

Toughening of Recycled Poly(ethylene terephthalate) with Clay-Compatible Rubber Phase

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ABSTRACT: Recycled bottle-grade PET (rPET) is a valuable low-cost polymeric material. However, enhancement of its mechanical properties is necessary for many applications. This work is focused on clay-reinforced/compatibilized rPET/elastomer system. Although the clay addition to various rPET/elastomer blends caused a remarkable refinement of structure, more pronounced for clay with less polar modification, both a gain or decrease in strength and toughness occurred, whereas an increase in modulus was found for all systems. This is a consequence of simultaneous complex affecting many parameters by clay

and both antagonistic and synergistic combination of respective effects. Best results were found for low contents of EPR rubber and its preblending with clay. The presented results indicate that a suitable combination of nanosilicates with rubber can lead to rPET materials with fairly enhanced properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3621–3628, 2010

Key words: recycled poly(ethylene terephthalate); nanocomposite; clay compatibilization; polymer blend; toughness

INTRODUCTION

The application range of most polymer materials is limited mainly by their low stiffness and toughness. Enhancement of toughness of most thermoplastics like PET is achieved by addition of finely dispersed low-modulus polymer particles, which enhance their ability to absorb mechanical energy absorbing capacity. Simultaneous loss in strength and stiffness¹ occurs. Stiffness is enhanced mostly by addition of more rigid components like micron-size fibers, particles, platelets, etc., but a simple combination of both methods leads mostly to a not very favorable compromise.^{2–4} More advantageous is the modification of polymers with nanosize inorganic fillers, in particular layered silicates. Because of their extremely large specific surface, enhancement of a wide range of properties including inflammability is achieved, whereas toughness is mostly unchanged or slightly decreased.⁵ Therefore, an increasing amount of papers indicate the effort to improve the balance of mechanical properties of polymeric nanocomposites using rubber phases with varying mixing protocols.^{6–12} Favorable results were obtained for

clay reinforced/compatibilized systems like PA6/rubber¹³ or reactively compatibilized PET/EMAGMA/clay nanocomposite.¹⁴ The combined compatibilizing and reinforcing effect (usually without detrimental effect on toughness) of clay can lead to enhanced strength, stiffness and toughness with upgrading further parameters by clay. Formation of the structure of rubber particles embedded in layers of clay stacks even increases the toughening ability.^{13,15}

In spite of the expected good affinity of PET and other thermoplastic polyesters with organophilized clay, the degree of clay dispersion in melt-mixed nanocomposites is relatively low. As a result, enhancement of stiffness is accompanied by a decrease in strength and toughness.^{16–19} One of the reasons seems to be the instability of ammonium salt-based modifiers at processing temperatures, as confirmed by more successful results using clays with more stable modification.^{20–22}

The affinity of thermoplastic polyester to clay is further increased by application of ionomers,^{23,24} dual functionalization of clay, mostly by condensation of epoxy group bearing alkoxy silanes^{25,26} or by application of a low amount of epoxy resin.²⁷

The ability of clay to influence structure of polymer blends is also of importance. The compatibilizing activity of clay^{13,28} was successfully demonstrated for many polymer pairs but there are only few reports dealing with PET blends, in particular PET matrix systems.^{29–31} At the same time, the rising

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TABLE I
Mechanical Properties of PET Nanocomposite Containing 3% Clay

Composition	a_t (kJ/m ²)	E (MPa)	σ (MPa)	ε_B (%)
PET-M	12	1510	60	135
PET/30B	14	1766	58.5	13
PET/C25A	11.5	1850	62	130
PET/C15A	14	1830	64.5	90

production of recycled bottle-grade PET brings a valuable new low-cost polymeric material. This fact is confirmed also by several studies of nanocomposites with recycled PET matrix.^{32–35}

In this work we focus on upgrading bottle-grade recycled PET (rPET) using nonreactive rubbers in combination with clay for simultaneous compatibilization and reinforcement.

EXPERIMENTAL

Materials

Recycled bottle-grade poly(ethylene terephthalate) (rPET) PET-M chain extended by organosilanes, Plastic Technology and Products, was used as a matrix.

