Recycled PET-Organoclay Nanocomposites with Enhanced Processing Properties and Thermal Stability

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ABSTRACT: Preparation of thermally stable recycled PET-organoclay nanocomposites with improved processing and mechanical properties is a challenging task from the environmental as well as industrial and commercial point of view. In this work, both modification of sodium-type montmorillonite with 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride and additional treatment with [3-(glycidyloxy)propyl]trimethoxysilane was performed. Thermal stability of the organoclays and nanocomposites prepared by melt compounding was tested by thermogravimetric analysis, differential scanning calorimetry, and melt rheology. In comparison with the organoclays modified with quaternary ammonium compounds, the prepared clays showed substantial suppression of matrix degradation during melt mixing. The increase in inter-layer distance of silicate platelets and homogeneity of dispersions in the recycled and virgin PET matrices have been evaluated by transmission electron microscopy and wide-angle X-ray scattering. The higher degree of delamination in the nanocomposites filled with imidazole organoclays was in a good agreement with improved rheological characteristics and led to significant enhancement in mechanical properties and thermal stability. A difference in structure (besides the level of delamination and homogeneity of silicate platelets) of recycled versus virgin PET nanocomposites was detected by X-ray diffraction patterns. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2092–2100, 2007

Key words: recycled PET; organoclay; melt compounding

INTRODUCTION

Recycling of poly(ethylene terephthalate) (PET), in particular beverage bottles, is not yet satisfactorily solved. The European average of PET recovery is approximately 30% and in the United States 20% only.[1,2] During the recycling procedure and each processing step of thermoplastic materials, the melt viscosity decreases as a result of chain scission. As a key parameter in processing of recycled materials, their melt strength has to be held at a sufficient level. The low viscosity of recycled PET causes problems in the employment of some technologies (e.g. flat-die extrusion, blow molding) for reprocessing. Hence, only limited applications of this high-tech material (mostly staple fibers, packaging, films, and strips) have appeared on the market.[3] The addition of highly dispersed silicate particles to recycled PET increases melt consistence, leading to more opportu-nities of further processing. Nanocomposites prepared by melt mixing introduce an interesting method of polymer recycling especially with regard to the properties enhancement via intercalation/exfoliation of silicate platelets. To our knowledge, only few papers dealing with recycled PET-organoclay nanocomposites have been published so far. The presented materials exhibited poor processing as well as utility characteristics (deterioration of mechanical properties, melt viscosity decrease, etc.).[4–6]

In our previous work, we studied the nanocomposites of recycled PET with commercial organoclays and we obtained an increase in melt viscosity due to the formation of a physical network between polymer and organoclay.[7] However, a problem occurred with the thermal stability of commercial organic modifiers (quaternary ammonium salts), leading to the matrix degradation during melt mixing. The low thermal stability of commercial organoclays resulted in chemical decomposition by α, β elimination (Fig. 1).[8–12] To reduce degradation processes and to enhance delamination in the system, we modified the selected commercial organoclays by silanization with [3-(glycidyloxy)propyl]trimethoxysilane, hexadecyltrimethoxysilane and (3-aminopropyl)trimethoxysilane.[13] The epoxy functional groups attached to

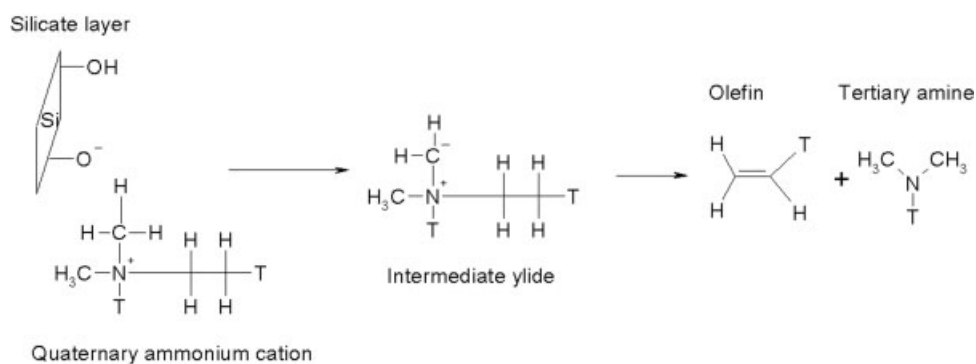**WILEY InterScience®**
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Figure 1 Scheme of α, β elimination. Where T is a hydrogenated tallow (mixture of 65% C18, 30% C16, and 5% C14).

the silicate surface facilitated interactions between the filler and polymer matrix and reduced the adverse effect of the silicate hydroxyl groups. Moreover, the epoxy-silanized organoclay could be directly bound to polymer chains, resulting in higher delamination of silicate platelets (Fig. 2). With the view of complete suppression of degradation reactions during compounding, the sodium montmorillonite was modified with spacers based on an imidazolium salt (Fig. 3). The ''imidazolium organoclay'' was further modified by silanization. The effect of various organoclay surface modifications on the processing and utility properties of recycled and virgin PET was the main object of interest in this work.

