



## Review

## Recent progress on preparation and properties of nanocomposites from recycled polymers: A review

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## ABSTRACT

Currently, the growing consumption of polymer products creates the large quantities of waste materials resulting in public concern in the environment and people life. Nanotechnology is assumed the important technology in the current century. Recently, many researchers have tried to develop this new science for polymer recycling. In this article, the application of different nanofillers in the recycled polymers such as PET, PP, HDPE, PVC, etc. and the attributed composites and blends is studied. The morphological, mechanical, rheological and thermal properties of prepared nanocomposites as well as the future challenges are extensively discussed. The present article determines the current status of nanotechnology in the polymer recycling which guide the future studies in this attractive field.

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## 1. Introduction

## 1.1. Polymer recycling

Polymers are the most widely used materials in various fields due to their valuable properties such as good mechanical properties, low density, rather low cost, and also ease of processing (Ansari and Alikhani, 2009; Rahimi and Shokrolahi, 2001). The total production of plastics is more than 230 million tonnes per year which will reach to 400 million tonnes in 2020 based on a more conservatively annual growth rate of about 5% (Braun, 2004; Simoneit et al., 2005).

Every year, large quantities of waste polymers are produced from industrial, agricultural and household activities. It has been reported that plastics make up more than 12% of municipal solid waste stream, a dramatic growth from 1960, when plastics were only 1% of the waste stream (<http://www.epa.gov/osw/conservation/materials/plastics.htm>). The new environmental, economic, and petroleum considerations have induced the scientific communities to increasingly deal with polymer recycling (Fall et al., 2010; Salmiaton and Garforth, 2007, 2011; Taurino et al., 2010).

The efficient treatment of waste polymers is still a difficult challenge. The traditional methods such as combustion or burying underground show a negative effect on the environment like formation of dust, fumes and toxic gases in the air, and the pollution of underground water and other resources. The recycling process is the best way to manage the waste polymers. There are various techniques for recycling of waste polymers including primary

recycling, mechanical recycling, chemical or feedstock recycling and energy recovery (García et al., 2009; Sadat-Shojai and Bakshandeh, 2010; Zhang et al., 2009b). The recycling rate for different types of plastic significantly varies, leading to an overall recycling rate of only 8% or 2.4 million tons in 2010 (<http://www.epa.gov/osw/conservation/materials/plastics.htm>).

However, there are some main problems for polymer recycling such as separation (Burat et al., 2009). For example, PVC bottles are difficultly identified from PET ones, but one stray PVC bottle in a melt of 10,000 PET bottles can ruin the whole batch. For ease of separation, most manufacturers determine the type of plastics by the numerical coding system created by Society of Plastics Industry in 1980s (<http://www.epa.gov/osw/conservation/materials/plastics.htm>). The identification codes can be found at the bottom of most plastic packaging. Table 1 shows the identification codes and some household applications of commonly used polymers. However, plastic tarps, pipes, toys, household coverage, and a multitude of other products do not fit into the numbering system. So, there are not usually collected as well as the thousands of different polymers. Moreover, after several processing cycles, the structure of polymer is degraded introducing the poorer mechanical properties than those of a virgin one (Goto et al., 2006; Oromiehie and Mamizadeh, 2004). To overcome these limitations, it seems that the easiest way to recycle the waste plastics is development of blends and composites.

## 1.2. Why nanotechnology?

Nanotechnology is assumed as one of the key technologies in the recent century (Shabani et al., 2012, 2011a, 2011b, 2009). We can obtain the substantial enhancements of mechanical, thermal,

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**Table 1**

The identification code and some household applications of most consumed polymers.

Polymer	Identification code	Applications
PET	1	Fizzy drink bottles, Waterproof packaging
HDPE	2	Milk, oil and detergent Bottles, toys and plastic bags
PVC	3	Food trays, cling film, liners, blister packages
LDPE	4	Carrier bags and bin Liners, shrink wrap, garment bags
PP	5	Margarine tubs, Refrigerated containers, bags, bottle tops, carpets, some food wrap
PS	6	Yoghurt pots, foam Plastic cutlery, protective packaging for electronic goods and toys, throw-away utensils

optical and barrier properties using the nanofillers (Frounchi et al., 2006; Shahabadi and Garmabi, 2012; Zare and Garmabi, 2012a; Zare et al., 2011). The nano-additives increase the interphase surface of components and superficial area/volume ratio leading to improvement of overall performances. In comparison to traditional micro-fillers, very low loading of nanoclay is sufficient to achieve the excellent development of properties without substantially increasing the density and cost or reducing the light transmission properties of base polymer (Jafari et al., 2012; Ramezani-Dakhel and Garmabi, 2010; Zare and Garmabi, 2012b).

Further, the reduced melt strength of recycled polymers in extrusion process causes the inconsistency of material after leaving the die which makes the production of sheets or profiles impossible (Hamzehlou and Katbab, 2007; Kráčalík et al., 2007b). Also, reprocessing of waste PET with very small intrinsic viscosity is not feasible (Kráčalík et al., 2007c). Nanofillers can increase the melt strength and viscosity of recycled polymers in addition to improvement of various properties. The recent studies on polymer recycling by nanofillers are presented in Table 2.

In this review paper, a comprehensive study on the application of nanofillers in the recycling process of polymers, composites and blends is carried out. Moreover, the future challenges in this area are discussed which can help the researchers in the potential works.

