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Effect of 3D structures on recycled PET/organoclay nanocomposites

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Summary

Formation of physical network in PET/organoclay nanocomposites leads to significant improvement of processing and utility properties. The state of dispersion of silicate platelets in PET by melt mixing depends on shear forces as well on surface chemical treatment of the filler. The level of dispersion was determined by X-ray diffraction analysis and transmission electron microscopy. Melt rheology was used to examine the presence of network particles. It was shown that the addition of 5 wt. % of organo-modified montmorillonite into recyclate leads to a 3D network structure with secondary plateau of G' at lowest frequencies. XRD and TEM experiments supported the conclusion.

Introduction

Investigation of relationship between the structure and processing properties has an important impact on various branches of materials science. Understanding the influence of processing parameters on final properties is the key to preparation of new materials for specific purposes.

Polymer/clay nanocomposites with a relatively low loading of the filler are interesting in terms of improvement of barrier, mechanical and rheological properties, dimensional stability, heat, flame and oxidative resistance [1]. Melt mixing as the most industrially attractive method for nanocomposite production requires study of rheological properties during compounding and their effect on the state of dispersion (delamination level) in the resulting polymer system. Up to now, a few papers have dealt with this topic for some polymer matrices [2, 3, 4, 5], but no mention for recycled PET (which is interesting particularly from the environmental point of view) was found in available literature. The difficulties that accompany processing of PET

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with commercial organoclays arise from thermally limited stability of the quaternary ammonium salts used for modification of montmorillonite (MMT). Davis et al. [6] reported black, brittle and tarlike nanocomposites prepared from PET and ammonium-salt-based organoclay. In our work, transparent nanocomposites with improved processing, mechanical and barrier properties from recycled PET and commercially modified MMT were prepared, although moderate degradation of the matrix was observed in rheological measurements. Thus prepared nanocomposites could find applications in industry on account of continuously decreasing price of commercial organoclays. Description of physical as well as chemical phenomena which occur during compounding and their effect on the material structure are investigated by rheological and morphological testing.

Experimental

Materials

Organo-modified clays were supplied by Southern Clay Products, Inc., Gonzales, TX, U.S.A.

Table 1. Characteristics of organoclay fillers [a]

Organoclay	Organic modifier [b]	Modifier concentration [mequiv/100 g clay]	Moisture [%]	Weight loss on ignition [%]
Cloisite 6A	2M2HT	140	< 2	45
Cloisite 15A	2M2HT	125	< 2	43
Cloisite 20A	2M2HT	95	< 2	38
Cloisite 10A	2MBHT	125	< 2	39
Cloisite 25A	2MHTL8	95	< 2	34
Cloisite 30B	MT2EtOH	90	< 2	30

[a] according to the manufacturer

[b] quaternary ammonium chlorides: dialkyldimethyl- (2M2HT), alkyl(benzyl)dimethyl- (2MBHT), alkyl(2-ethylhexyl)dimethyl- (2MHTL8), alkylbis(2-hydroxyethyl)methyl- (MT2EtOH). Alkyls are a mixture of 65 % C18, 30 % C16 and 5 % C14, derived from hydrogenated tallow.

Recycled poly(ethylene terephthalate) from colour-selected beverage bottles (PET-R), with the intrinsic viscosity 0.73 dl/g was delivered by Polymer Institute Brno, Ltd., Czech Republic.

Preparation of nanocomposites

Organoclays were dried at 80 °C and PET regranulate at 110 °C in an oven at least for 12 h. PET-R was compounded with 5 wt. % of organoclay in a co-rotating twin-screw micro-extruder (DSM Research, Netherlands) under nitrogen environment. The mixing temperature 255 °C was set in order to exert maximal shear stress and minimal thermal degradation on the modified MMT during processing. The blending time was 10 min at the speed 200 rpm.

Structure of nanocomposites

WAXS (wide-angle x ray scattering) analysis was performed with a HZG 4/4A diffractometer (Praezisionsmechanik Freiburg, Ltd., Germany) at room temperature at a scanning rate of 1.5°/min. The Ni-filtered Cu Kα radiation generator was operated at 30 kV accelerating voltage and 30 mA current. The TEM measurements were carried out with a Zeiss LEO 912 Omega transmission electron microscope using an acceleration voltage of 120 keV. The samples were prepared using a Leica Ultracut UCT ultramicrotome equipped with a cryo-chamber. Thin sections of about 50 nm were cut with a Diatome diamond knife at -120 °C.

