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Preparation, mechanical and rheological properties of a thermoplastic polyolefin (TPO)/organoclay nanocomposite with reference to the effect of maleic anhydride modified polypropylene as a compatibilizer

Joy K. Mishra, Keun-Joon Hwang, Chang-Sik Ha*

Department of Polymer Science and Engineering, Pusan National University, Keumgjung Ku, Pusan 609-735, South Korea

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Abstract

A thermoplastic polyolefin (TPO)/organoclay nanocomposite has been successfully prepared by using maleic anhydride modified polypropylene as a compatibilizer. The nanocomposite was characterized by IR spectra, X-ray diffraction and Transmission Electron Microscope. The nanocomposite exhibited remarkable improvement of tensile and storage modulus over its pristine counterpart. Enhancement of storage modulus (in melted state) and decrease in terminal slope of the nanocomposite (over its pristine equivalent in the frequency sweep experiment) confirms the fact that a strong interaction exists between clay platelet and polymer molecules in the melted state. For both the nanocomposite and its pristine counterpart, strong shear thinning behavior was observed in the melted state (as examined by frequency sweep experiment).

Keywords: Thermoplastic polyolefin (TPO); Nanocomposite; Organoclay

1. Introduction

Polymer layered silicate nanocomposites have received significant research attention because they often exhibit remarkable improvement of mechanical properties, enhanced barrier properties, reduced flammability and enhanced biodegrability of a biodegradable polymer [1–7]. In an intercalated polymer layered silicate nanocomposite the extended polymer chains remain between the host layers whereas in an exfoliated nanocomposite they are randomly dispersed in a continuous polymer matrix such that interlayer distances are comparable to the radius of gyration of polymers.

Thermoplastic elastomer compositions based on uncured ethylene propylene diene teropolymer (EPDM) rubber and polypropylene (PP) is referred as thermoplastic polyolefin (TPO) whereas blends of PP and dynamically vulcanized EPDM rubber are termed as thermoplastic vulcanizates (TPV). In one extreme when PP content is very high (hardest grade that contains more than 80% PP) the material (TPO) shows properties like an impact toughened PP (elastomer modified thermoplastics), on the other hand when the PP content is less than 30% the material behaves as thermosetting rubber (another extreme, softest or rubbery grade) [8,9]. Thus it is possible to prepare various TPO compounds (by changing PP and EPDM ratio) for suitable end use application by changing PP and EPDM composition. Most attractive feature of these materials is that they can be processed like thermoplastic while exhibiting the resilience and elasticity characteristics like an elastomer.

TPO find wide application in automotive parts, extruded profile for windows, cable insulation, footwear, packaging industry etc. Automotive parts constitute the largest single market of the TPO compounds. Their excellent weatherability, low density, and relatively low cost make them a common component in a number of interior and exterior applications (such as sight shields, grills, conduit, interior trim etc). Filler is required for achieving the stiffness of the

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* Corresponding author. Tel.: +82 51 510 2407; fax: +82 51 514 4331.
E-mail address: csha@pusan.ac.kr (C.-S. Ha).

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TPO compounds. The traditional reinforcements and fillers must be used at high loading levels, which increase the weight and cause an adverse effect in automotive applications area, because 90% of the total energy used by automobile during its life cycle is from fuel consumed by its own weight [10]. Small amount of nanofiller can improve the stiffness of the material substantially, thus cost effective where the weight of the material part is a concern.

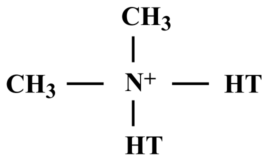
Though polymer/clay nanocomposites based on PP and EPDM were prepared successfully by many groups [11–17], till date there is very little information available regarding TPO/clay nanocomposite [18,19]. Recently, Mehta et al. [19] studied TPO/clay nanocomposite where the TPO contains 70% isotactic PP and 30% EPDM. They observed substantial improvement in mechanical properties even at small clay content. Very recently we successfully prepared and studied TPV/organoclay nanocomposite [20]. The results were encouraging enough for us to study TPO/organoclay nanocomposite where PP/EPDM ratio of the TPO is 25:100 by weight (soft rubbery grade type).