Impact modifiers: Ethene-propene elastomer (EPR) Buna AP 331, Degussa Hüls, Germany.

Ethene-methyl acrylate copolymer (EMA) Lotril 28MA07 (30% MA) (Atofina).

Organophilized clays based on natural montmorillonite: Cloisite 15A (modified with dialkyldimethylammonium chloride 95 meq/100 g) (C15), Cloisite 20A (modified with dialkyldimethylammonium chloride 125 meq/100 g, with alkyls derived from hydrogenated tallow) (C20), Cloisite 30B (modified with

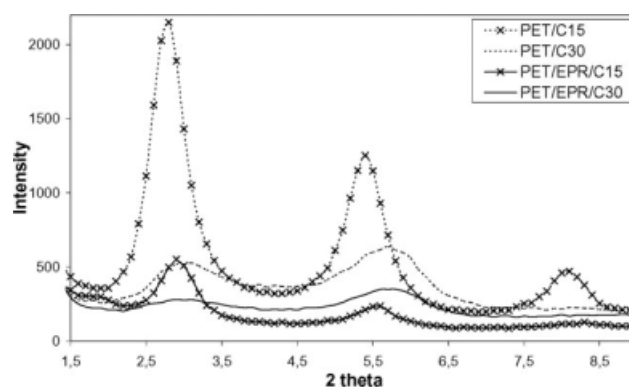


Figure 1 XRD patterns of nanocomposites with rPET matrix.

alkylbis(2-hydroxyethyl)methylammonium chloride 90 meq/100 g) (C30), Cloisite 25A (modified with alkyl2-ethylhexyldimethylammonim methylsulphate 95 meq/100g with alkyl derived from hydrogenated tallow)) (C25) (Southern Clay Products, Inc.)

Nanocomposite preparation

Before mixing, rPET and clay were dried at 90°C and 70°C, respectively, in a vacuum oven for 12 h. The blends were prepared by mixing the components in the W 50 EH chamber of a Brabender Plasti-Corder at 270°C and 60 rpm for 10 min. The material was immediately compression-molded at 260°C to form 1-mm-thick plates. Strips cut from the plates were used for preparation of dog-bone specimens (gage length 40 mm) in a laboratory microinjection molding machine (DSM). The temperature of barrel was 270°C, that of mold 50°C.

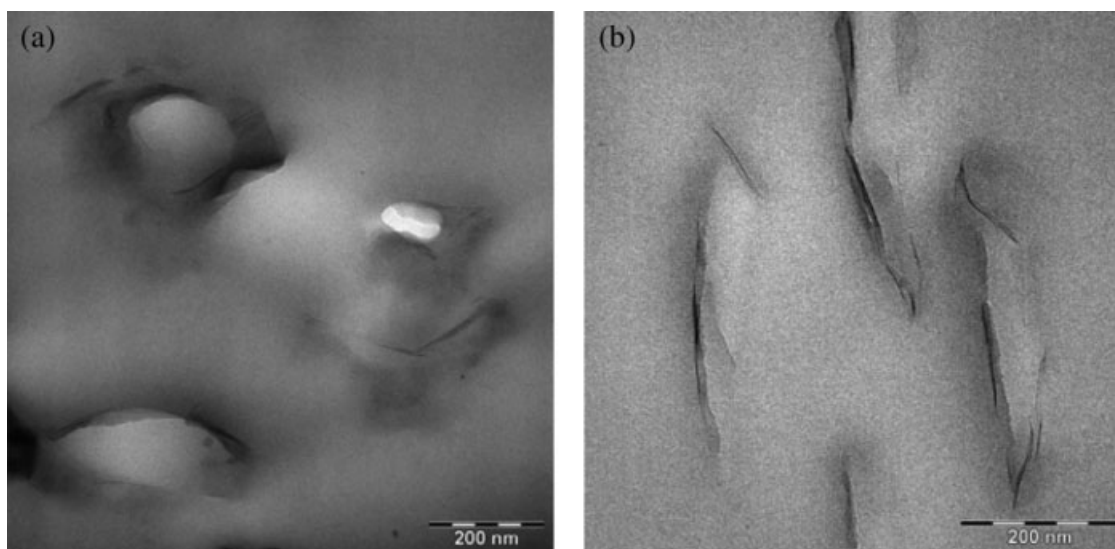


Figure 2 TEM of nanocomposites (a) rPET/EPR/C15 90/10/3 and (b) rPET/(EPR/C15pb)/C15 90/10/3.