Melt rheology

An ARES 3 Rheometer (Advanced Rheometric Expanded System, Rheometric Scientific, Inc., U.S.A.) with 25 mm parallel plate geometry was employed for rheological characterization. Dynamic frequency sweep measurements (at the strain level 2 % for the nanocomposites and 30 % for the matrix) as well as time sweep tests were performed at 270 °C under nitrogen.

Results and discussion

As seen in Table 1, the difference between various types of the Cloisite nanofillers comes from the ammonium cations located in the gallery of silicate layers. With two long alkyl groups, the ammonium cations in Cloisite 6A, 15A and 20A are non-polar, while those in Cloisite 30B (two 2-hydroxyethyl groups), 10 A (one hydrogenated alkyl replaced by benzyl group) and 25 A (one hydrogenated alkyl group replaced by a short 2-ethylhexyl group) are more polar. To obtain well-intercalated and exfoliated structure, the surface polarities of polymer matrix and organoclay must be matched [7]. Polar interactions are also crucial for the formation of well-dispersed systems via polymer melt intercalation [8]. These assumptions are confirmed by the results obtained.

Nanofillers Cloisite 6A, 15A and 20 A show a large initial gallery spacing, allowing an easier penetration of polymer chains, but they are exceedingly hydrophobic and do not match the polarity of PET. Subsequently, the weak interactions between the ammonium cations of fillers Cloisite 6A, 15A, 20 A and chains of PET resulted in inferior PET intercalation (Figure 1a, Table 2). On the other hand, due to the moderate surface polarity of Cloisite 30B and 10A, highly delaminated structures of recycled PET nanocomposites were obtained (Figure 1b, Table 2).

The WAXS diffractograms of nanocomposites (Figure 1a, 1b) showed that the first peaks of the pure fillers Cloisite 6A and Cloisite 15A as well as of composites PET-R/Cloisite 6A and PET-R/Cloisite 15A occur in similar positions (Table 2), indicating only very low interactions of the matrix with these organoclays. For PET-R/Cloisite 30B, PET-R/Cloisite 10A, PET-R/Cloisite 25A and PET-R/Cloisite 20A systems, the peaks of fillers were shifted to lower angular values. The increased basal spacing d_{001} showed that the polymer chains were intercalated in the gallery of silicate layers (Table 2). The obviously larger interlayer distance of Cloisite 30B, 10A and 25A in recycled PET nanocomposites demonstrates the efficiency of filling. The highest decrease in the first peak in WAXS patterns (Figure 1b) corresponds with partial exfoliation (exfoliation of a certain number of tactoids) in the systems mixed with Cloisite 30B and 10A. Cloisite 25A exhibits also a high level of intercalation, which is attributed to the hydrophobicity decrease resulting from the loss of one hydrogenated alkyl group (Figure 1a, Table 2).

Table 2. WAXS analysis of organoclays in nanocomposites*

Organoclay	XRD peak position (°)	Basal Spacing (Å)	Δ d_{001} (Å)
Cloisite 6A	2.8 (2.64)	31.5 (33.4)	-1.9
Cloisite 15A	2.9 (2.8)	30.4 (31.5)	-1.1
Cloisite 20A	3 (3.65)	29.4 (24.2)	5.2
Cloisite 10A	3 (4.6)	29.4 (19.2)	10.2
Cloisite 25A	3.1 (4.75)	28.5 (18.6)	9.9
Cloisite 30B	2.9 (4.77)	30.4 (18.5)	11.9