EXPERIMENTAL

Materials and methods

All chemical compounds were purchased from Fluka or Aldrich in sufficient purity. The synthesized compounds were characterized by elemental analysis, and melting point, if possible. The MMT-IM and MMT-IME organoclays have been synthesized using the molar excess of modifiers in order to achieve maximal modification efficiency.

Recycled poly(ethylene terephthalate) from color-sorted beverage bottles (PET-R), with the intrinsic viscosity 0.73 dL/g, was supplied by Polymer Institute Brno, Czech Republic. Virgin bottle grade PET Elixir (PET-V) with the intrinsic viscosity 0.8 dL/g was delivered by EKO PET, Czech Republic.
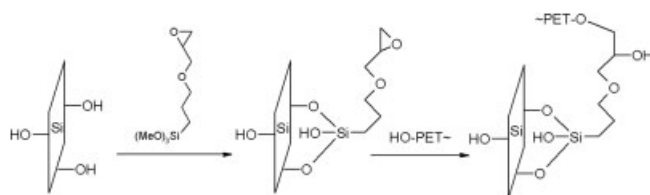
Synthesis of 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride[14]

1,2-Dimethyl-1H-imidazole (18 g, 0.188 mol) was suspended in 1-chloroctadecane (65 g, 0.225 mol) and the mixture was homogenized by stirring at 100°C for 12 h. The reaction mixture was cooled to 50°C and shaken with 200 mL of benzene. Precipitated crystals were filtered off, washed with a small amount of benzene and dried under vacuum [Fig. 4(a)].

The yield was 49.3 g (68%) and the melting point 93–95°C.

Preparation of organoclay with 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium (MMT-IM)

Cloisite Na$^+$ (20.6 g of dry matter) was stirred in 1000 mL of deionized water and the suspension was kept at room temperature for 12 h. The suspension was heated at 80°C under vigorous stirring and the warm (60°C) solution of 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium chloride (7.85 g, 20.38 mmol) in 200 mL water was slowly added. The thick suspension was stirred for 90 min at 80°C, filtered off while hot, and washed with a high amount of boiling water. The filtration cake was suspended in 1000 mL of hot water (80°C) and vigorously stirred for 1 h. The final suspension was filtered off, washed, and the described procedure was repeated. The properly washed organoclay was air-dried and then dried under vacuum at 110°C [Fig. 4(b)]. The yield of the product was 25.6 g.

Elemental analysis (Perkin Elmer CHNSO Analyzer Series II 2400): Found C 20.70%, H 3.83%, N
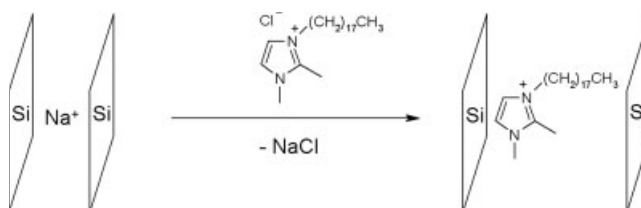

Figure 2 The scheme of epoxy-silanization and subsequent bonding of polymer chain to the silicate layer.

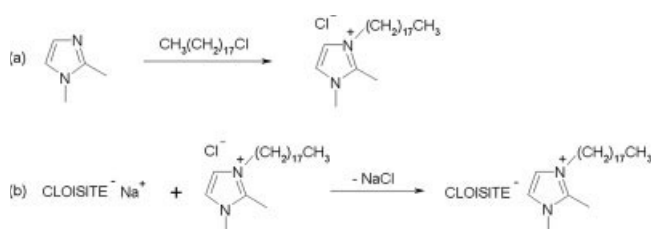**Figure 3** The scheme of ion exchange.

Figure 4 MMT-IM organoclay preparation.

1.60%, ash 68.39%. The 23% fraction of organic phase was calculated from TGA measurement.

Epoxy-silanization of 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ium organoclay (MMT-IME)

The MMT-IM organoclay (1 g) was suspended in 50 mL of a methanol–water mixture (10:1) and [3-(glycidyloxy)propyl]trimethoxysilane (0.3 g) was added. The mixture was stirred at room temperature for 2 days and the precipitate was filtered off and thoroughly washed with methanol. The solid was dried under vacuum at 50°C for 4 h. This procedure has been performed according to scheme in Figure 2.

Preparation of nanocomposites

Organoclay powder was dried at 80°C and PET pellets at 110°C in an oven overnight. Polymer was compounded with 5 wt % of organoclay in a co-rotating twin-screw microextruder (DSM Research, Netherlands) at 255°C under nitrogen. The mixing time was 10 min at a speed of 200 rpm. Immediately after blending cycle, the nanocomposite melt was injected into a form at 260°C using DSM micro-injection equipment.

Structure of nanocomposites

Wide-angle X-ray scattering (WAXS) was measured with a HZG 4/4A diffractometer (Praezisionsmechanik Freiburg, Germany) at room temperature at the scanning rate 1.5°/min. The Ni-filtered Cu Kα radiation generator operated on the accelerating voltage 30 kV and 30 mA current. Morphological analysis was made 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, from Rheometric Scientific, USA) with the 25-mm parallel-plate geometry was

employed for rheological characterization. Dynamic frequency sweep measurements were performed at 270°C under nitrogen at the strain level of 2% (nanocomposites) or 30% (neat matrices), respectively.