## 2. Results and discussion

### 2.1. Recycled polyethylene terephthalate (rPET)

#### 2.1.1. Nanoclay content

Hamzehlou et al. have found the optimal nanoclay (DK2) content of 3 wt.% for tensile strength of both recycled and virgin PET nanocomposites (Hamzehlou and Katbab, 2007). However, it was clearly observed that all samples prepared from rPET showed the higher tensile properties, compared to virgin PET (vPET). Also, the onset of thermal degradation has been delayed for rPET nanocomposites composed of 3 and 5 wt.% of nanoclay. It exhibited the enhanced melt elastic modulus and pseudo solid-like behavior of nanocomposite at low shear frequencies compared to unfilled PET indicating the formation of nanoscopic network structure by the clay platelets. At low shear frequencies, the samples containing 3 and 5 wt.% of nanoclay demonstrated the higher storage modulus while more Newtonian behavior was shown in the samples with nanoclay concentration of lower than 5 wt.%. The oxygen permeation of virgin and recycled PET nanocomposites is observed in Fig. 1. The permeation of neat rPET was larger than neat vPET, due to the smaller chain size of rPET; but, the addition of nanoclay

**Table 2**

Recent studies on the polymer recycling via nanotechnology.

Polymer	Nanofiller	References
PET	Nanoclay	Basilia et al. (2011), Bizarria et al. (2007), Giraldi et al. (2008), Hamzehlou and Katbab (2007), Karabulut (2003), Kráčalík et al. (2007a), Kráčalík et al. (2007b, 2007c) and Pegoretti et al. (2004)
PET/rubber	Nanoclay	Kelnar et al. (2010)
PET/PMMA	Nanoclay	Kerboua et al. (2010)
PET/ABS	SiO <sub>2</sub>	Shi et al. (2011)
PP	Nanoclay	Cengiz (2008), Tri Phuong et al. (2008)
PP	CaCO <sub>3</sub>	Elloumi et al. (2010)
PP	CNTs	Gao et al. (2011)
PP/HIPS	Nanoclay	Mural et al. (2011)
HDPE	Nanoclay	Hill (2005) and Lei et al. (2007)
HDPE	Graphene	Jannapu Reddy (2010)
HDPE/baggase	Nanoclay	Hemmasi et al. (2011)
PVC	Nanoclay	Yoo et al. (2004)
PVC/PP	CaCO <sub>3</sub>	Andričić et al. (2008)
PS	Nanoclay	Liu et al. (2007)
PMMA	Nanoclay	Martin et al. (2008)
PBT/glass fiber	SiO <sub>2</sub> , MMT, mica	Zhang et al. (2009a)

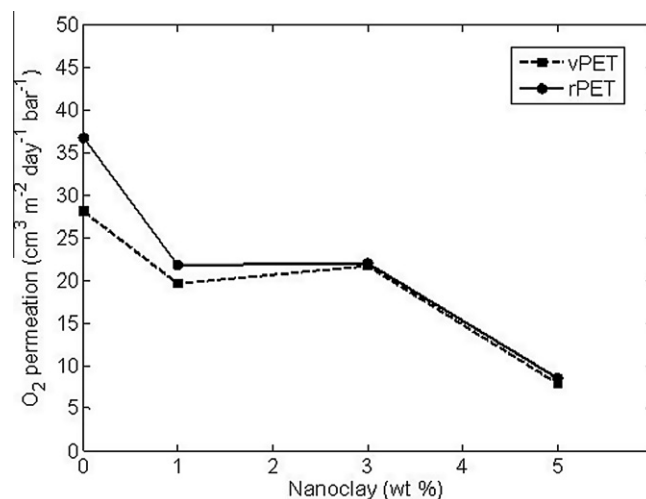


Fig. 1. The oxygen permeation of virgin and recycled PET nanocomposites at different nanoclay content (Hamzehlou and Katbab, 2007).

decreased the permeation in both rPET and vPET nanocomposites and the permeation became similar for both nanocomposites at higher contents of nanoclay (>3 wt.%).

Basilia et al. (2011) also reported that the 5 wt.% of synthesized Philippine MMT (Na-MMT) offered the best improvement of tensile properties. Furthermore, Giraldi et al. (2008) have found that the optimized values of strength and toughness were obtained at 2.5 wt.% of nanoclay instead of 5 wt.%.

Pegoretti et al. (2004) and Bizarria et al. (2007) prepared the rPET/organoclay nanocomposites at several nanoclay content (1, 3 and 5 wt.%). Both works suggested the highest stiffness and tensile strength at 5 wt.% of nanoclay. In Bizarria study, T<sub>g</sub> slightly decreased by the clay content, may be due to clay agglomeration which occurred above a critical clay loading (Chang et al., 2005; Haddad and Lichtenhan, 1996; Xu et al., 2002).

Karabulut compounded the rPET with commercial nanoclay (Cloisite 30B) in the contents of 1, 2, and 5 wt.% (Karabulut, 2003). The mechanical properties such as tensile, flexural and impact results showed the highest improvement in the clay content of 2 wt.%.

As a result, the highest level of stiffness and strength were obtained at the larger contents of nanoclay while the optimized level of strength and toughness was achieved in the lower nanoclay loading (about 2 wt.%) due to the lower mobility of chains introduced by mechanical involvement of chains with nanoclay which decrease the toughness.

### 2.1.2. Nanoclay type

Kráčalík et al. (2007a) incorporated the 5 wt.% of different Cloisite organoclays in rPET. The increased basal spacing after the diffusion of polymer chains into the gallery of silicate layers ( $\Delta d_{001}$ ) is observed in Fig. 2. The ammonium cations in Cloisite 6A, 15A and 20A with two long alkyl groups are non-polar, while those in Cloisite 30B, 10A and 25A are more polar. To obtain a well-intercalated and exfoliated structure, the surface polarities of polymer matrix and organoclay should be matched (LeBaron et al., 1999; Xie et al., 2001). Therefore, Cloisite 6A, 15A and 20A nanofillers showed the weak interactions leading to less intercalation. The maximum level of homogeneity and delamination was found in samples composed of Cloisite 25A and 30B.