* manufacturer´s data for neat organoclays are given in parentheses

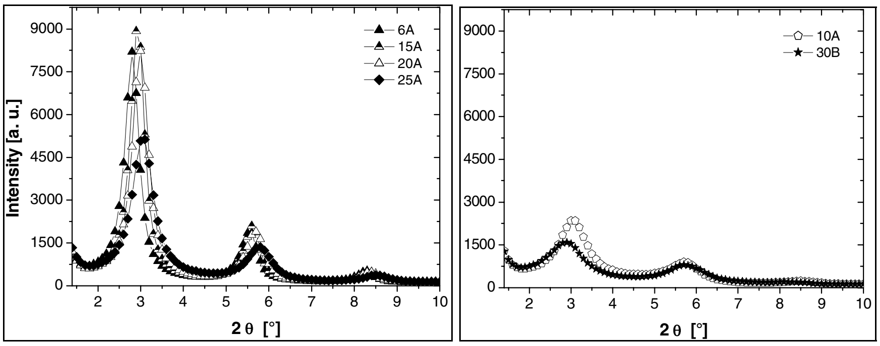

Figure 1a, 1b. WAXS patterns of the matrix and nanocomposites.

According to TEM micrographs, the highest level of homogeneity and delamination was found in the system filled with Cloisite 25A (Figure 2A). The nanocomposites with Cloisite 30B and 10A showed heterogeneous structure, which manifested itself by both exfoliated platelets and their stacks (Figure 2B, C). On the other hand, materials containing Cloisite 6A, 15A and 20A exhibited poor dispersion due to highly hydrophobic nature of these organoclays (Figure 2D, Table 2).

Processing properties of nanocomposites are characterized by rheological measurements. The flow curves (Figure 3) indicate the efficiency of the organoclay filling which manifests itself as a significant increase in melt viscosity in the range of low shear rates. At higher frequencies, the complex viscosity of nanocomposites decreased below the value of the unfilled matrix with the same processing history as the nanocomposites. The wall slip of filled melts between the parallel plates and matrix degradation during the rheological measurements were disproved by the time sweep tests, performed at various frequencies and plotted in Figure 4. The reason for the observed phenomenon could then be a slip between the polymer matrix and filler particles or a decrease in the complex viscosity of PET-R matrix in nanocomposites.

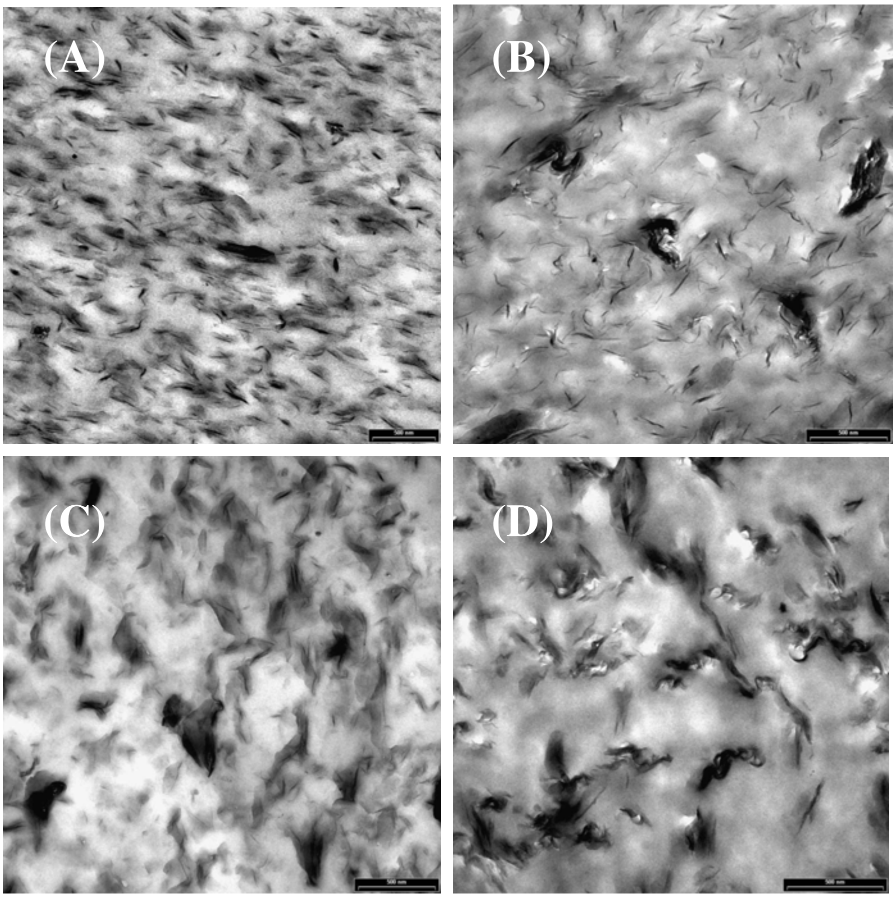

Figure 2. TEM photomicrographs of PET-R/organoclay nanocomposites; (A) Cloisite 25A, (B) Cloisite 30B, (C) Cloisite 10A, (D) Cloisite 6A.