Thermal properties

Thermal characterization of the polymer matrices and nanocomposites was carried out by a differential scanning calorimetry (Perkin Elmer, Pyris 1 DSC) using a common mode: (1) holding at 30°C for 3 min; (2) heating from 30 to 280°C at 10°C/min; (3) holding at 280°C for 2 min.

The glass transition temperature (T_g), cold crystallization temperature (T_c), melting temperature (T_m), enthalpy of cold crystallization (ΔH_c), and enthalpy of melting (ΔH_m) were recorded. The relative crystalline content (X_c) in nanocomposites was calculated by taking the value 117.6 J/g as ΔH_m of a hypothetical 100% crystalline poly(ethylene terephthalate).[15]

Thermal stability of organoclays was evaluated using Perkin Elmer TGA 7 instrument equipped with the software Pyris 1. The samples were heated from 40°C up to 750°C at 10°C/min under a nitrogen flow of 20 mL/min.

Mechanical testing

Mechanical properties of the prepared materials were measured on an Instron 5800 R test instrument. The experiments were carried out according to ISO 527 and ISO 1873-2 standards. The crosshead speed was set to 1 mm/min (tensile modulus) or to 50 mm/min (other characteristics).

RESULTS AND DISCUSSION

Dispersibility of organo-clays in recycled PET

The morphological analysis revealed a similar level of dispersion and homogeneity of silicate platelets in PET/MMT-IM and PET/MMT-IME nanocomposites. According to Table I and Figure 5(A,B), a slight increase in intercalation, expressed by the difference in basal spacing Δd_{001}, was achieved in the systems containing the filler treated with [3-(glycidyloxy)pro-

TABLE I
WAXS Analysis of Organoclays in PET Nanocomposites[a]

Nanocomposite	XRD peak position (°)	Basal spacing (Å)	Δd_{001} (Å)
PET-R/IM	3.1 (4.3)	28.5 (20.5)	8
PET-R/IME	3 (4.6)	29.4 (19.3)	10.1
PET-V/IM	3 (4.3)	29.4 (20.5)	8.9
PET-V/IME	3.1 (4.6)	28.5 (19.3)	9.2

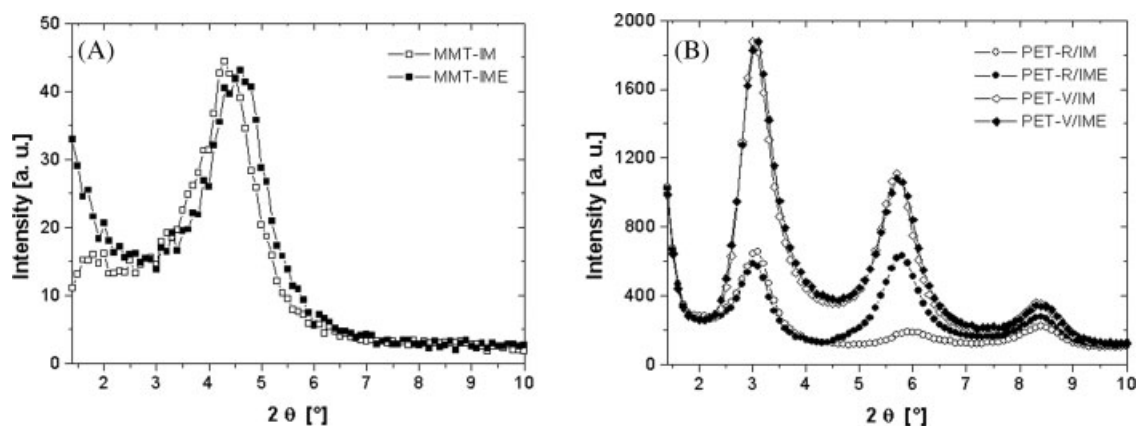[a] Data of neat organoclays are given in parentheses.

Figure 5 WAXS patterns of the neat organoclays (A) and nanocomposites (B).

