to Figure 1(a), where the blending process has divided the organic particles into lighter portions. That being said, PPKS acts as

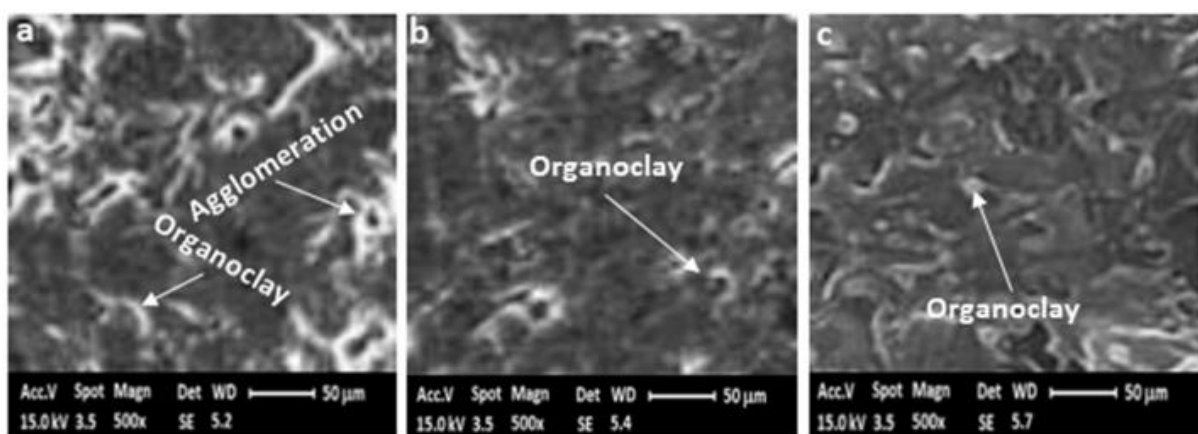


an intercalator between PP and organoclays, so adding it will result in a better dispersion (Figure 1, c). Because the PPKS system's PP matrix has less black shape than the PPMA systems, the organoclay dispersion in PPKS systems is better and more consistent. To enhance the mechanical qualities and more evenly distribute OM throughout the matrix, compatibilizers should be combined with OM and matrixes.

Fig. 1. TEM images for three nanocomposites: (a) PPC5, (b) PPC5M1, and (c) PPC5M2.

SEM Examination

Figure 2 shows SEM photomicrographs of PPC5, PPC5M1, and PPC5M2 nanocomposites. Large sections of the OM components of Figure 2(a) were exposed above the fracture surface, and they were dispersed randomly throughout the PP matrix. The PP to PPC5 nanocomposite has large particles distributed throughout it, preventing the presence of functional polymer and giving the impression that the component adhesion is weak or individually moist at each contact. Photomicrographs of PPC5M1 and PPC5M2 nanocomposites are shown in Figures 2(b) and 2(c). The average particle size of the PPC5M1 system was smaller than that of the PPC5, and it contained some big components. The PPC5M2 system was more evenly distributed throughout the PP matrix than the PPC5M1 system, as seen in Figure 2(c).



PPC5M1 or PPC5M2 aids in the breakdown of particles and the modification of interfacial interactions, as evidenced by changes in both particle size and interface characteristics. This finding is consistent with Table 2's mechanical property results.

Fig. 2. A set of SEM photomicrographs showing the nanocomposites (a) PPC5, (b) PPC5M1, and (c) PPC5M2.

Evaluation of Tensile Properties

Without compatibility, immiscible mixtures typically have weak interfacial bonds between the components, which results in weak tensile properties such as tensile strength (TS), tensile modulus (TM), and elongation at break (Eb (%)). In both pure PP and PP/OM nanocomposites, tensile characteristics were assessed at certain loading percentages of OM (5 weight percent) and compatibilizer (15 weight percent). How both compatibilizers handled tensile characteristics was a significant point to note. Table 2 contains the testing findings for the tensile characteristics. By adding organoclays and PPMA or PPKS, the tensile characteristics of neat PP were noticeably enhanced. The nanocomposite's TS and TM were increased to 37.6 and 1365 MPa, respectively, from the roughly 32.5 and 1158 MPa of the neat PP. Due to the long aliphatic chain in OM, which creates a rich interfacial bond between the matrix and the OM, increased tensile characteristics may also result in rich interfacial bonding between the matrix and OM. Furthermore, among all the examples studied on a specific OM content, the TS and TM of the nanocomposites linked to PPC5M2 were the highest values. The greatest values attained were 40.5 MPa and 1813 MPa, which compared to virgin PP were increases of 25 and 57%, respectively. On the other hand, the TS of the PPC5M1 nanocomposites did not increase further. The compatibilizer's fine dispersion and improved solid-state adhesion, which can transmit more stress from the matrix to the dispersion stage, are typically cited as the reasons for the compatibilized system's higher tensile characteristics as compared to the unmodified system. These results align with the findings of studies carried out by W.C. Chen et al. [14]. One important attribute of tensile strength for materials is the elongation at break. In general, OM decreases the elongation at break in polymeric materials. Observe the elongation trend at nanocomposites break, as indicated by Table 2, using the same OM and PPMA or PPKS content.