Pegoretti et al. (2004) prepared the rPET nanocomposite with non-modified natural (Cloisite Na<sup>+</sup>) and modified (Cloisite 25A) nanoclays. The observations confirmed that the Cloisite 25A particles were much better dispersed in the rPET matrix compared to Cloisite Na<sup>+</sup>. Also, the tensile tests illustrated that both nanoclays increased the modulus of rPET but Cloisite 25A was more effective. Furthermore, the compliance of the nanocomposites was only slightly lower than that of neat rPET and both nanoclays had a beneficial effect on the dimensional stability of rPET.

The rPET nanocomposites containing 2 wt.% of different nanoclays, Cloisite 15A, 25A, and 30B were prepared by Karabulut (2003). The Cloisite 25A having long alkyl side-groups provided the best dispersion of clay platelets along with the most mechanical results owing to its branched nature.

Eventually, it seems that the Cloisite 25A type of nanoclay presents the better properties in the rPET nanocomposites.

### 2.1.3. Nanoclay modification

Kráčalík et al. (2007b) performed the two step modification of sodium type MMT with 1,2-dimethyl-3-octadecyl-1 H-imidazol-3-ium chloride (MMT-IM) and then with [3-(glycidyoxy)propyl] trimethoxysilane (MMT-IME). The filling of MMT-IM and MMT-IME into the rPET led to the substantial enhancement of Young's modulus especially by MMT-IME. The rPET/MMT-IME

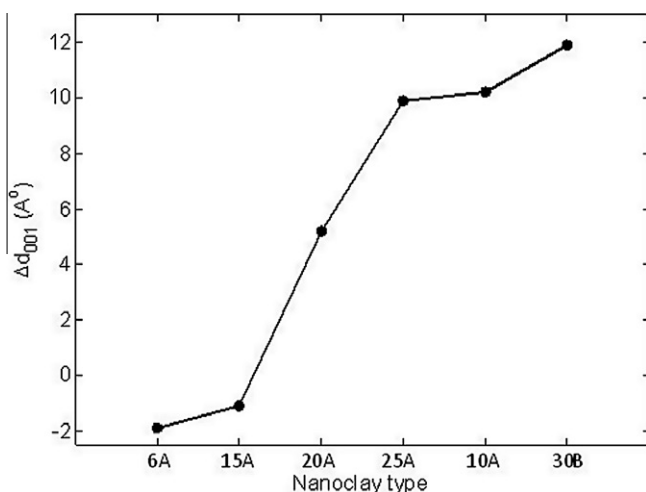


Fig. 2. The increased basal spacing ( $\Delta d_{001}$ ) of rPET/clay nanocomposites (Kráčalík et al., 2007a).

nanocomposite presented a better melt viscosity and storage modulus compared to MMT-IM system. Although the neat matrices showed a Newtonian behavior within the whole range of shear rates, the addition of modified organoclays caused an increase of one order of magnitude in complex viscosity at low shear rates. As suggested, the enhanced melt viscosity and elasticity of the rPET nanocomposites even at higher shear rates can be applied in extrusion, injection and blow molding technologies.

Kráčalík et al. (2007c) also silanized the commercial organoclays, Cloisite 25A, 10A, and 30B. The modification of Cloisite 25A with [3-(glycidyoxy) propyl] trimethoxysilane increased the homogeneity of silicate layers in rPET whereas the additional modification of Cloisite 10A and 30B led to the slighter level of both delamination structure and melt viscosity. The silanization of Cloisite 10A and 30B caused the significant loss of melt strength attributed to the higher water retention of silicate layers together with chemical reactions between the organic groups of organoclays and [3-(glycidyoxy)-propyl] trimethoxysilane modifier. Also, all prepared nanocomposites showed a shear thinning behavior, caused by disruption of network structures and orientation of nanoparticles in flow. The modified Cloisite 25A only presented the highest level of elongation at break while the largest improvement of tensile modulus was obtained using Cloisite 25A.

### 2.1.4. Process condition

The rPET nanocomposites were prepared by a corotating twin-screw extruder at two screw rotation speeds of 150 and 250 rpm (Giraldi et al., 2008). At lower screw speed, the exfoliation of clay platelets and also, the Young's modulus of rPET/clay nanocomposites were better than those at higher screw speed.

The rPET nanocomposites were also prepared at three different screw speeds: 150, 350 and 500 rpm (Karabulut, 2003). The maximum exfoliation and viscosity took place at 350 rpm exhibiting more desirable impact, tensile and flexural properties. Actually, the average screw speeds provide a good balance between the induced shear stress and residence time of melt mixing which establish desirable properties.

### 2.1.5. Ternary nanocomposites

Kelnar et al. (2010) focused on the rPET/nanoclay nanocomposites with Ethene-propene (EPR) and Ethene-methyl acrylate copolymer (EMA) elastomers for simultaneous compatibilization and reinforcement of rPET. The enhancement of stiffness, strength, and toughness was obtained applying 5 wt.% of preblended EPR or EMA and Cloisite 15A (3 wt.%) or particularly, simultaneously added Cloisite 30B and Cloisite 15A. The increment of EPR content did not practically lead to an increase in toughness, most possibly due to an extremely rough structure.