In this article we highlight the preparation and properties of a TPO/clay nanocomposite. As TPO (Both PP and EPDM are non polar) is not polar to improve the dispersion of clay we have used maleic anhydride (MA) modified PP as a compatibilizer [18,19,21] for the nanocomposite preparation.

2. Experimental

2.1. Materials

A commercial grade TPO with a hardness of 63 (shore A) and specific gravity of 0.959 was used. The ratio of PP and EPDM in the TPO is (25:100 by weight). The compatibilizer used in this study is maleic anhydride modified polypropylene (hereafter referred as m-PP) with melt flow index 250 g/10 min at 230 °C. The MA possessing 1% functionality was supplied by Uniroyal Chemical Co. Cloisite 20A was purchased from Southern Clay, TX, USA. The structure of the organic modifier is shown below; in which HT represents the hydrogenated tallow (∼65% C18, ∼30% C16, and 5% C14).



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle HT}{N^+}}-HT$$

2.2. Sample preparation

The composition of the prepared samples is listed in Table 1. They are explained as below:

TPON5. It is a TPO/organoclay nanocomposite containing TPO, Cloisite 20A, and m-PP. The organoclay and compatibilizer ratio in the hybrid is 1:3 (by weight) [21] and the hybrid contains 5% organoclay. In earlier study [21] for the preparation of PP/clay nanocomposite it was observed that when the clay/compatibilizer (m-PP) ratio became 1:3 by weight; the dispersion of clay in the polymer matrix is highest.

TPOE5. It is composed of TPO and m-PP in the same weight ratio as is used in TPON5. This sample is equivalent with TPON5 as far as the weight ratio of the TPO and m-PP is concerned. This sample is the pristine equivalent of sample TPON5. This sample is necessary to study the property enhancement of nanocomposite over its pristine counterpart.

TPON2.5 and TPOE2.5. TPON2.5 consists of 2.5 wt % clay, m-PP (1:3 ratio by weight) and TPOE2.5 is its pristine equivalent.

TPOtM20. It is a 20 wt % talc based microcomposite.

TPO/20A. It is a 5 wt % organoclay base nanocomposite (without any compatibilizer).

Mehta et al. [19] studied TPO/clay nanocomposite where the TPO contains 70% isotactic PP and 30% EPDM. They did not prepare any pristine equivalent sample like us for the comparison of mechanical properties. Their TPO contains 70 wt % PP and they have used very little amount of compatibilizer. In their case, variation of mechanical properties of the nanocomposite due to a compatibilizer (there is no drastic change in the thermoplastic elastomer composition) is very little (although theoretically it can not be ruled out).

2.3. Measurements

The samples were prepared by melt mixing method. The mixing was carried in a Haake Rheocorder at 190 °C and 50 rpm rotor speed with a mixing time of 10 min. X-ray diffraction (XRD) studies of the samples were carried out (to examine the basal spacing of the pure clay as well as in nanocomposite) using a Rigaku D/max 2200 H X-ray diffractometer operating at 40 kV, and 50 mA (Cu K_α radiation). The scanning rate was 0.5 °/min. The microstructure of the nanocomposite was examined by Phillips CM-20 Transmission Electron Microscope (TEM). The accelerating voltage was 120 KV. Tensile properties of the samples were measured with a Universal Tester (H.T.E, H 25 km and 500 Lm extensometer) at a strain rate of 100 mm/min. At least six dog-bone shape replica of each samples were used. Dynamic mechanical analysis of samples was carried out using a dynamic mechanical analyzer (Rhevibron DDV-25 F; Orientec Co.) in tension mode with following parameters: frequency 1 Hz; scan rate 5 °C/min, in the temperature range of −100–+150 °C.

Melt rheological measurement (small amplitude oscillatory shear rheometry) was carried out on RDA II instruments. Dynamic oscillatory shear measurements were performed using a set of 25 mm diameter parallel plate and a sample thickness of 1–2 mm, at 200 °C. Strain

Table 1
Composition of various samples

Sample Code	TPO (gm)	Talc (gm)	MA functionalized PP (gm)	Cloisite 20A*	TPO: MA functionalized PP (by weight)
TPON5	40	–	7.5	2.5	5.33
TPOE5	42.1	–	7.9	–	5.33
TPON2.5	45	–	3.75	1.25	12
TPOE2.5	46.15	–	3.85	–	12
TPOtM20	40	10	–	–	–

sweep experiment was first carried out at frequency of 6.28 rad/s. Then, frequency sweep experiment was carried out at a range of frequency 0.05–100 rad/s at a strain 0.07% (which is clearly in the linear viscoelastic range).