Monitoring the melt compounding process, it was found that the most significant degradation during the processing of recycled PET and organoclay is attributed to chemical reactions between the functional groups of organic modifiers, free water of silicate and the polymer chains. These reactions lead to a decrease in molecular weight, which is indicated by decreasing values of load force (F_L) during mixing in microextruder (Figure 5). For a constant volume of the compounded material and the same processing speed, the F_L magnitude is proportional to the viscosity of the material. The sharpest decrease in F_L with time was observed for the system containing Cloisite 30B, which is attributed to the presence of hydroxyl groups in the nanofiller. The clays treated with organic compounds, which show a higher reactivity to PET (Cloisite 30B, 10A) manifesting itself by a decrease in F_L (Figure 5), support a much higher level of delamination (changes in the intensity and shape of basal reflections) than the other nanocomposites (Figure 1a, b). This phenomenon could be explained by easier penetration of shorter, degraded polymer chains into the gallery of silicate layers.

The melt viscosity decrease of nanocomposites at higher frequencies compared with PET-R matrix is caused by inert low-molecular-weight compounds formed by thermal degradation of alkylammonium tethers as well as by chain scission due to water and hydroxyl groups of silicate and especially due to the hydroxyalkyl groups of Cloisite 30B. Thermal decomposition of quaternary ammonium tethers proceeds by Hofmann elimination. The silicate anion abstracts hydrogen from the β-carbon of an alkyl, yielding an olefin, tertiary amine and acid, a protonated site of silicate. An excess surfactant chloride over the montmorillonite cation exchange capacity which is in Cloisite 6A, 15A and 10A, decomposes also by S_N2 nucleophilic substitution yielding alkyl chloride and tertiary amine [9].

Although organoclays are conventionally considered hydrophobic, water absorption still proceeds on the outer surface of particles, along the hydrophilic layer edges and on polar groups of alkylammonium tethers. The water content in dried, mostly hydrophobic Cloisites 6A, 15A and 20A is up to 0.6–0.7 wt. % [9]. Hydrolytic degradation of PET proceeds under the catalysis with Bronsted and Lewis acid sites of silicate. The nanocomposite with 5 wt. % of Cloisite 30B contains an amount of 2-hydroxyethyl groups comparable with that of PET, whose M_n is ca. 10000. This means that every PET molecule can be split once on average due to transacylation during the melt mixing process. This is the main cause of significant viscosity and storage modulus decrease in the nanocomposite mentioned.

Except the composites containing Cloisite 30B and 10A (due to the degradation mentioned above), a relationship between rheological properties and structure of

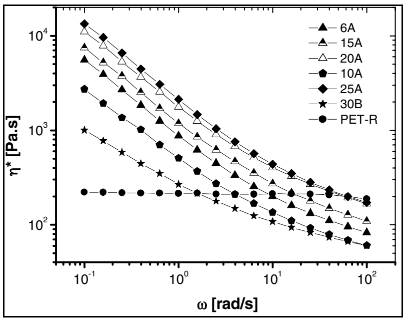

Figure 3. The dynamic flow curves of the matrix and nanocomposites.

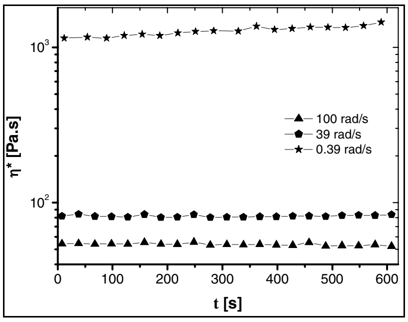

Figure 4. Time sweep test of the nanocomposite with Cloisite 10A.