Kerboua et al. (2010) studied the blend of rPET and virgin poly methyl methacrylate (vPMMA) with nanoclay. By addition 2 wt.% of nanoclay (Nanofil2), the morphology of blend significantly changed and the particle size reduced, dramatically. An increase in nanoclay loading from 2 to 5 wt.% led to a more reduction in particle size while it became impossible to distinguish the dispersed PMMA domains. These remarks indicated the strong interfacial activity of nanoclay for this polymer pair. Also, the enhancement of strength, modulus, viscosity and dynamic storage at low frequencies was noticed by addition of nanoclay.

Shi et al. (2011) mixed the SiO<sub>2</sub> nanoparticles with rPET/ABS/AES (acrylonitrile-acrylic-styrene copolymer) blend. In the SiO<sub>2</sub> content of 1 phr, uniform dispersion of nanoparticles in rPET/ABS was illustrated and the SiO<sub>2</sub> nanoparticles were mainly distributed in rPET phase. As the content of SiO<sub>2</sub> increased, larger ABS domains was shown. The rPET/ABS/AES blends did not behave as a tough polymer but by incorporation of nano-SiO<sub>2</sub>, a significant improvement of impact and tensile strength was provided.

Fig. 3 shows the most improvement percentage of tensile modulus obtained in each study on rPET nanocomposites. The minimum improvement was observed in Kerboua work (Kerboua et al., 2010) about 18% whereas the maximum enhancement was achieved in Basilia study (Basilia et al., 2011) about 173%.

Accordingly, the concentration of 2–5 wt.% of Cloisite 25A at screw speeds of 150–350 rpm can be chosen as an optimized condition for recycling of rPET by nanoclay. Furthermore, the simultaneous addition of nanofillers and other polymer components to waste PET can be more efficient technique for improvement of rPET properties as discussed.

## 2.2. Recycled polypropylene (rPP)

### 2.2.1. Nanoclay

Tri Phuong et al. (2008) prepared the rPP/nanoclay nanocomposite at different concentrations of nanoclay and PP grafted with maleic anhydride (PPgMA) compatibilizer. They found that the nanoclay loading of 4 wt.% and PPgMA content of 20 wt.% created the best results of impact and tensile strength, even better than those of virgin PP (vPP). Further addition of PPgMA does not improve the performance of nanocomposite. The concentration of compatibilizer may surpass a saturation level and a part of this compatibilizer may be located in the interphase between polymer matrix and organoclay and another one being dispersed in the matrix which disturb the homogeneity of system.

Cengiz studied the rPP/organoclay nanocomposite containing Ethylene–methyl acrylate–glycidyl methacrylate (E–MA–GMA) and PPgMA compatibilizers (Cengiz, 2008). The organoclay loading over 2 wt.% prevented the intercalation mechanism suggesting the minor properties even in the presence of compatibilizer. The PPgMA was pronounced as a better compatibilizer and also, the improvement of both tensile and impact properties were greater at compatibilizer to organoclay ratio of three. The nanocomposite of rPP and Cloisite 15A provided the highest improvement in mechanical properties. In addition, the remarkable enhancement of dispersion level and mechanical properties was observed when the extrusion temperature and screw speed were kept at 180 °C and 350 rpm, respectively.

### 2.2.2. CaCO<sub>3</sub> nanoparticles

Elloumi et al. (2010) studied the effect of CaCO<sub>3</sub> nanoparticles on the virgin and recycled PP. Although CaCO<sub>3</sub> nanoparticles were

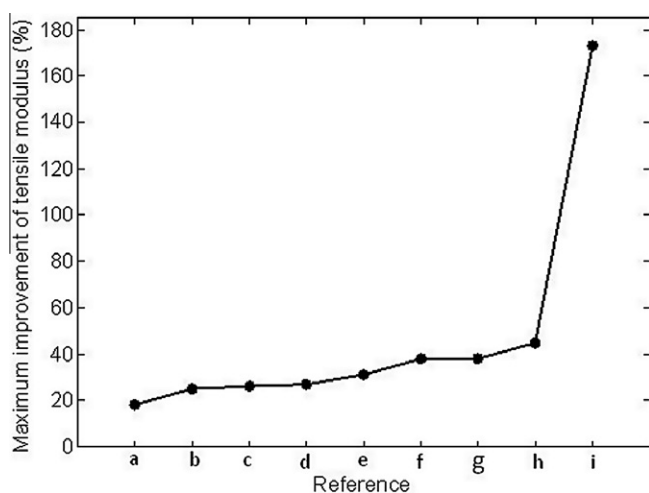


Fig. 3. The maximum improvement percentage of tensile modulus for rPET nanocomposites in Refs: (a) Kerboua et al., 2010; (b) Bizarria et al., 2007; (c) Kráčalík et al., 2007b; (d) Giraldo et al., 2008; (e) Pegoretti et al., 2004; (f) Kráčalík et al., 2007c; (g) Kelnar et al., 2010; (h) Hamzehlou and Katbab, 2007 and (i) Basilia et al., 2011.

surface modified, non-uniform dispersion of nanoparticles in the matrix was shown. Also, the reduction of ductility by the addition of CaCO<sub>3</sub> nanoparticles indicated to a reduction in the matrix deformation attributed to the introduction of mechanical stresses by non-deformable filler particles. At low frequencies, the loss modulus ( $G''$ ) of rPP was greater than the storage modulus ( $G'$ ) and the material behaved as a viscous liquid until the crossover whereas after reaching the crossover frequency, the material behaved as a solid material. The yield strength and strain of vPP decreased gradually by increasing CaCO<sub>3</sub> loading, while its Young's modulus increased slightly. These phenomena were less pronounced for rPP.