pyl]trimethoxysilane. However, TEM micrographs (Figs. 6 and 7) showed a moderate delamination decrease in the MMT-IME-filled nanocomposites observable both on 500 and on 1000 nm scale (Figs. 6 and 7: A, C). At the 100 nm scale (Figs. 6 and 7: B, D), individual sheets of silicate and a slightly higher delamination level in the systems containing MMT-IME organoclay can be seen. Concerning the neat organoclays, a higher interlayer distance was achieved in MMT-IM silicate (20.5 Å) than in MMT-IME, whose intercalation reached 19.3 Å. Nevertheless, the MMT-IM organoclay resulted in a higher final interlayer distance only in the virgin PET.
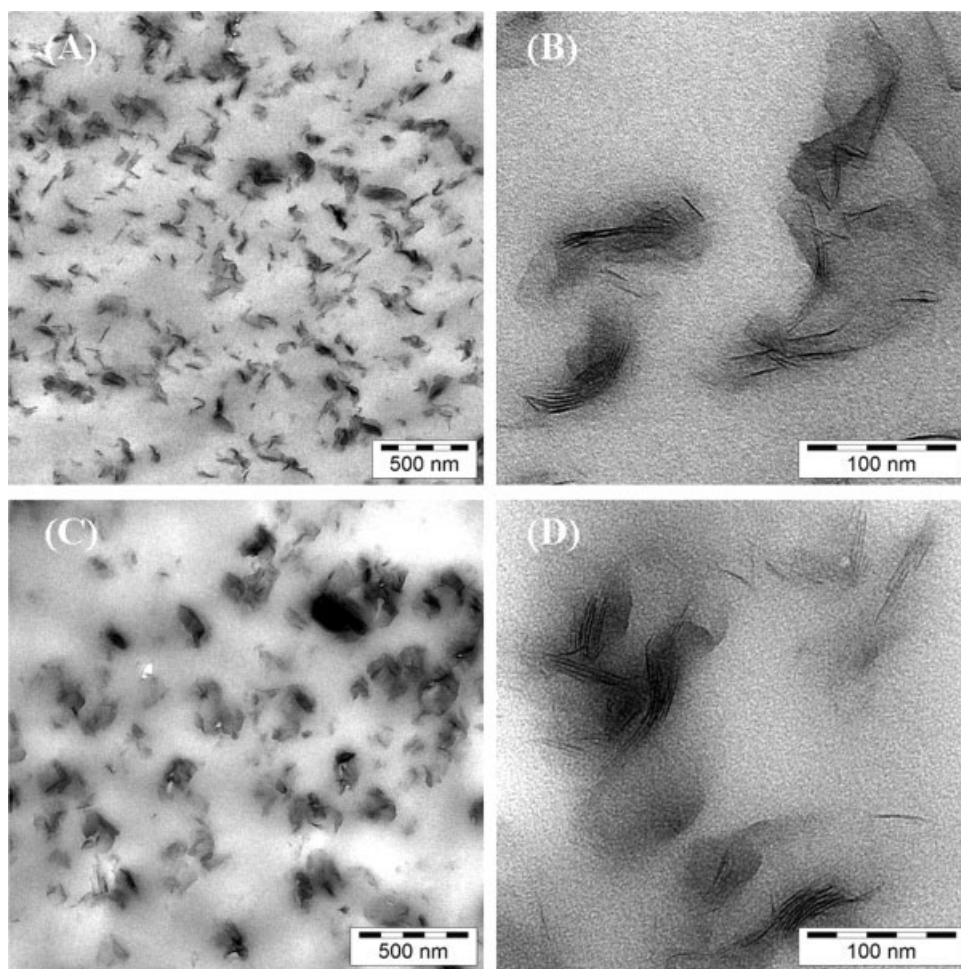

Figure 6 TEM micrographs of PET-R/organoclay nanocomposites: (A, B) MMT-IM; (C, D) MMT-IME.
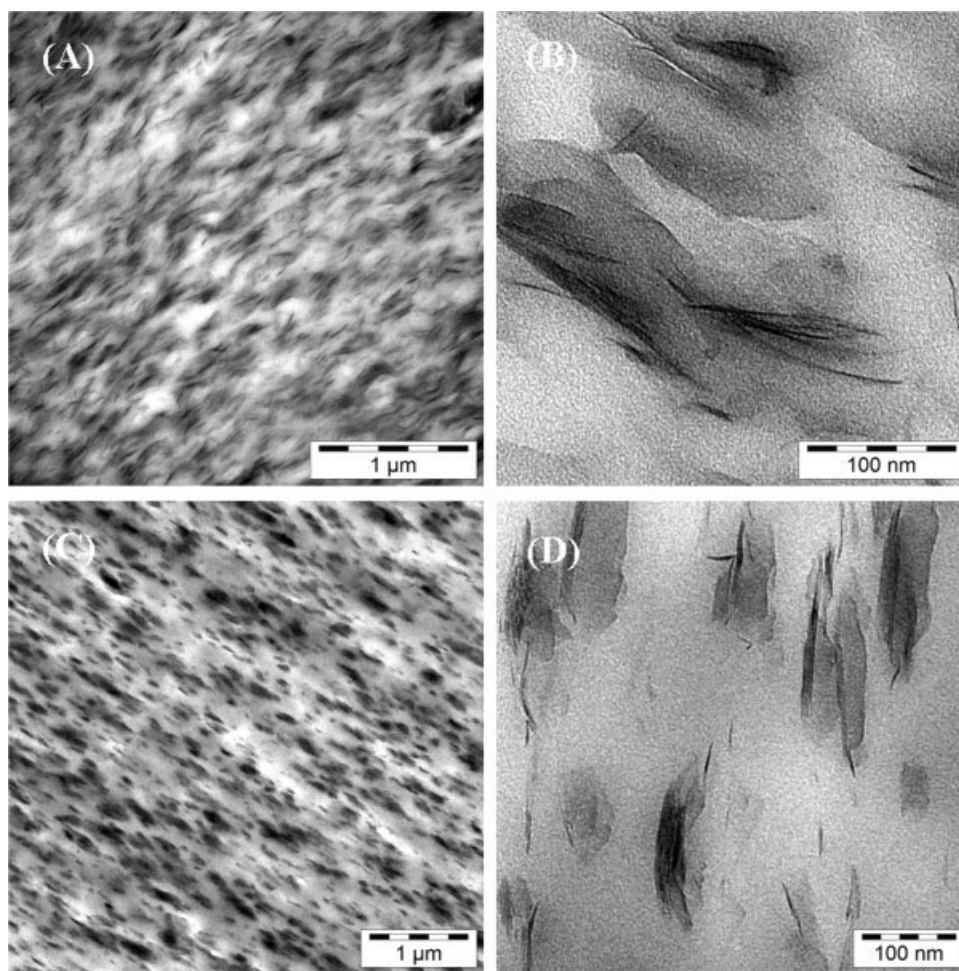
Figure 7 TEM photomicrographs of PET-V/organoclay nanocomposites: (A, B) MMT-IM; (C, D) MMT-IME.