Table 2. Tensile characteristics and composition of PP/OM nanocomposites.

Samples	PP wt%	OM wt%	PPMA wt%	PPKS wt%	TS (MPa)	TM (MPa)	Eb (%)
PP	100	-	-	-	32.5 ± 0.9	1158 ± 45	96 ± 1.5
PPC5	95	5	-	-	37.6 ± 0.7	1365 ± 51	88 ± 1.2
PPC5M1	85	5	15	-	38.6 ± 0.8	1118 ± 53	77 ± 1.4
PPC5M2	85	5	-	15	40.3 ± 1.1	1619 ± 62	74 ± 1.6

PPMA: Maleated polypropylene; PPKS: potassium succinate grafted polypropylene

DSC Evaluations

As can be shown in Figures 3(a) and 3(b), respectively, the crystalline and melting peak temperatures of neat PP and its nanocomposites. The enhancement in the crystallization peak temperature (T_c) of the PPC5 nanocomposite was seen in Figure 3(a), rising from 111.6°C for PP to 113.2°C. PPC5M2's T_c improved to 116.3°C, which is notable because it is substantially larger than both PP and PPC5M1's nanocomposite. As a result, the compatibilizer and OM are more significantly impacted by the PP crystallization process. This is most likely because the compatibilizer in PPC5M2 creates a more uniform network structure and the OM's PP melt viscosity increases, increasing the local shear stress. In addition, the addition of compatibilizers and/or OM had no discernible impact on PP's T_m [Figure 3(b)]. Figure 4(a) shows the percentage of neat PP's crystallinity as well as that of its nanocomposites. Since the compatibilizer significantly improves crystallinity between the PPC5M1 and PPC5M2 systems, OM has an imperfect effect on crystallinity. One might take up the fact that the compatibilizer, not the OM, determines the crystallinity of PP in PPC5M2 in order to examine the nucleation impact of the compatibilizer on PP. Because of its superior surface area when exfoliated, OM was thought to be an excellent nucleating agent, as evidenced by the aforementioned results, which were very naturally attractive. However, the interface nucleation effectiveness is reduced because of the impacts of welding, plasticizing, and/or flaws mentioned. In particular, a significant concentration of compatibilizers hindered the high nucleating efficiency of OM [15].

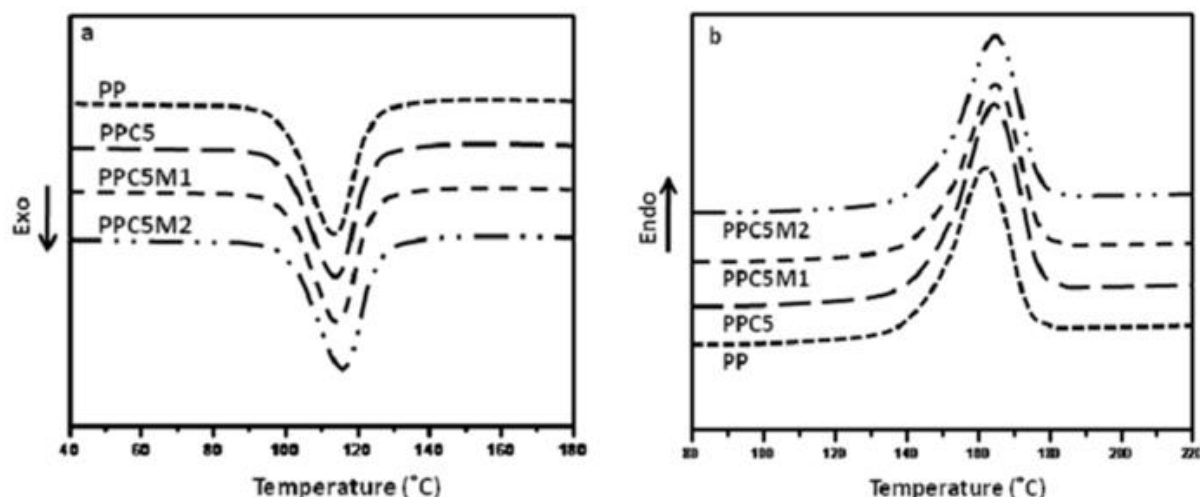


Fig. 3. Polypropylene (PP) and its nanocomposites: (a) crystallization and (b) melting curves using differential scanning calorimetry (DSC).