3. Results and discussion

3.1. IR spectroscopy

The IR spectra of the TPO/organoclay nanocomposite and their pristine counterpart are displayed in Fig. 1. The IR spectra of the TPON5 and the TPON2.5 show a peak at 3628 and 3621 cm^{-1}, respectively. These two peaks are attributed to the stretching frequency of O–H group, which emanates from the terminal hydroxyl group of the montmorillonite of the Cloisite 20A [22,23]. However, in the IR spectra of TPOE5 and TPO E2.5, no peak is observed within the range of 3400–3700 cm^{-1} due to the absence of organoclay. However there appears a weak peak at 3183 cm^{-1} for TPON5, 3621 cm^{-1} for TPON2.5, 3183 cm^{-1} for TPOE2.5 and 3190 cm^{-1} for TPOE5 (which is absent in Cloisite 20A). These peaks are due to the =C–H stretching frequency, which arise from the MA group in the m-PP compatibilizer. The peaks at 517 and 462 cm^{-1} in TPON5 as well as TPON2.5 are attributed to the Al–O stretching and Si–O bending frequency of the montmorillonite (generates from the organoclay Cloisite 20A).

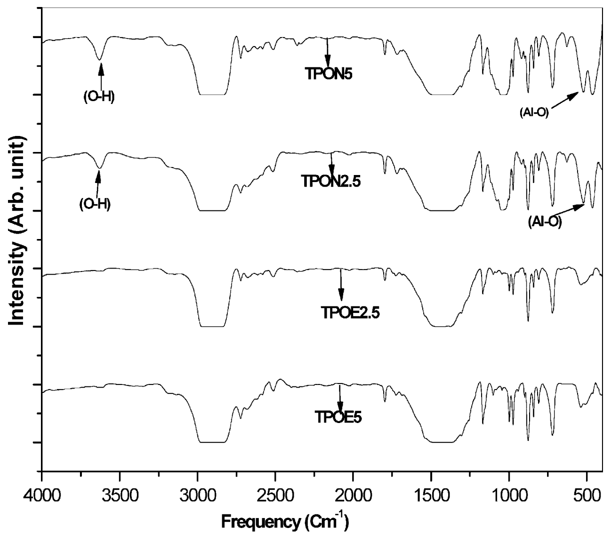


Fig. 1. FTIR spectra of TPON5, TPON2.5, TPOE5 and TPOE2.5.

3.2. X-ray diffraction (XRD) and transmission electron microscope (TEM)

XRD is the most powerful and reliable technique to study the dispersion of organoclay inside the polymer matrix. The X-ray diffraction pattern in the range of $2\theta = 1.5$–$12°$ is shown in Fig. 2. It is observed from Fig. 2 that the peak corresponding to the basal spacing (d_{001}) of the Cloisite 20A (the used organoclay) appears at $2\theta = 3.48°$ (corresponding d_{001} spacing is 2.47 nm). In nanocomposites the d_{001} peak of the clay has been shifted to low angle corresponding to an increase in d-spacing from 2.47 to 4.3 nm and 3.9 nm for TPON2.5 and TPON5, respectively. The higher basal spacing of clay in the nanocomposites as compared to virgin Cloisite 20A (organoclay) is due to the intercalation of polymer chains inside the clay layers. Again in TPO/20A (absence of the m-PP compatibilizer) the basal spacing of the clay is 3.4 nm. Thus intercalation in TPO/20A is less compared to TPON5. Higher intercalation means higher the dispersion of organoclay inside the polymer matrix. When m-PP is used for nanocomposite preparation as a compatibilizer it can diffuse easily (because it is polar) into the organoclay layers and increase its basal spacing. After that it is easy for PP and EPDM (although they are non polar) to intercalate inside the silicate layers as the space available for intercalation between clay galleries have already increased. At low clay content (2.5 wt %) the insertion of the polymer into the silicate gallery led to the disordering of the layered silicate structure, which decreased the peak intensity as compared to Cloisite 20A [20,24,25]. However after further addition of the clay in case of TPON5, the intensity of the d_{001} peak increased, confirming the intercalation of the clay layers inside the silicate gallery without the disruption of the ordered structure [25,26].