### 2.2.3. Carbon nanotubes (CNTs)

Long et al. prepared the rPP/CNTs nanocomposite by melting method (Gao et al., 2011). The thermal degradation of nanocomposite shifted to higher temperatures as the content of CNTs increased. More, no additional mass loss has been noticed as the temperature of the rPP/CNTs nanocomposite increased from 700 °C to 1000 °C. The mechanical properties of prepared nanocomposite are observed in Fig. 4. With increasing CNTs content up to 3 wt.%, the tensile strength and elongation at break increased but a downturn in mechanical properties occurred at 5 wt.% of CNTs attributed to the presence of small bundles of CNTs in the prepared samples.

### 2.2.4. Ternary nanocomposites

Mural et al. (2011) optimized the blend of rPP and waste high impact polystyrene (rHIPS) at a composition of 70/30 wt.% based on the mechanical performance. Then, this composition was mixed with a SEBS triblock copolymer and Cloisite 20A nanoclay. The samples prepared with 3 wt.% of nanoclay displayed the absence of characteristics peak of nanoclay in XRD, indicating a mixed intercalated and exfoliated clay layers where the intercalated layers were further pushed toward the interphase (Santana and Manrich, 2003). The incorporation of compatibilizer and nanoclay improved the thermal stability of PP/HIPS blend. The SEBS and nanoclay acted as an interfacial compatibilizer, which led to the reduction in particle size of rHIPS and promotion of effective interfacial adhesion.

The optimized parameters for preparation of rPP nanocomposites are briefly observed in Table 3. It is shown that the lower concentration of different nanofiller such as nanoclay, CaCO<sub>3</sub> and CNTs has a positive effect on the rPP properties. Also, the application of PPgMA compatibilizer causes a more improvement of performance. In addition, the nanofiller could develop the blend of two waste polymers, especially in the presence of a compatibilizer for enhancement of interfacial adhesion.

## 2.3. Recycled high density polyethylene (rHDPE)

### 2.3.1. Nanoclay

Lei et al. (2007) used both maleated polyethylene (MAPE) and titanate for compatibilization of rHDPE with nanoclay. Both compatibilizers could improve the compatibilization of components but the best results of mechanical properties were obtained at equivalent contents of nanoclay and MAPE at 1 wt.%. Without compatibilizers, the addition of nanoclay reduced the temperature and rate of crystallization and also, the degree of crystallinity while the addition of 2.5 wt.% of MAPE increased them. Moreover, the samples produced by a two-step blending method demonstrated the completely exfoliated clay platelets because more shear stress is applied for dispersion of the silicate layers.

Hill (2005) focused on the improvement of mechanical properties of rHDPE through the addition of MMT and bentonite types of nanoclay, cellulose fibers, and a combination of nanoclay and

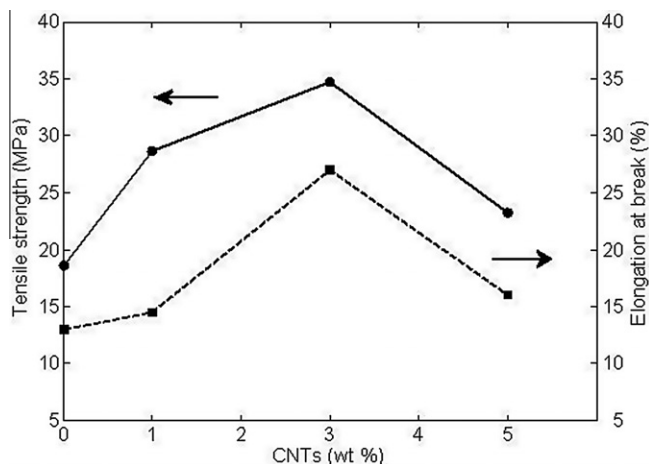


Fig. 4. The mechanical properties of rPP/CNTs nanocomposite (Gao et al., 2011).

cellulose fibers. The Cloisite 20A was found as the most compatible clay for this system due to its nature. The interactions between the PEGMA and the clay introduced the PEGMA as a more effective compatibilizing agent at higher clay loadings. Also, it was shown that the bentonite could compete with the Cloisite 20A nanoclay in the imparted mechanical properties. More, the grafting of maleic anhydride onto rHDPE during compounding provided a better tensile modulus. For all clay types, an increase in modulus was observed by addition of 1 vol.% of nanoclay. However, only Cloisite 20A showed the enhancement of modulus with addition of more nanoclay in this system. In the hybrid system, the nanoclay provided the effective stiffening while the cellulose caused an efficient strengthening.

Hemmasi et al. (2011) studied the influence of nanoclay loading on the water absorption and thickness swelling of rHDPE/wood composite. The nanoclay inhibited the water permeation in the polymer matrix based on its hydrophilic nature while the surface tended to immobilize some of the moisture (Rana et al., 2005), or surfactant-covered clay platelets formed a tortuous path for water transport (Alexandre et al., 2009; Bharadwaj et al., 2002). Also, the possible reason for less water uptake could be the existence of nanoclay as a nucleating agent.

### 2.3.2. Graphene nanoparticles

Reddy investigated the effect of graphene nanoparticles on the properties of rHDPE (Jannapu Reddy, 2010). The large improvement of properties was observed only with a little content of graphene due to the separation of single graphene sheet to 1 nm. It was reported that only about 0.25 wt.% of graphene introduced more tensile modulus, dielectric constant ( $k$ ) and thermal conductivity in rHDPE nanocomposite and the properties improved more, when the graphene content increased. Fig. 5 illustrates the tensile

modulus of rHDPE/graphene nanocomposite. As shown, the graphene has a most positive effect on the tensile modulus of rHDPE.

The most favorable condition for obtaining the optimized rHDPE nanocomposites is observed in Table 4. It is concluded that only extremely slight contents of nanofillers can significantly improve the properties of rHDPE.