Results of XRD measurements [Fig. 5(B)] indicate an organized structure of silicate platelets in nanocomposites based on the virgin PET matrix (manifested by the regularity of XRD patterns). On the other hand, the same organoclays mixed with recycled PET exhibited a rather disordered structure of clay layers, manifesting itself by specific XRD peaks [Fig. 5(B)]. This observation is in a good agreement with transmission microscopy measurements (Figs. 6 and 7). In our previous work,[13] a rather low level of delamination was observed using commercial fillers silanized with [3-(glycidyloxy)propyl]trimethoxysilane. A similar adverse effect of epoxy-silanization on the overall dispersion of silicate platelets was observed in this study (Figs. 6 and 7; A, C), although the average interlayer distance was slightly increased with MMT-IME loading (Table I, Figs. 6 and 7; B, D).

Melt rheology

Dynamic rheological behavior of the prepared nanocomposites was investigated in the region of linear viscoelasticity. The dynamic strain sweep test ($G'(\gamma)$) revealed the linearity region of $1-100\%$ strain (the matrices) or $1-15\%$ strain (the composites), respectively. The processing properties of the prepared materials are characterized by flow curves (Figs. 8 and 9). In comparison with neat matrices (showing a Newtonian behavior within the frequency dependence $\eta^*(\omega)$ nearly in the whole range of tested shear rates), filling with imidazole organoclays led to an increase of an order of magnitude in complex viscosity at low shear rates. A typical shear thinning effect can be observed as a result of physical network destruction and particle orientation in flow direction.

In the case of systems based on recycled PET matrix, the epoxy-silanization of MMT-IM silicate had a remarkable impact on the melt viscosity increase of resultant nanocomposite (Fig. 8). On the other hand, the virgin PET filled with MMT-IME organoclay showed a lower melt viscosity than the system containing the MMT-IM silicate in the range of low shear rates (Fig. 9).

The G' secondary plateau at low frequencies (Figs. 10 and 11), observable for all nanocomposites,
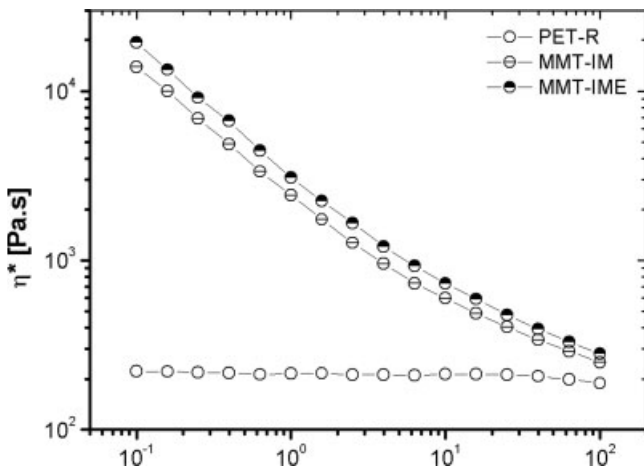
Figure 8 The dynamic flow curves of the PET-R matrix and nanocomposites.
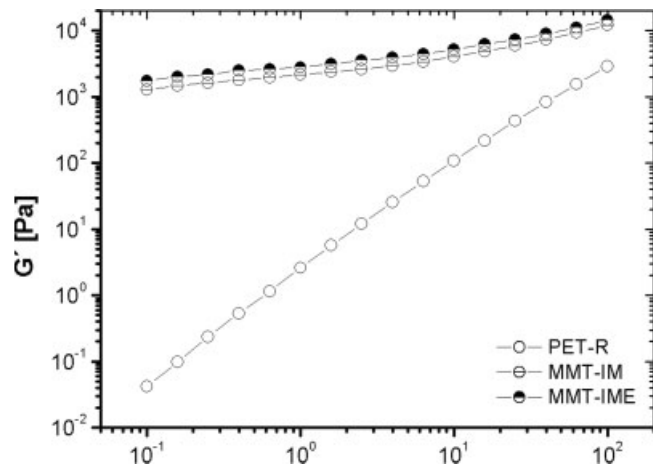