The TPON5 nanocomposite was further characterized by TEM and shown in Fig. 3 (as a representative sample). The dark lines in the TEM image are silicate layers. It is revealed that majority of silicate layers are in the intercalated state (label ‘A’). However, few silicate layers are in the exfoliated state (label ‘B’) also. The average thickness of the clay layers are ~1 nm. The average distance between the two silicate layers is 3.8 nm.

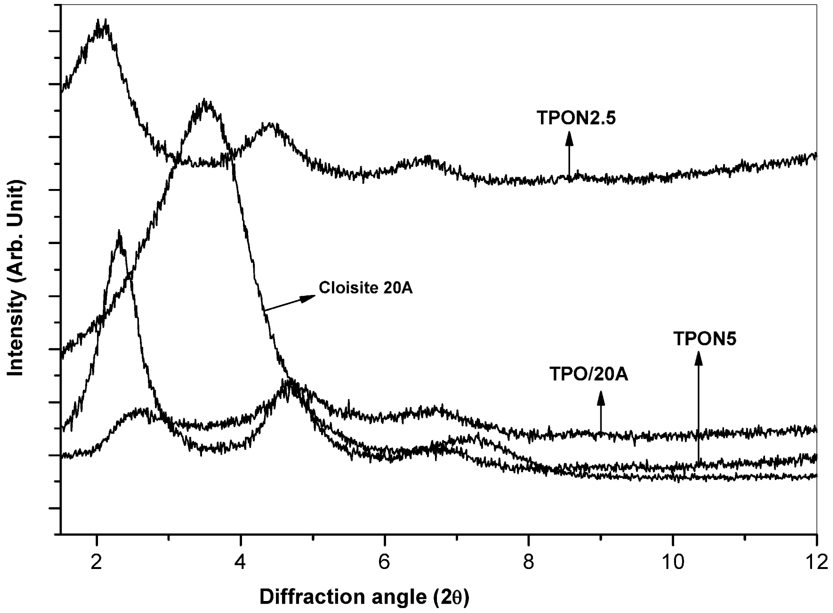


Fig. 2. XRD patterns of the TPO/organoclay nanocomposites and Cloisite 20A.

3.3. Change of thermoplastic elastomer composition of TPO and its effect on hardness

m-PP compatibilizer in the TPO/organoclay nanocomposite system plays a dual role. In one hand, it enhances intercalation of polymer chains inside the clay gallery, which has already been discussed (in the XRD portion). On the other hand, m-PP changes thermoplastic elastomer composition of the TPO/organoclay nanocomposite system.

It is observed from Table 2 that the hardness of TPOE2.5 is 73 and TPOE5 is 82 (hardness of the virgin TPO is 63). Thus the rubbery grade TPO material tends to be changed as an impact toughened PP (from one extreme to another) depending on the compatibilizer weight. Thus not only clay but also the compatibilizer plays an important role for the end use application of the TPO/organoclay nanocomposite.

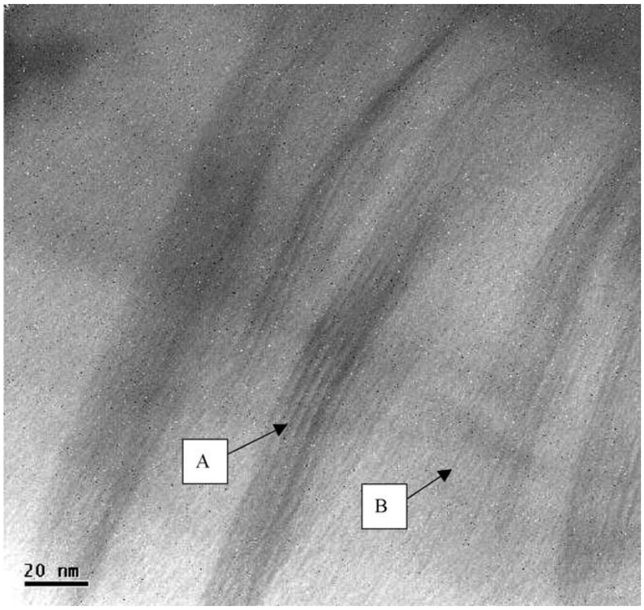


Fig. 3. TEM image of TPON5.