Heat Distortion Temperature (HDT)

The HDT measurements of PP and its nanocomposites' thermal behavior are shown in Figure 4(b). Observably, the PPC5 system's HDT was around 2.1°C higher than the neat PP's. Because of the supporting OM particles in it, PPC5 systems have improved thermal stability. This supports the TEM results that were previously presented. The strong hydrogen connections that exist between the OM surface and the polymer matrix are responsible for the HDT improvement. An additional explanation for this was that the nanocomposite's superior mechanical stability was to blame, not the molten temperature rising above what it was in comparison to the neat PP. Since OM is more dispersed and exfoliated in the polymer matrix, the PPC5M1 system has demonstrated a more advanced improvement in HDT when compared to the PPC5 system. In addition, every sample displays the greatest HDT value for the PPC5M2 system. As demonstrated by the TEM studies that were previously described, this can be attributable to the PPC5M2 nanocomposite's more well-exfoliated structure. Stated differently, compatibilizers enhance the thermal characteristics of polypropylene in a complementary manner.

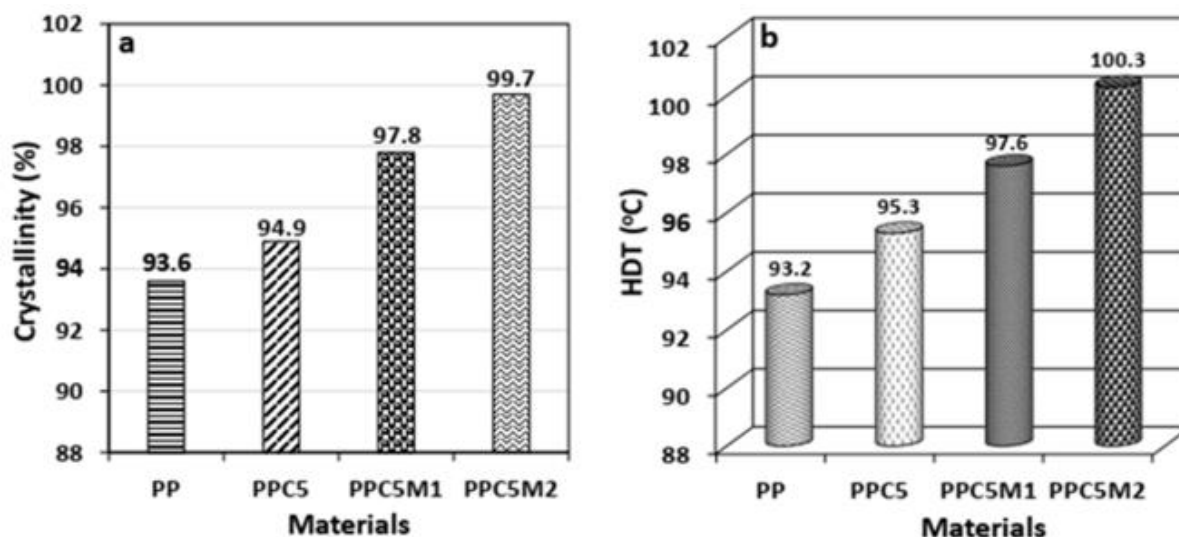


Fig. 4. (a) The PP, PPC5, PPC5M1, and PPC5M2 nanocomposites' crystallinity; and (b) the nanocomposites' hardness characteristics.