## 2.4. Recycled Polyvinyl chloride (rPVC)

### 2.4.1. Nanoclay

Yoo et al. (2004) prepared the rPVC/clay nanocomposite by melt mixing. In the case of 10 wt.% of nanoclay, the characteristic peak of clay was completely disappeared. Also, the coefficient of thermal expansion decreased with addition of nanoclay. The mechanical properties of the nanocomposite increased simultaneously for various clay loadings, 1, 3, 5 and 10 wt.%. Further, the thermal decomposition behavior and linear dimensional of nanocomposite improved proportionally to the contents of nanoclay. The thermal degradation of PVC leads to the evolution of hydrogen chloride gas, wide discoloration of PVC and reduction of physical and mechanical properties. It was also found that at 55 °C, the storage modulus of nanocomposite composed of 10 wt.% of nanoclay was 11 times higher than that of neat rPVC.

### 2.4.2. CaCO<sub>3</sub> nanoparticles

Andričić et al. (2008) added the virgin PVC (vPVC) and CaCO<sub>3</sub> nanoparticles to a waste laminate containing PVC, CaCO<sub>3</sub> and PP in the contents of 40, 25, and 10 wt.%, respectively. SEM images showed the agglomeration of the nanofiller most probably due to the differences in polarity of polymer and nanofiller as well as the insufficient dispersion in the mixing process. The filler made a new interlayer between two polymer phases which could improve their compatibility. The tensile strength and elongation at break of PVC sheets containing 10, 20 and 30 wt.% of waste laminate (1, 2 and 3 wt.% of PP) decreased as PP content increased. In the samples with lower PP content, mechanical properties got better as the filler content increased, while with higher PP content, mechanical properties reached its maxima at about 6 wt.% of CaCO<sub>3</sub> content. It was clear that PVC and PP could not be efficiently recycled without some compatibility improvement.

In conclusion, rPVC and also the waste blends and composites can be recycled by nanoclay and CaCO<sub>3</sub> at different concentrations. Especially in the case of blends and composites, some compatibility should be induced for efficient improvement of properties.

## 2.5. Recycled polystyrene (rPS)

### 2.5.1. Nanoclay

Liu et al. (2007) prepared a novel superabsorbent nanocomposite based on partially neutralized acrylic acid, rPS foam, and sodium type MMT (Na-MMT) through emulsion polymerization. The results showed that acrylic acid monomer successfully grafted onto the PS chain and the layers of Na-MMT were exfoliated after

Table 3  
The best condition for manufacturing rPP nanocomposites.

Parameter	Optimal condition	References
Nanofiller condition	4 wt.% of nanoclay 2 wt.% of Cloisite 15A 3 wt.% of CaCO <sub>3</sub> 3 wt.% of CNTs	Tri Phuong et al. (2008) Cengiz (2008) Elloumi et al. (2010) Gao et al. (2011)
Compatibilizer content	20 wt.% of PPgMA Compatibilizer to organoclay ratio of three	Tri Phuong et al. (2008) Cengiz (2008)
Process condition	180 °C and 350 rpm	Cengiz (2008)
Optimization of PP/HIPS	70/30 wt.% of blend with 3 wt.% of nanoclay and 5 wt.% of SEBS compatibilizer	Mural et al. (2011)

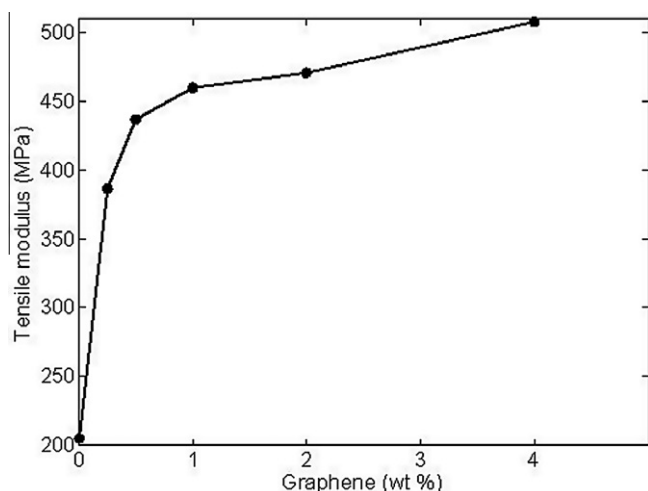


Fig. 5. The tensile modulus of rHDPE/graphene nanocomposite (Jannapu Reddy, 2010).

Table 4

The most favorable condition for fabrication of rHDPE nanocomposites.

Parameter	Optimal condition	References
Nanofiller condition	1 wt.% of nanoclay Cloisite 25A Higher contents of graphene (maximum 8 wt.% was reported)	Lei et al. (2007) Hill (2005) Jannapu Reddy (2010)
Compatibilizer	1 wt.% of MAPE MAPE especially at higher clay loadings	Lei et al. (2007) Hill (2005)

copolymerization. The addition of Na-MMT not only enhanced the thermal stability of the composite, but also increased the content and rate of water absorbency.

### 2.6. Recycled polymethyl methacrylate (rPMMA)

Martin et al. (2008) investigated the nanocomposite of rPMMA with both natural and organically modified silicate layers. There was no improvement in thermal properties of nanocomposites but at higher dispersion degree, the nanocomposites showed higher transparency extent. The tensile modulus increased with nanoclay content for both nanoclays which introduced nanocomposites with attractive properties by the maintenance of transparency and thermal properties of waste matrix.