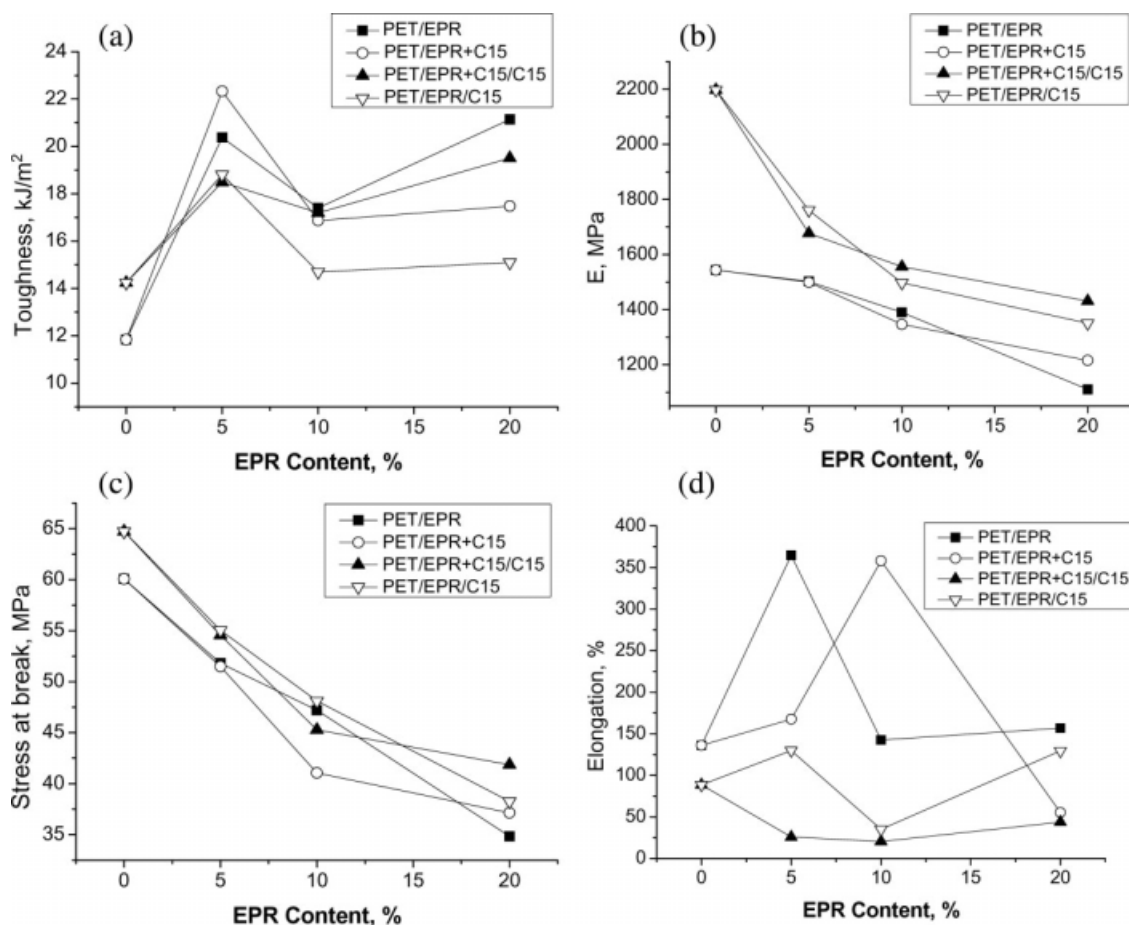


Figure 3 Mechanical properties of nanocomposites in dependence on the EPR content (a) Young's modulus, (b) stress-at-break, (c) elongation, and (d) tensile impact strength.

Testing

Tensile tests were carried out at 22°C using an Instron 5800 apparatus at a crosshead speed of 20 mm/min. At least eight specimens were tested for each sample. The stress-at-break, σ_b , elongation at break, ε_b , and Young's modulus, E , were evaluated. The corresponding variation coefficients do not exceed 2, 15, and 5%, respectively.