3.4. Dynamic mechanical properties

Dynamic mechanical analysis (DMA) measures the response of a given material to a cyclic deformation as a function of temperature. The storage modulus vs temperature curve is shown in Fig. 4. The improvement of the storage modulus of the nanocomposite over their pristine counterpart is more prominent in the rubbery region because in this region the material is soft and flexible. As emanates from Table 2 at room temperature storage modulus of the TPON5 is 44% higher than TPOE5 whereas in case of TPON2.5 it is 35% higher over its pristine counterpart (TPOE2.5).

The enhancement of storage modulus strongly depends on the aspect ratio [27] of the dispersed clay particles and the intercalation of the polymer chains inside the clay matrix. When polymer matrix is reinforced with rigid filler particles the polymer interface adjacent to the clay particle is highly restrained mechanically. Platelet edges (of the clay particle) act as a week point and are sites of high stress concentration of the matrix. As the aspect ratio of the filler increases these week points are decreased which results in the higher amount of stress transfer between the matrix and filler particles. Active surface area of the filler increases due to the intercalation of the polymer chains inside the clay galleries. Polymer chains inside the clay galleries are immobilized and the effective immobilization of these chains is responsible for the enhancement of the hydrodynamic storage modulus [28].

Table 2
Mechanical properties of various samples

Sample code	Tensile modulus (kgf/cm^2)	Tensile strength (kgf/cm^2)	Elongation at break (%)	Storage modulus (at 25 °C) (Pa)	Hardness (Shore A)
TPON5	230	80	271	13.7×10^7	–
TPOE5	159	76	431	9.5×10^7	82
TPON2.5	160	71.6	502	6.3×10^7	–
TPOE2.5	135	68	604	4.7×10^7	73
TPOtM20	96	47.5	280	–	–

3.5. Tensile properties

The tensile properties of the nanocomposite and their pristine counterpart are shown in Table 2. It is observed from Table 2 that tensile modulus of the nanocomposite is higher than that of their pristine equivalent. Tensile modulus of the TPON5 is 45% higher than that of TPOE5 whereas tensile modulus of the TPON2.5 is 18% higher than that of TPOE2.5. Tensile modulus expresses the stiffness of the material at the start of tensile test and generally increased when nanocomposites are formed. The insertion of the polymer chain inside the silicate layers leads to an increase in the surface area of interaction between clay and polymer matrix, thus causing enhancement of modulus over the entire composition range. However the tensile modulus of 20 wt % talc filled microcomposite is lower than 2.5 wt % organoclay based nanocomposite. In case of talc filled microcomposite the surface area of interaction is less, thus to enhance stiffness very high loading of talc is necessary, which is not cost effective in the automobile applications or other areas where minimization of weight is main motivation for the material selection. The tensile strength of the nanocomposite increases slightly as compared to their pristine equivalent. The tensile strength of the nanocomposite depends on several factors, such as interaction of clay and matrix, compatibity of PP phase and EPDM phase of TPO, and filler–filler interaction [29]. Low matrix filler interaction (as the matrix is non polar) is responsible for the small increment of tensile modulus of the nanocomposite over its pristine counterpart. The elongation at break of the nanocomposite is less as compared to their pristine counterpart. The presence of filler may increase the stress concentration, which causes the composite to fail in a brittle manner as compared to their pristine equivalent, resulting in the decrease of the elongation at break of the nanocomposite as compared to their pristine counterpart.

3.6. Melt rheological behavior

Melt rheology study is very important from processing point of view. Fig. 5 depicts the elastic modulus dependence on strain for TPON5 and TPOE5 (pristine counterpart) at melted state. Fig. 5 reveals that linear viscoelastic range is widespread. It is 6% for TPON5 but is 11% (almost doubled) for TPOE5 (the linear viscoelastic range is the limit of strain (%) up to which the storage modulus is independent of strain). Thus filler decreases the linear viscoelastic range of the nanocomposite. The TPOE5