### 2.7. Recycled polybutylene terephthalate (rPBT)

Zhang et al. (2009a) improved the mechanical properties of recycled glass fiber reinforced flame retardant PBT with three types of nanoparticles including SiO<sub>2</sub>, MMT and mica. Fig. 6 presents the impact strength of prepared samples with different nanoparticles. The samples containing SiO<sub>2</sub> and mica show the best improvement of impact strength at 1 wt.% concentration. In these nanocomposites, a strong adhesion which acts as an effective bridge for the organic resin to pass the stress to the inorganic particles was provided. The MMT inversely caused the reduction of impact strength due to reduction in chain mobilities. Also, the tensile and flexural strength of nanocomposites showed this trend but, the heat distortion temperature (HDT) increased with addition of SiO<sub>2</sub> and mica. Further, the addition of nanoparticles did not significantly affect the electrical and flame retardant properties.

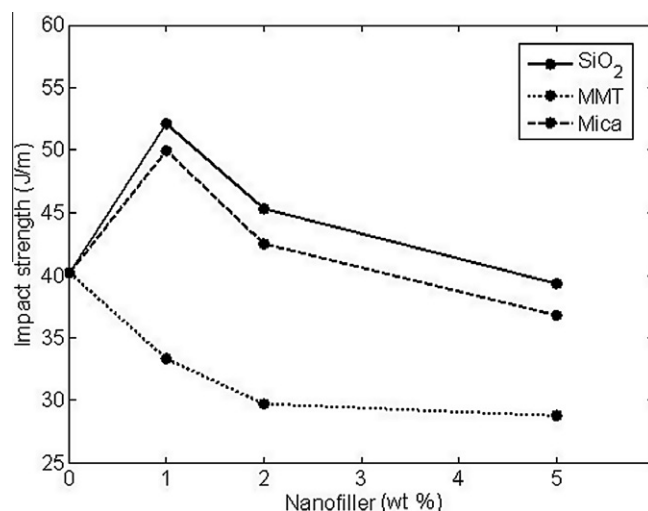


Fig. 6. The impact strength of rPBT nanocomposite containing different nanoparticles (Zhang et al., 2009a).

Lastly, it is demonstrated that the different nanofillers have a dissimilar effect on the waste polymers and the optimized condition should be determined for development of nanocomposites from waste products.

## 3. Conclusion and future trends

The current study shows that the application of much low content of nanofillers can be an efficient technique for recycling of polymers, composites and blends. Various nanoparticles such as nanoclay, CaCO<sub>3</sub>, CNTs, SiO<sub>2</sub>, mica and graphene have been used for recycling which should be developed for all waste polymers. Also, it is indicated that the application of a compatibilizer for recycling of polymers, particularly blends and composites are more useful.

However, with the objective to a successful and economic recycling in which the recycled polymer has more acceptable characteristics, more investigation must be made on the whole aspect of recycling process to enhance the competitiveness in these systems. The first step may be the improvement of interaction and interfacial adhesion in prepared nanocomposites. Compatibilizing, functionalizing and surface modification procedures can be developed in the future works. Further, the addition of effective nanofillers including available nanofillers or a combination of nanofillers is suggested which will provide further progress and new opportunities in these materials. In addition, the development of various preparation techniques and also, optimization of melt mixing process should be carried out attributed to its important effect on the final properties.

Finally, it is indicated that the products prepared through the addition of nanoparticles to the recycled polymers can offer the unexpected combinations of improved properties, low-weight, ease of processing, and low cost which is not easily and concurrently found in other manufactured goods.

## References

- Alexandre, B., Langevin, D., Médéric, P., Aubry, T., Couderc, H., Nguyen, Q., Saiter, A., Marais, S., 2009. Water barrier properties of polyamide 12/montmorillonite nanocomposite membranes: structure and volume fraction effects. *Journal of Membrane Science* 328, 186–204.
- Andričić, B., Kovačić, T., Klarić, I., 2008. Properties of recycled material containing poly (vinyl chloride), polypropylene, and calcium carbonate nanofiller. *Polymer Engineering & Science* 48, 572–577.
- Ansari, R., Alikhani, A.H., 2009. Application of polyaniline/nylon composites coating for corrosion protection of steel. *Journal of Coatings Technology and Research* 6, 221–227.