Figure 10 The storage modulus of the PET-R matrix and nanocomposites.

reflects highly delaminated structure of clay platelets in the polymer matrix. According to previous studies,[16–18] the structural changes in nanocomposites in the molten state can be evaluated from frequency dependences of the storage (G') and loss (G'') moduli. Addition of silicate platelets to the polymer melt causes an increase in the dynamic moduli, particularly in G' (Figs. 10 and 11). The unfilled PET behaves as a viscoelastic liquid ($G'' > G'$). The higher value of G' than that of G'' in nanocomposites indicates a different viscoelastic behavior, i.e. a liquid–solid transformation through filling with clay.[7] This pseudo-rubber response in the range of low shear rates (up to 10^0 s^{-1}) reflects a strong rigidity of a 3D structure, where the action of moderate shear forces on delaminated silicate platelets results in entirely elastic response (without viscous factor) of the whole physical network. Furthermore, the power-law dependence of dynamic moduli at low shear rates

(characteristic of neat PET) was not observed in the nanocomposite systems. The G' becomes nearly frequency-independent. In comparison with other physical methods, the evaluation of dynamic moduli gives information about network structure associated with the level of delamination in the molten state. Moreover, the substantial storage modulus increase of the filled systems in comparison with neat matrices proves an enhancement of melt strength that plays an important role in processing of recycled materials.

In our previous work,[7,13] incorporation of commercial or silanized commercial organoclays into recycled PET led to certain degradation during compounding process. This degradation was indicated by a decrease in the complex viscosity and the storage modulus in the region of higher shear rates. Overall rheological characteristics in this work confirmed the nondegrading effect of imidazole organo-
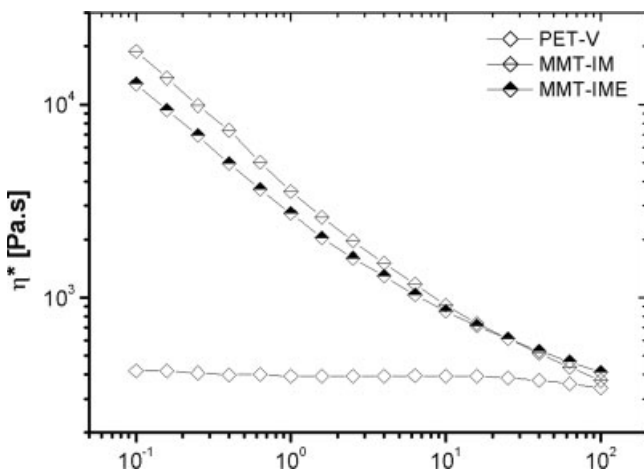

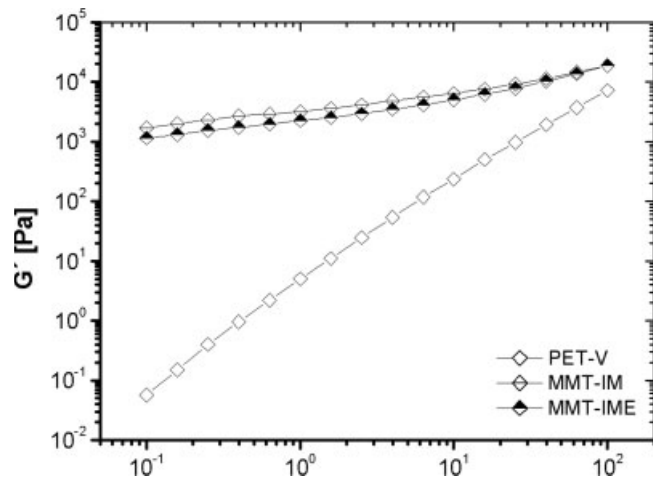**Figure 9** The dynamic flow curves of the PET-V matrix and nanocomposites.

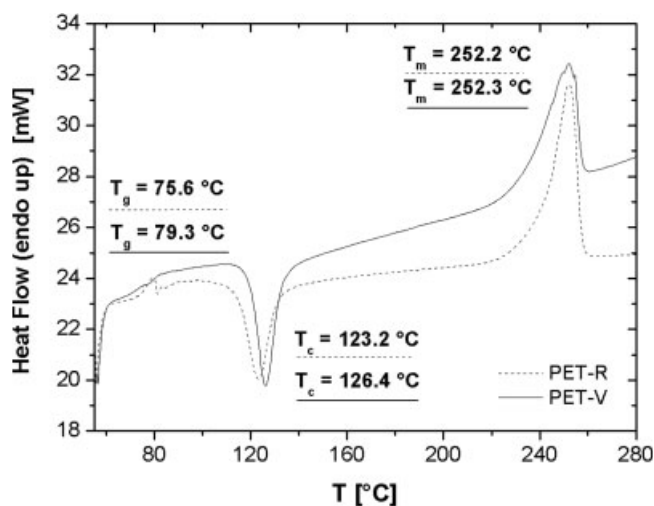**Figure 11** The storage modulus of the PET-V matrix and nanocomposites.