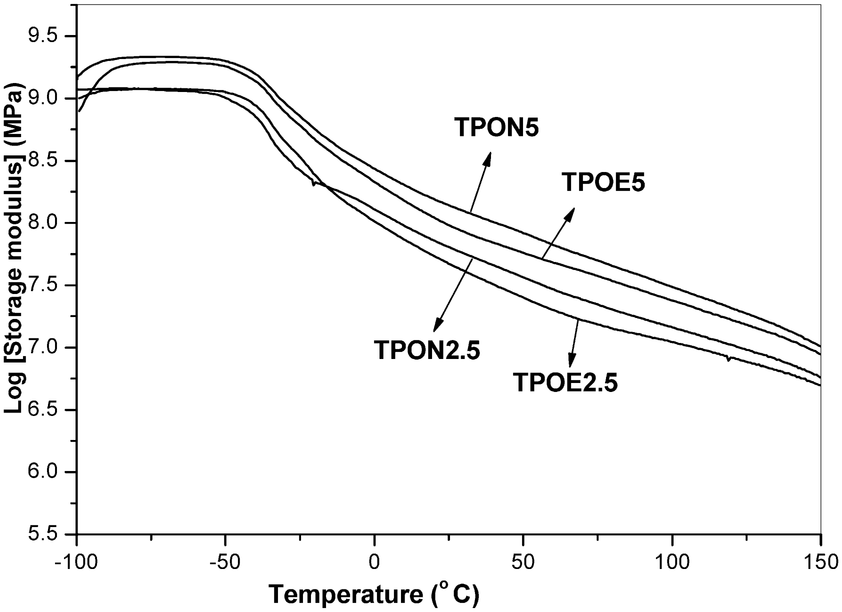


Fig. 4. Dynamic storage modulus of the TPO/organoclay nanocomposites and their pristine counterpart as a function of temperature.

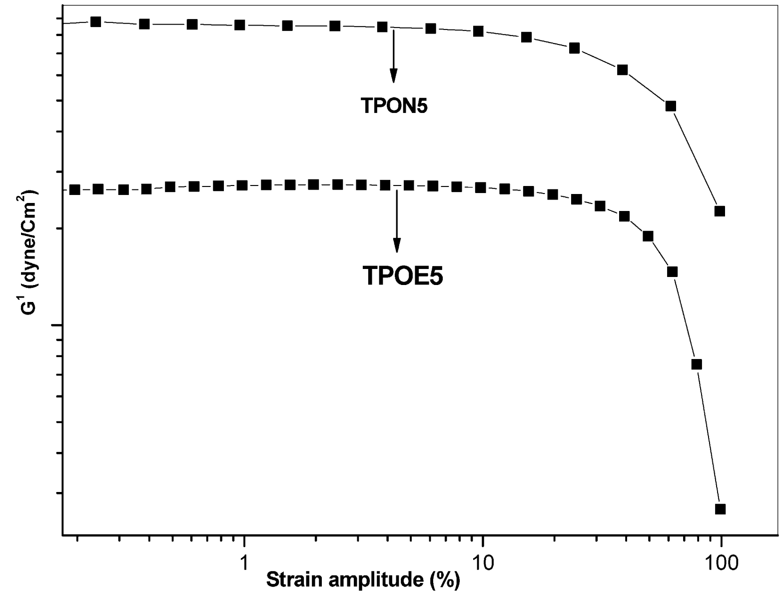


Fig. 5. Storage modulus vs strain amplitude of TPON5 and TPOE5.

contains PP and EPDM. The network structure of the sample emanates from the presence of entanglements of amorphous EPDM rubber, entanglements in the amorphous zone of PP and ordered crystalline domain of PP. This network structure sustains in large deformation in strain sweep experiment. But in nanocomposite there occurs a formation of new microstructure (layered filler decreases the entanglement density of amorphous zone and the network structure becomes weak), which does not resist large deformation like its pristine counterpart.

The elastic modulus (G'), loss modulus (G'') of TPO/organoclay nanocomposite and their pristine counterpart are shown in Figs. 6 and 7, respectively. In entire studied frequency range the storage and loss modulus of the nanocomposite are substantially higher than that of their pristine counterpart. The storage modulus and loss modulus increase with the increased frequency of all the studied samples. This is due to the fact that at low frequency, time is large enough to unraveling of the entanglements so a large amount of relaxation occur results in a low value of storage and loss modulus. However, when a polymer sample is deformed at large frequency the entanglement chains do not have time to relax, so modulus goes up.