Tensile impact strength, a_t , was measured with one-side notched specimens, using a Zwick hammer with an energy of 2 J (variation coefficient 10–15%).

The reported values are averages of 14 individual measurements.

Morphological observations

Phase structure was observed on cryo-fractured samples using scanning electron microscopy (SEM). The elastomer phases were etched with *n*-heptane for 1 h or with boiling toluene for 2 min. The size of dispersed particles was evaluated from their micrographs using a MINI MOP image analyzer (Kontron

TABLE II
Mechanical Properties of rPET/EPR 95/5 Nanocomposites

Composition	a_t (kJ/m ²)	E (MPa)	σ (MPa)	ε_B (%)	P.S. ^a (nm)
PET/EPR 95/5	20	1490	51.8	365	2035
PET/EPR/C15 95/5/3	19	1735	55	130	300
PET/EPR+C15 95/5	22.5	1520	51.5	170	725
PET/EPR+C15/ ^b C15 95/5/3	19	1750	54.5	25	–
PET/EPR+C15/ ^b C30 95/5/3	18	1690	50.5	30	–

^a Particle size

^b Preblend EPR/C15 90/10

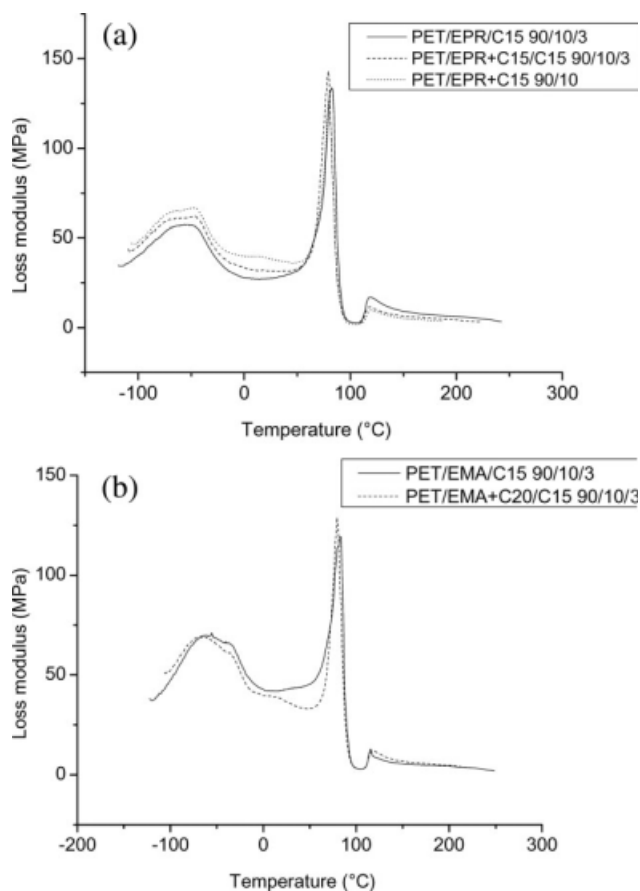


Figure 4 Dynamic mechanical analysis: Temperature dependence of loss modulus of nanocomposite containing (a) 10% EPR (b) 10% EMA.

Co., Germany). For transmission electron microscope (TEM) observations, ultrathin (60 nm) sections were cut, under liquid nitrogen, from a stained (RuO_4 vapor for 90 min) sample using an Ultracut UCT (Leica) ultramicrotome.

Wide-angle X-ray diffraction (XRD) patterns were obtained with a powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Germany) and monochromatic $\text{CuK}\alpha$ radiation

RESULTS AND DISCUSSION

Effect of clay on properties of rPET

The results in Table I indicate fair properties of nanocomposites with rPET matrix as a consequence of an enhanced molecular weight and silane-modification due to chain extension by silanes³⁶ leading to higher clay affinity. Especially in case of the C30, high degree of exfoliation was observed [Fig. 1]. Though the best strength and toughness were found for C15 in spite of the most significant portion of clay platelets retaining parallel registry within the used clays [Fig. 1], this may be explained by TEM [Fig. 2(a)] observation showing that the periodicity originates from high content of fine tiny stacks of clay with high aspect ratio. Moreover, less exfoliated clay leads to higher toughness.³⁷