Figure 12 DSC thermograms of the recycled and virgin PET matrix.

Figure 13 Thermogravimetrical decomposition curves of organoclays.

clays on recycled and virgin PET matrix, manifesting itself by higher η^* and G' values compared with unfilled matrices in the whole range of applied shear rates. The obtained frequency dependences of the measured rheological characteristics indicate that the enhanced melt viscosity and elasticity of the recycled PET nanocomposites should persist also at higher shear rates applied in processing technologies (extrusion, injection molding, blow molding).

Thermal characterization

Judging from differential scanning calorimetry experiments, PET-R exhibits usual thermal behavior (similar to PET-V) because no remarkable decrease in T_g and T_m values was observed (Fig. 12).

The DSC spectra of nanocomposites (Table II) based on recycled and virgin PET matrix show no fundamental differences. Nanocomposites prepared from recycled PET revealed a decrease in total crystallinity 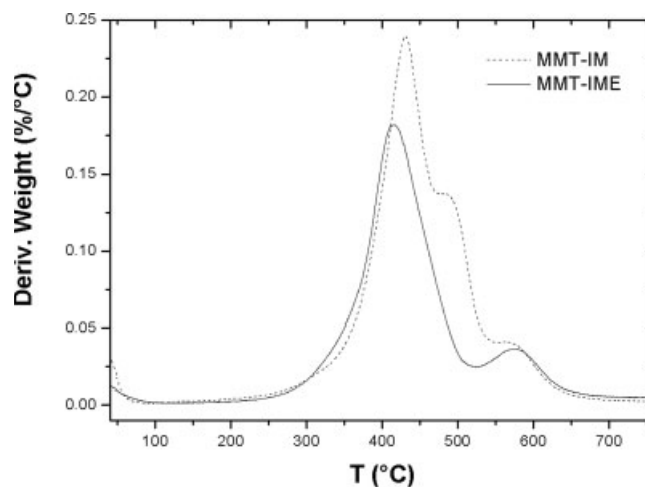and melt temperature, a faster formation of crystalline nuclei, an increase in glass transition and cold crystallization temperature compared with the neat matrix. The systems containing virgin PET showed similar level of total crystallinity, a higher crystallization rate, and a lower glass transition temperature compared with the unfilled matrix. The recycled PET exhibited lower values of T_g and T_c temperatures, a higher crystallization rate, and a higher total crystallinity than virgin PET. The faster formation of crystalline nuclei in recycled PET in relation to virgin polymer could be attributed to the lower value of melt viscosity (Figs. 8 and 9) associated with a faster translation of polymer chains and easier arrangement into lamellar structure. The higher crystallization rate of nanocomposites when compared with neat matrices is explained by the nucleating effect of silicate particles on heterogeneous crystallization of PET chains.

Results of thermogravimetrical measurements (Fig. 13, Table III) revealed the first decomposition peak of MMT-IM at 430°C and MMT-IME at 416°C. Surprisingly, the second decomposition peak at 500°C is

TABLE II
Thermal Properties of the Matrices and Nanocomposites

Nanocomposite/matrix	$T_g{}^a$ (°C)	$T_c{}^b$ (°C)	$T_m{}^c$ (°C)	$\Delta H_c{}^d$ (J/g)	$\Delta H_m{}^e$ (J/g)	$X_c{}^f$ (%)
PET-R/IM	75.8	124.7	250.3	20.7	40.2	34.2
PET-R/IME	75.4	122.9	253.9	17.4	42.9	36.5
ET-V/IM	76.3	124.7	250.9	17.8	37.5	31.9
PET-V/IME	75.6	131.5	252.1	21.9	36.5	31.1
PET-R	72.8	118.1	254.6	25.5	46	39.1
PET-V	79.3	126.4	252.3	27.9	37.1	31.6

[a] Glass transition temperature.
[b] Cold crystallization temperature.
[c] Melting point.
[d] Enthalpy of cold crystallization.
[e] Enthalpy of melting.
[f] Relative crystalline content.

absent in the MMT-IME organoclay. This evidence suggests that more rigid structure of silanized groups leads to a higher clustering tendency of particles and, consequently, to the uniform main decomposition peak. A higher level of clustering of nanocomposites containing MMT-IME silicate than that filled with MMT-IM clay is also obvious in TEM micrographs (Figs. 6 and 7: A, C). The different shape of MMT-IME main decomposition peak will be further investigated. Comparing to commercially available organoclays, the thermal stability of prepared immidazole organoclays has been substantially enhanced (Table III).[13]