It is observed from Fig. 6 that there is a dramatic increase in the storage modulus of the nanocomposite over its pristine counterpart. At 1 rad/s the storage modulus of

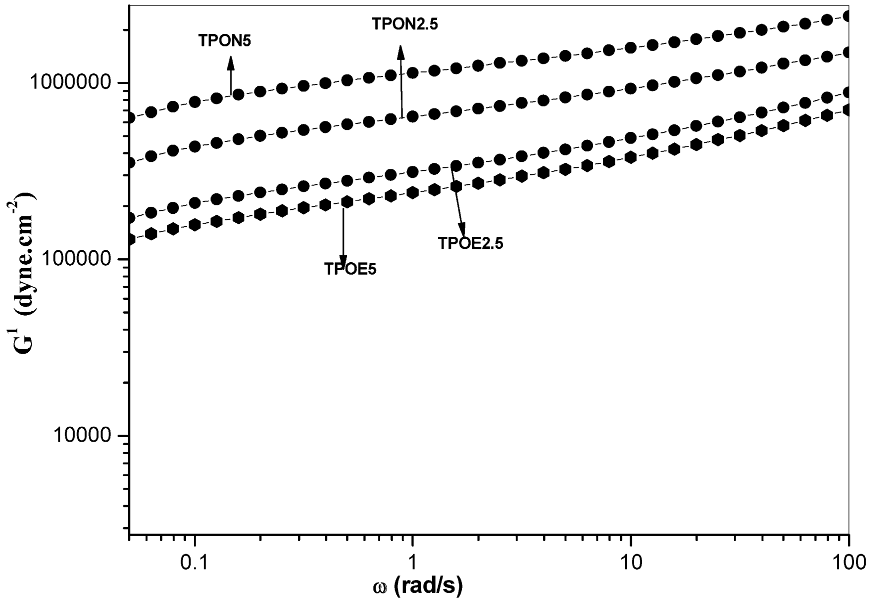


Fig. 6. G' (storage modulus) vs frequency (ω) of TPO/organoclay nanocomposites.

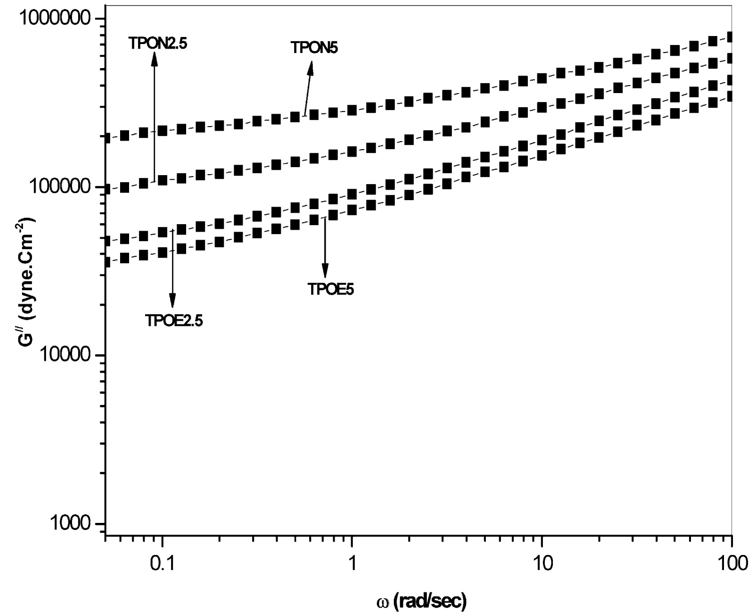


Fig. 7. G'' (loss modulus) vs frequency (ω) of TPO/organoclay nanocomposites.

TPON5 is 376% higher than that of TPOE5 whereas for TPO N2.5 it is 106% higher that TPON2.5.

The slopes in the terminal zone were calculated at low ω region (below 5 rad/s) and listed in Table 3. It is observed from Table 3 that the slope of G' and G'' of the nanocomposites are smaller as compared to their pristine counterpart. The higher the G' and smaller the terminal slope of the nanocomposite over their pristine equivalent indicates the formation of three dimensional superstructure. These results are showing a good agreement with other studied nanocomposite systems [30–34].