Effect of rubber content

It is clear from Figure 3 that, except for a decrease in modulus, strength and elongation [Figs. 3(a–c) respectively], increasing the EPR content practically does not lead to an increase in toughness [Fig. 3(d)], most probably due to a very rough structure. For example, at the 20% EPR content, an average particle size of about 3 μm with significant polydispersity (particles up to 10 μm) was found. The fact that an analogous clay-containing system has even lower toughness, in spite of the structure refinement by clay to an average particle size about 2 μm , with largest particles approaching 5 μm (not shown), indicates that also this structure is still too rough and the interparticle distance (ca. 0.8 μm) apparently exceeds its critical value. This is supported by the fact that clay increases toughness of rPET matrix (Table I). Additionally, the more favorable interparticle distance in a clay-compatible system is most probably eliminated by a clay-induced change in matrix parameters (blocking effect), leading to a decrease in critical interparticle distance.¹² The relatively higher toughness of the system with EPR/C15

TABLE III
Mechanical Properties of rPET/EPR 90/10 Matrix Nanocomposites

Composition	ΔT (kJ/m ²)	E (MPa)	σ (MPa)	ϵ_B (%)	P.S. ^a (nm)
PET/EPR 90/10	17.5	1390	47	142	2800
PET/EPR/C25A 90/10/3	17.5	1575	48	70	–
PET/EPR/C30 90/10/3	21	1460	46	12	1230
PET/EPR/C15 90/10/3	2220	1510	48	35	600
PET/EPR+C15 90/10	17	1410	45	360	–
PET/EPR+C15/ ^b C15 90/10/3	17	1630	45.5	20	–
PET/EPR+C15/ ^b C30 90/10/3	22	1610	49.5	28	460