Mechanical properties

According to tensile tests (Table IV), a higher stiffness and extensibility of the PET-V matrix than that of recycled PET was revealed. Filling of MMT-IM and MMT-IME organoclays into the recycled as well virgin matrix led to a substantial increase in the Young modulus and to satisfactory values of extensibility, which could be used in the spinning technology (e.g. preparation of fibers with quite a high stiffness). The nanocomposite with the best mechanical properties was prepared by the addition of MMT-IME organosilicate to the virgin PET. On the other hand, the highest stiffness combined with an acceptable level of tensile strength and extensibility was achieved in the PET-V/MMT-IM system. Therefore, various materials for specific purposes could be prepared using different organoclays. The higher tensile strength of nanocomposites containing the MMT-IME filler than those filled with MMT-IM organoclay could result from the presence of polar epoxy functional groups, leading to lower interfacial stress accumulation in a hydrophilic PET matrix. This explanation is in a good accordance with rheological measurements, where the PET-R/MMT-IME system revealed higher melt viscosity and storage modulus than that filled with MMT-IM organoclay. The higher level of melt strength in PET-R/MMT-IME nanocomposite resulted in high interfacial shear strength also in solid state.

TABLE III
Thermogravimetric Decomposition Characteristics of Organoclays

Organoclay	5% mass loss (°C)	10% mass loss (°C)	500°C mass loss (%)
Cloisite 10A	224.6	244.1	34.3
Cloisite 30B	279.1	324.2	17.7
Cloisite 25A	298.5	321.0	30.6
MMT-IME	379.4	412.4	18.8
MMT-IM	381.5	416.6	23.7

TABLE IV
Mechanical Properties of the Matrices and Nanocomposites

Nanocomposite/ matrix	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PET-R/IM	2628	20.6	210.4
PET-R/IME	2743	37.7	192.3
PET-V/IM	2898	30.4	227
PET-V/IME	2460	51.9	253.1
PET-R	2170	54.7	316.5
PET-V	2286	57.1	327.2

CONCLUSIONS

Nanocomposites using both recycled and virgin bottle-grade PET with improved thermal stability and processability were prepared. Rheological investigations revealed a typical shear thinning behavior with organoclay addition and a higher melt viscosity of nanosystems in the whole measured range of shear rates compared with unfilled matrices. These nondegrading organoclays could be used for the preparation of multilayer beverage bottles without admixture of polyamide and, consequently, the recycling of multilayer bottles would be simplified. In comparison with the unfilled matrix, the melt strength of all the nanocomposite systems was significantly enhanced by the formation of 3D physical network made of silicate platelets. Therefore, more processing technologies for the recycled PET can be employed. Differential scanning calorimetry and thermogravimetrical analysis supported the evaluation of thermal behavior from rheological experiments. According to transmission electron microscopy, addition of MMT-IM organoclay to recycled or virgin PET led to a better dispersion of silicate platelets than in the MMT-IME filled systems. However, the average increase in interlayer distance determined by WAXS showed a slightly higher level of intercalation in PET/MMT-IME systems. The results of tensile testing showed that specific materials can be prepared by organoclay variation, which leads to different values of tensile strength, Young modulus, and extensibility.

References

1. The Container Recycling Institute; http://www.container-recycling.org.
2. PETCORE association (PET containers recycling Europe); http//www.petcore.org.
3. PET recycling association; http://www.petrecycling.cz.
4. Pegoretti, A.; Kolarik, J.; Peroni, C.; Migliaresi, C. Polymer 2004, 45, 2751.
5. Sanchez-Solis, A.; Romero-Ibarra, I.; Estrada, M. R.; Calderas, F.; Manero, O. Polym Eng Sci 2004, 44, 1094.
6. Sanchez-Solis, A.; Garcia-Rejon, A.; Manero, O. Macromol Symp 2003, 192, 281.

7. Kráčalík, M.; Mikešová, J.; Puffr, R.; Baldrian, J.; Thomann, R.; Friedrich, C. Polym Bull 2007, 58, 313.
8. Weygand, F.; Daniel, H.; Simon, H. Chemische Berichte 1958, 91, 1691.
9. Bach, R. D.; Andrzejewski, D.; Bair, K. W. J Chem Soc: Chem Commun 1974, 20, 820.
10. Bach, R. D.; Knight, J. W. Tetrahedron Lett 1979, 40, 3815.
11. Wittig, G.; Polster, R. Ann 1957, 612, 102.
12. Wittig, G.; Burger, T. F. Ann 1960, 632, 85.
13. Kráčalík, M.; Studenovský, M.; Mikešová, J.; Sikora, A.; Thomann, R.; Friedrich, C.; Fortelný, I.; Šimoník, J. Recycled PET nanocomposites improved by silanization of organoclays. J Appl Polym Sci, to appear.
14. Webb, P. B.; Sellin, M. F.; Kunene, T. E.; Williamson, S.; Slawin, A. M. Z.; Cole-Hamilton, D. J. J Am Chem Soc 2003, 125, 15577.
15. Metha, A.; Wunderlich, B. J Polym Sci Polym Phys Ed 1978, 16, 289.
16. Krishnamoorti, R.; Giannelis, E. P. Macromolecules 1997, 30, 4097.
17. Krishnamoorti, R.; Vaia, R. A.; Giannelis, E. P. Chem Mater 1996, 8, 1728.
18. Khan, S. A.; Pru'homme, R. K. Rev Chem Eng 1987, 4, 205.