The Viscoelastic Performance

Melt rheology research is important from the standpoint of polymer processing. It also provides the impression of a molten microstructure. The storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) of the neat PP, PPC5, PPC5M1, and PPC5M2 systems are shown as functions of frequency in Figures 5(a)–(c). When compared to linear viscoelastic responses, significant effects of nanocomposites demonstrate organoclay. Organoclays were recruited in order to boost the G' , G'' , and η^* of the PP matrix. PPC5M2 has been shown to have the largest range among the frequencies examined in G' and G'' (Figures 5a and 5b). It has been discovered that the G' and G'' frequencies become distinct for PPC5M2 and PPC5M1, which are typical behaviors of hard-core materials, especially in the low-frequency area. Lower frequency increases in G' and G'' signify a stronger contact between the OM and the polymer matrix. The results suggest that the OM and the PP chain do not interact, and PPC5 was unable to show any discernible filler effect in the absence of a compatibilizer. However, when taking into account the increase in G' and G'' terminal areas, it has been shown that PPC5M1 causes a significant interaction at the polymer-OM interface, albeit less than the sample sorted with PPC5M2 at a particular OM content. For the sample composition supplied, anticipate that OM will exhibit better dispersion in the PPC5M2 system than in the PPC5M1 system.

For the PP, PPC5, PPC5M1, and PPC5M2 systems, the complex viscosity (η^*) vs frequency obtained from the frequency sweep test is shown in Figure 5(c). With an increase in η^*

frequency, the nanocomposite diminishes and exhibits "non-Newtonian behavior". Strong molecular chain adaptation of the polymer nanocomposite during applied shear stresses is responsible for the shear-thinning nanocomposites' observed behavior. Because polymer nanocomposites exhibit strong shear-thin behavior, compatibilizers have a greater influence on the strength of the nanocomposites at lower frequencies than at higher ones. However, as compatibilizers are added, this influence reduces with increasing frequency. At a particular OM content, it was found that PPC5M2 generated a significant interaction at the polymer-OM interface that was superior to that of the prepared sample containing PPC5M1. The significant increase in the G' or G'' was closely linked to this enrichment effect.

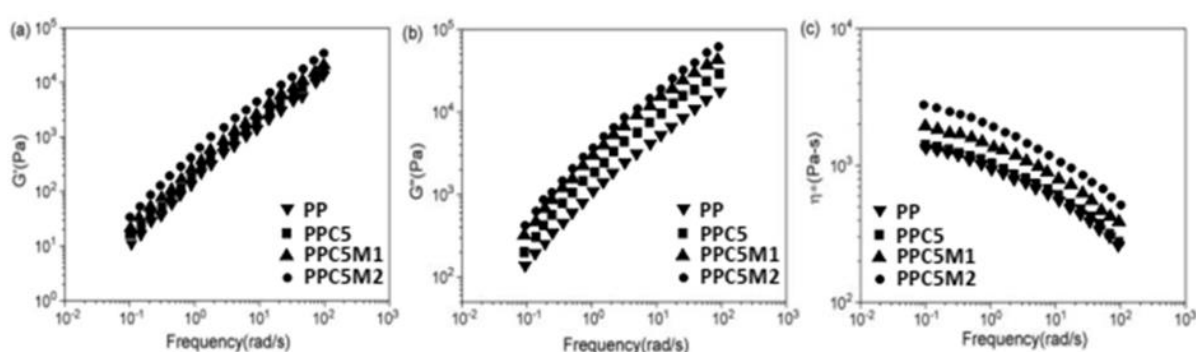


Fig. 5. Neat PP, PPC5, PPC5M1, and PPC5M2 nanocomposites of (a) G' , (b) G'' , and (c) η^* as a function of the frequency.

Conclusions

This study effectively created PP/OM nanocomposites by utilizing a melt mixing process with two distinct compatibilizers: maleated polypropylene (PPMA) and potassium succinate modified polypropylene grafted maleic anhydride (PPKS). Investigations were conducted into compatibilizers' impacts on the morphological, mechanical, thermal, and rheological characteristics of PP/OM nanocomposites. The final morphological characteristics demonstrated that the OM platelet delamination was supported by both compatibilizers. In comparison to the PPC5M1 compatible system, the PPC5M2 compatible system exhibited a partial exfoliation of PP/OM nanocomposites. This result was also validated by the sample's rheological characteristics. Compared to the PP/OM case and the PPMA compatible system, the PPKS compatible system offers better tensile qualities. According to DSC thermograms, compatibilized nanocomposites with lower crystallization temperatures exhibit a protective shield and/or error effect from the more compatibilizers. This is particularly true for PPMA compatibilized nanocomposites, which have a tendency to contain more compatibilizers than

PPKS. The results show how crucial it was to include compatibilizers with different matrix properties as a result of OM dispersion in order to get the best possible mechanical, thermal, and rheological properties.

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