^a Particle size

^b Preblend EPR/C15 90/10

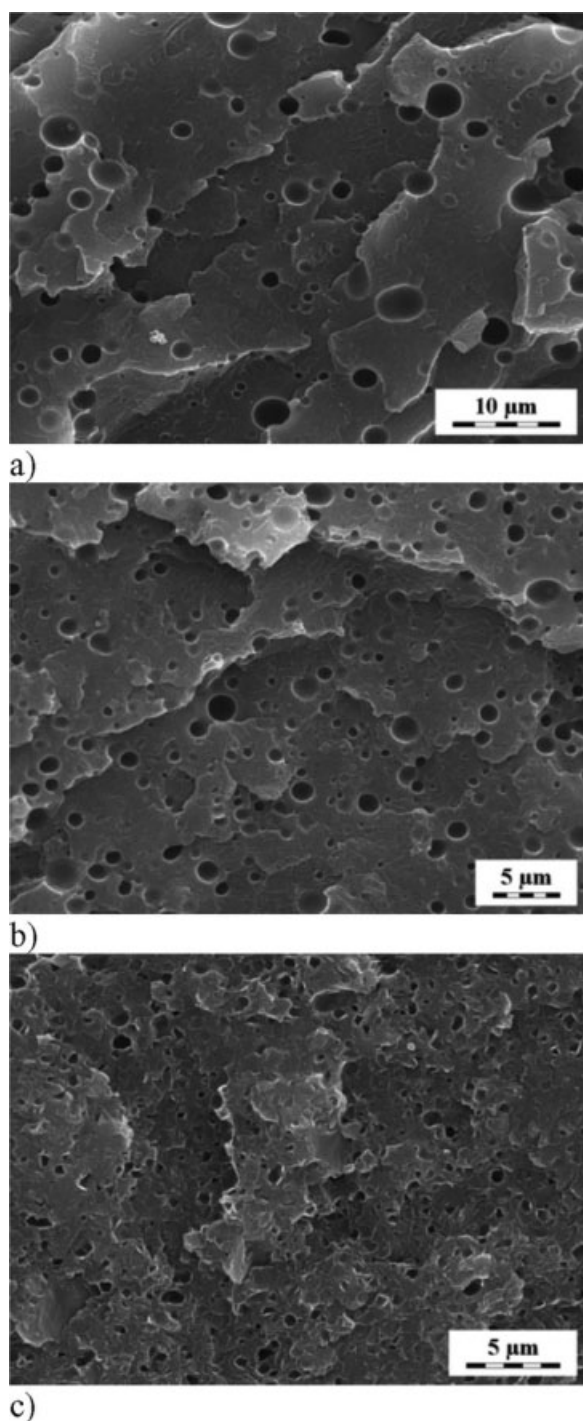


Figure 5 SEM images indicating the effect of C 15 clay on EPR particle size in (a) PET/EPR 90/10 (b) PET/EPR/C15 90/10/1.5, and (c) PET/EPR/C15 90/10/10.

preblend confirms the higher toughening effect of this preblend similar to analogous PA6 matrix nanocomposite.¹³ From Figure 3 it follows that addition of clay increases the modulus of all the systems whereas a relative gain in strength was most significant at the 20% EPR content and its decrease was found in the 90/10 system. Also, this last result indi-

cates a complex effect of clay on the system behavior (see below).

Because of sufficient toughening effect of low amounts of rubber, we focussed on the systems with 5 and 10% rubber contents.

Effect of clay type and mixing protocol

From the results in Table II it follows that the use of 5% of EPR/C15 preblend and in particular its combination with simultaneously added C 30 or C15 leads to fair balance of properties, i.e., simultaneous enhancement of stiffness, strength, and toughness. This confirms the effectivity of preblending clay/EPR found for the PA6 matrix systems¹³ as a consequence of advantageous core shell structure (the layer of clay stacks around an elastomer particle) indicated by TEM [Fig. 2(b)], most significant in the case of clay-rubber preblend. The relatively lower toughening effectivity of clay-embedded rubber particles in comparison with analogous PA6 systems seems to be due to significantly less regular layer of clay stacks around rubber particles, which are less circular [Fig. 2]. The corresponding change in interface parameters due to clay stacks around rubber particles is also confirmed by the different course (formation of a new peak at $\sim 20^\circ\text{C}$) of temperature dependence of loss modulus in DMA measurement [Figs. 4(a,b)].

The slight decrease in toughness on clay addition, not corresponding to the practically unchanged or enhanced toughness of rPET by clay [Table I, Fig. 6(a)], can be explained by blocking of the overlap of stress volume around rubber particles by clay reinforcement of the matrix.¹²

With the 90/10 rPET/EPR matrix composition (Table III), the toughness does not exceed that of the 95/5 composition, most probably due to a rougher

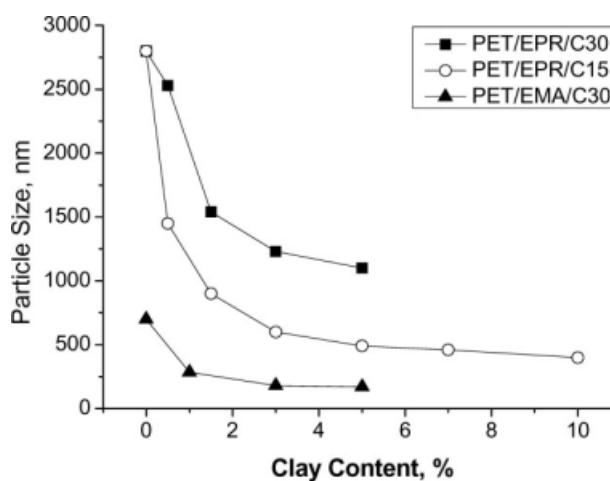


Figure 6 Effect of clay content and type on elastomer particle size.