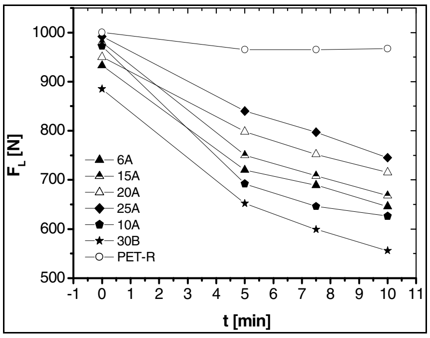

Figure 5. Time dependence of the load force during melt mixing of the matrix and nanocomposites.

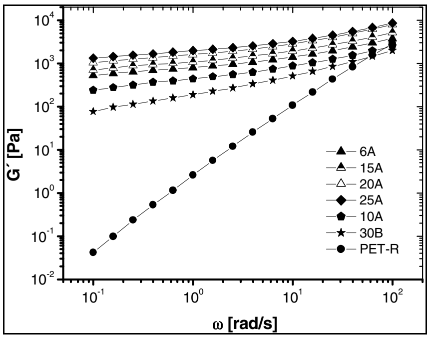

Figure 6. Dependence of storage modulus on frequency for the matrix and nanocomposites.

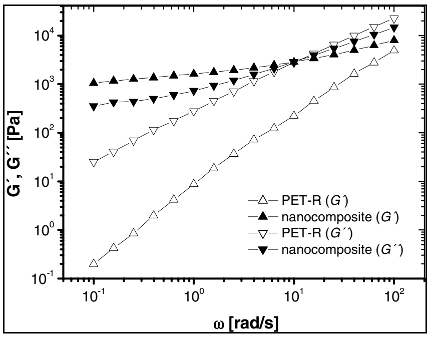

Figure 7. Comparison of viscoelastic properties of the matrix and the nanocomposite with Cloisite 6A.

prepared nanocomposites was revealed. The higher increase in interlayer distance Δd_{001} (level of intercalation of the silicate platelets, Figure 1a, b; Table 2) resulted in an enhancement of the complex viscosity and storage modulus (dispersion of clay particles forms stronger physical network in the polymer matrix, Figure 3, 6).

Compared with the unfilled polymer, all nanocomposites show rubber-like behaviour which is indicated as *G´* secondary plateau in the range of low frequencies. This phenomenon is especially distinct in Figure 7, where the viscoelastic liquid of recycled PET (*G´´*>*G´*) is transformed into rubber-like nanocomposite (*G´*>*G´´*). These properties are attributed to physical network structures in nanocomposites.

Conclusions

Morphological investigations (WAXS and TEM) revealed partial exfoliation in nanocomposites prepared from recycled PET and commercial organoclays Cloisite 25A, 30B and 10A. The dynamic flow properties of the prepared composites related to structural changes associated both with the reinforcing effect (formation of physical network with organoclay loading) and degrading aspect (chain scission of PET and organoclay decomposition tendency). Moderate matrix degradation caused by some organoclays did not affect visual properties (transparency) of composites.

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References

1. Ray SS, Okamoto M (2003) Prog Polym Sci 28:1539
2. Hoffmann B, Dietrich C, Thomann R, Friedrich C, Mülhaupt R (2000) Macromol Rapid Commun 21:57
3. Reichert P, Hoffmann B, Bock T, Thomann R, Mülhaupt R, Friedrich C (2001) Macromol Rapid Commun 22:519
4. Lim YT, Park OO (2001) Rheol Acta 40:220
5. Incarnato L, Scarfato P, Scatteia L, Acierno D (2004) Polymer 45:3487
6. Davis CH, Mathias LJ, Gilman JW, Schiraldi DA, Shields JR, Trulove P, Sutto TE, Delong HC (2002) J Polym Sci, Part B Polym Phys 40:2661
7. Lebaron PC, Wang Z, Pinnavaia TJ (1999) Appl Clay Sci 15:11
8. Khan SA, Prud'homme RK (1987) Rev Chem Eng 4:205
9. Xie W, Gao Z, Pan WP, Hunter D, Singh A, Vaia R (2001) Chem Mater 13:2979