The change in complex viscosity (η^*) of nanocomposite and its pristine counterpart is shown in Fig. 8. It is observed from Fig. 8 that the complex viscosity decreases with increased frequency. This is due to the strong shear thinning behavior of the polymer nanocomposite and their pristine equivalent at the melted state. The viscosity of the nanocomposites is higher than their pristine counterpart. At 1 rad/s the viscosity of the TPON5 is 379% higher than TPOE5 whereas it is 104% higher in case of TPON2.5 (as compared to TPOE2.5). The increment of melt viscosity of the nanocomposite is attributed to the strong interaction of organoclay and polymer matrix. However viscosity of the TPOE5 is less than TPOE2.5. This is due to the fact that TPOE5 contains much lower molecular weight and very less viscous compatibilizer (m-PP, shown in Table 1) compared to TPOE2.5.

4. Conclusions

An intercalated thermoplastic polyolefin (TPO)/organoclay nanocomposite was prepared using maleic anhydride functionalized PP as a compatibilizer. The compatibilizer not only enhances the intercalation of the polymer chain inside the clay gallery but also change the thermoplastic elastomer composition (which is very important for end use application) of the TPO/clay nanocomposite. The tensile modulus as well as storage modulus of TPO/organoclay nanocomposite was substantially higher over their pristine counterpart and 20% talc based microcomposite.

It is observed from the dynamic mechanical analysis that storage modulus of the nanocomposite is higher over their pristine counterpart in the rubbery region. Enhancement of storage modulus (in the melted state) and decrease in terminal slope of the nanocomposite (over its pristine equivalent in the frequency sweep experiment) confirms the fact that a strong interaction exists between clay platelet and polymer molecules in the melted state. Nanocomposite as well as their pristine counterpart show strong shear thinning

Table 3
Terminal region slope of G' and G'' vs ω and complex viscosity of nanocomposites and their pristine equivalent

Sample	G' (dyne cm^{-2})	G'' (dyne cm^{-2})	Complex viscosity (at 1 rad/s) (dyne cm^{-2} s)
TPON5	0.09	0.08	11.7×10^5
TPON2.5	0.08	0.11	6.6×10^5
TPOE5	0.11	0.16	2.5×10^5
TPOE2.5	0.13	0.14	3.2×10^5

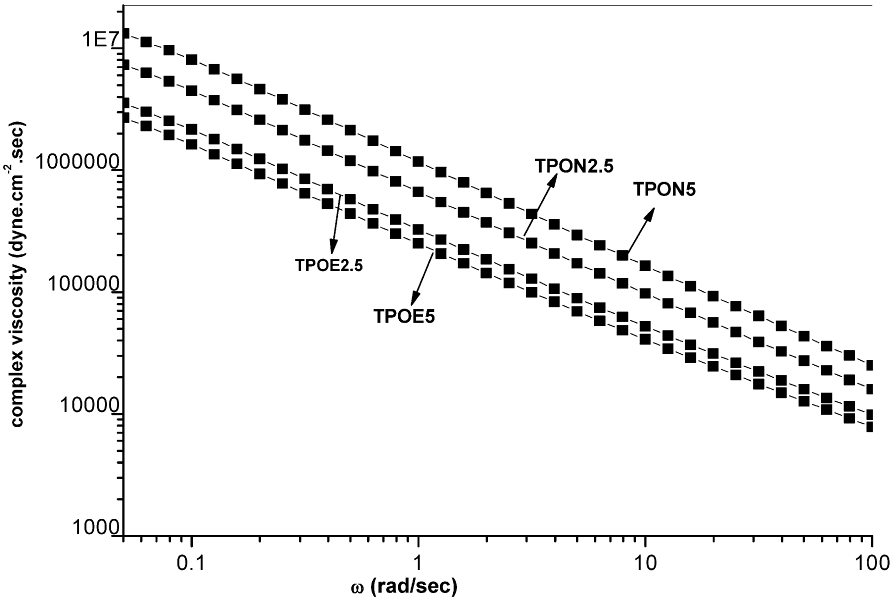


Fig. 8. η^* (complex viscosity) vs frequency (ω) of TPO/organoclay nanocomposites.

behavior at the melted state (as examined by frequency sweep experiment).

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