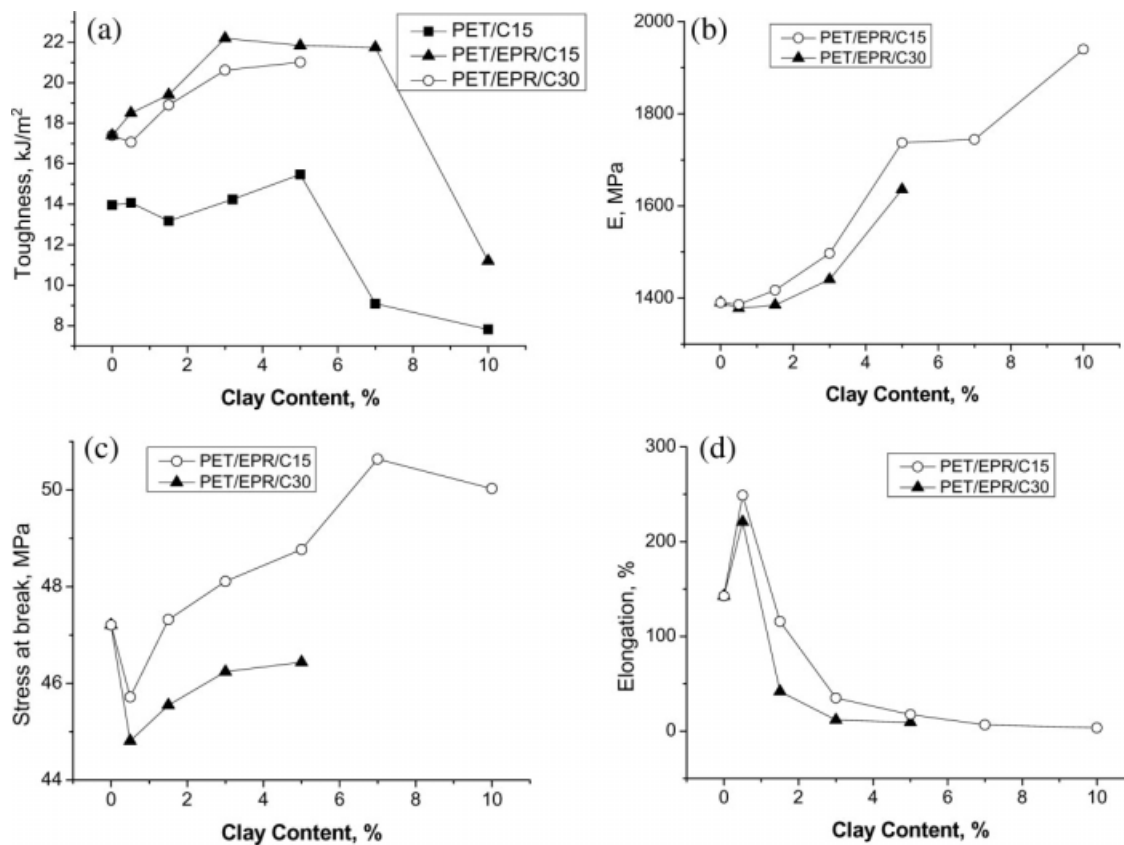


Figure 7 Effect of clay content on mechanical behavior of nanocomposite (a) tensile impact strength, (b) Young's modulus, and (c) stress-at-break, and (d) elongation.

particle size (Tables II and III). The difference from a sample containing 5% rubber consists in relatively low toughness for single EPR/C15 preblend and its enhancement with addition of C30. Further disadvantage of the 90/10 composition is that comparable values of modulus are found at a higher (5%) clay content [Fig. 5], but with lower strength in comparison with the 95/5 matrix.

TEM observation [Fig. 2(b)] indicates the presence of core-shell structure in the 90/10 system as well.

Though we have observed changes in crystallinity (in the range ~ 15 – 25%) in all the nanocomposites studied, practically no systematic correspondence with either modulus or toughness was found.

The differences in crystallinity and related changes in the rPET matrix affect the mechanical behavior most probably in combination (both synergistic and antagonistic) with other numerous "minor" effects of clay on the components (e.g., Poisson ratio and rigidity) and interface parameters and morphology.

Effect of clay content on structure and behavior of PET/EPR 90/10 system

SEM images in Figure 5. indicate significant refinement of dispersed particles by clay in rPET/EPR 90/10 system. From Figure 6 showing emulsification curves follows that C15 with less polar modification

TABLE IV
Mechanical Properties of Nanocomposite with rPET/EMA 95/5 Matrix

Composition	α (kJ/m ²)	E (MPa)	σ (MPa)	ϵ_B (%)	P.S. ^a (nm)
PET/EMA 95/5	13.5	1460	53.3	490	700
PET/EMA/C30 95/5/3	10.5	1615	53.7	76	170
PET/EMA/C15 95/5/3	14	1635	54.7	145	–
PET/EMA/C25 95/5/3	12.5	1668	54	95	–
PET/EMA+C20 ^b 95/5	12	1501	54.5	430	390
PET/EMA+C20/ ^b C15 95/5/3	8.5	1720	54.3	105	–
PET/EMA+C20/ ^b C30 95/5/3	8.5	1680	54	30	–

^a Particle size

^b Preblend EMA/C20 90/10

TABLE V
Mechanical Properties of Nanocomposites with rPET/EMA 90/10 Matrix

Composition	at (kJ/m ²)	E (MPa)	σ (MPa)	ϵ B (%)	P.S. ^a (nm)
PET/EMA 90/10	20	1375	51.5	215	400
PET/EMA/C30 90/10/3	20	1480	50	80	355
PET/EMA/C15 90/10/3	14	1590	52	120	300
PET/EMA+C20 ^b 90/10	18.5	1415	49	175	395
PET/EMA+C20/ ^b C15 90/10/3	20	1640	51.5	75	285
PET/EMA+C20/ ^b C30 90/10/3	11	1600	52.5	32	320

^a Particle size

^b Preblend EMA/C20 90/10

has a significantly better compatibilizing effect on the EPR phase in comparison with C30. The lower degree of exfoliation for C15 in comparison with C30 (Fig. 1) indicate that the clay with a lower affinity to matrix (and enhanced interaction with dispersed phase) has a higher "interfacial activity," as a result of more significant localization of clay at the interface and most probably also common intercalation of both components into clay tactoids.³⁸⁻⁴⁰ This result is similar to that found for the analogous PA6/EPR system.¹³ From Figure 1 further follows a lower intensity of peaks in the presence of EPR (and also EMA: not shown) in comparison with nanocomposite of neat rPET, i.e., addition of elastomers promotes clay exfoliation. Figure 7(a-d) also shows that addition of 3-7% of C15 leads to a system with well-balanced mechanical behavior. The increase in toughness, exceeding the effect of clay on single matrix, corresponds predominantly with structure refinement, whereas the subsequent decrease with higher clay content, more significant that a decrease in matrix toughness with the same amount of clay [Fig. 7(a)], corresponds with the blocking effect of dispersed clay¹² and a negligible further decrease in particle size (Fig. 6). Unexpected is a significant gain in elongation [Fig. 7(d)], not found in known nanocomposites including rPET/clay. Also, in this case, practically no correspondence with the observed changes in crystallinity found by XRD and DSC (not shown) documents that the effect is most probably caused by the complex effect of clay on the two-phase matrix nanocomposite.

Nanocomposites with rPET/EMA matrix

The results in Table IV show lower toughness of all rPET/EMA 95/5 systems in comparison with analogous EPR nanocomposite and its further decrease with increasing clay content. This is due to a lower toughening efficiency (and a lower critical interparticle distance) of EMA. SEM observations indicate that refinement of dispersed EMA particles by clay [Fig. 6] is less pronounced because of higher compatibility of components. The results in Table V

show that addition of clay to the 90/10 matrix can lead to a system with enhanced mechanical behavior, namely with 3% C30 addition, whereas combination of preblend EMA/C20 with C30 causes a very unexpected decrease in toughness. Quite an opposite situation is found with C15; lower toughness with 3% C15 addition was accompanied by its increase for a combination of preblend EMA/C20 with C15. This further confirms the expected complex influencing of the system by above mentioned synergistic or antagonistic cooperation of many "insignificant" effects (with respect to bulk phase behavior) induced by clay.

CONCLUSIONS

Combination of clay and rubber in rPET can lead to its better balanced mechanical behavior. The clay addition to various rPET/elastomer blends caused a remarkable refinement of structure, more pronounced for clay with less polar modification. At the same time, both a gain or decrease in strength and toughness occurred, whereas an increase in modulus was found for all systems. These rather contradictory results caused by changes in clay organophilization, concentrations and/or mixing protocol indicate a complex effects of clay on the system because of mutual influence of numerous clay induced changes in polymer components, interface, and morphology.

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