- Basilia, B.A., Mendoza, H.D., Cada, L.G., 2011. Synthesis and characterization of RPET/organo-montmorillonite nanocomposites. *Philippine Engineering Journal* 23, 19–34.
- Bharadwaj, R., Mehrabi, A., Hamilton, C., Trujillo, C., Murga, M., Fan, R., Chavira, A., Thompson, A., 2002. Structure–property relationships in cross-linked polyester–clay nanocomposites. *Polymer* 43, 3699–3705.
- Bizarria, M., Giraldi, A.L.F.M., de Carvalho, C.M., Velasco, J.I., d'Ávila, M.A., Mei, L.H.L., 2007. Morphology and thermomechanical properties of recycled PET–organoclay nanocomposites. *Journal of Applied Polymer Science* 104, 1839–1844.
- Braun, D., 2004. Poly (vinyl chloride) on the way from the 19th century to the 21st century. *Journal of Polymer Science Part A: Polymer Chemistry* 42, 578–586.
- Burat, F.I., Güney, A., Olgaç Kangal, M., 2009. Selective separation of virgin and post-consumer polymers (PET and PVC) by flotation method. *Waste Management* 29, 1807–1813.
- Cengiz, F., 2008. Preparation and characterization of recycled polypropylene based nanocomposites. M.Sc. Dissertation; The Graduate School of Natural and Applied Science of Middle East Technical University.
- Chang, J.H., Mun, M.K., Lee, I.C., 2005. Poly (ethylene terephthalate) nanocomposite fibers by in situ polymerization: the thermomechanical properties and morphology. *Journal of Applied Polymer Science* 98, 2009–2016.
- Elloumi, A., Pimbert, S., Bourmaud, A., Bradai, C., 2010. Thermomechanical properties of virgin and recycled polypropylene impact copolymer/CaCO<sub>3</sub> nanocomposites. *Polymer Engineering & Science* 50, 1904–1913.
- Fall, M., Célestin, J., Sen, H., 2010. Potential use of densified polymer–paste fill mixture as waste containment barrier materials. *Waste Management* 30, 2570–2578.
- Frounchi, M., Dadbin, S., Salehpour, Z., Noferesti, M., 2006. Gas barrier properties of PP/EPDM blend nanocomposites. *Journal of Membrane Science* 282, 142–148.
- Gao, J.L., Liu, Y.H., Li, D.M., 2011. Preparation and properties of recycled polypropylene/carbon nanotube composites. *Advanced Materials Research* 279, 106–110.
- García, M.T., Gracia, I., Duque, G., Lucas, A., Rodríguez, J.F., 2009. Study of the solubility and stability of polystyrene wastes in a dissolution recycling process. *Waste Management* 29, 1814–1818.
- Giraldi, A.L.F.M., Bizarria, M., Silva, A., Velasco, J., d'Ávila, M.A., Mei, L., 2008. Effects of extrusion conditions on the properties of recycled poly (ethylene terephthalate)/nanoclay nanocomposites prepared by a twin-screw extruder. *Journal of Applied Polymer Science* 108, 2252–2259.
- Goto, M., Sasaki, M., Hirose, T., 2006. Reactions of polymers in supercritical fluids for chemical recycling of waste plastics. *Journal of Materials Science* 41, 1509–1515.
- Haddad, T.S., Lichtenhan, J.D., 1996. Hybrid organic–inorganic thermoplastics: styryl-based polyhedral oligomeric silsesquioxane polymers. *Macromolecules* 29, 7302–7304.
- Hamzehlou, S., Katbab, A., 2007. Bottle-to-bottle recycling of PET via nanostructure formation by melt intercalation in twin screw compounder: Improved thermal, barrier, and microbiological properties. *Journal of Applied Polymer Science* 106, 1375–1382.
- Hemmasi, A.H., Ghasemi, I., Bazayr, B., Samariha, A., 2011. Influence of nanoclay on the physical properties of recycled high-density polyethylene/bagasse nanocomposite. *Middle-East Journal of Scientific Research* 8, 648–651.
- Hill, M.E., 2005. Adding Value to Recycled Polyethylene Through the Addition of Multi-Scale Reinforcements. M.Sc. Dissertation; The University of Akron. <<http://www.epa.gov/osw/conservematerials/plastics.htm>>.
- Jafari, S., Kalati-vahid, A., Khonakdar, H., Asadinezhad, A., Wagenknecht, U., Jehnichen, D., 2012. Crystallization and melting behavior of nanoclay-containing polypropylene/poly (trimethylene terephthalate) blends. *eXPRESS. Polymer Letters* 6, 148–158.
- Jannapu Reddy, R., 2010. Preparation, characterization and properties of injection molded graphene nanocomposites. M.Sc. Dissertation; Wichita State University.
- Karabulut, M., 2003. Production and Characterization of Nanocomposite Materials from Recycled Thermoplastics. M.Sc. Dissertation; Middle East Technical University.
- Kelnar, I., Sukhanov, V., Rotrekl, J., Kaprálková, L., 2010. Toughening of recycled poly (ethylene terephthalate) with clay-compatible rubber phase. *Journal of Applied Polymer Science* 116, 3621–3628.
- Kerboua, N., Cinausero, N., Sadoun, T., Lopez-Cuesta, J., 2010. Effect of organoclay in an immiscible poly (ethylene terephthalate) waste/poly (methyl methacrylate) blend. *Journal of Applied Polymer Science* 117, 129–137.
- Kráčálík, M., Mikešová, J., Puffr, R., Baldrian, J., Thomann, R., Friedrich, C., 2007a. Effect of 3D structures on recycled PET/organo clay nanocomposites. *Polymer Bulletin* 58, 313–319.
- Kráčálík, M., Studenovský, M., Mikešová, J., Kovářová, J., Sikora, A., Thomann, R., Friedrich, C., 2007b. Recycled PET–organoclay nanocomposites with enhanced processing properties and thermal stability. *Journal of Applied Polymer Science* 106, 2092–2100.
- Kráčálík, M., Studenovský, M., Mikešová, J., Sikora, A., Thomann, R., Friedrich, C., Fortelný, I., Šimoník, J., 2007c. Recycled PET nanocomposites improved by silanization of organoclays. *Journal of Applied Polymer Science* 106, 926–937.
- LeBaron, P.C., Wang, Z., Pinnavaia, T.J., 1999. Polymer-layered silicate nanocomposites: an overview. *Applied Clay Science* 15, 11–29.
- Lei, Y., Wu, Q., Clemons, C.M., 2007. Preparation and properties of recycled HDPE/clay hybrids. *Journal of Applied Polymer Science* 103, 3056–3063.
- Liu, P.S., Li, L., Zhou, N.L., Zhang, J., Wei, S.H., Shen, J., 2007. Waste polystyrene foam-graft-acrylic acid/montmorillonite superabsorbent nanocomposite. *Journal of Applied Polymer Science* 104, 2341–2349.
- Martin, L., Kortaberria, G., Vazquez, A., Fermeglia, M., Martinelli, L., Sinesi, S., Jimeno, A., de la Caba, K., Mondragon, I., 2008. A comparative study of nanocomposites based on a recycled poly (methyl methacrylate) matrix containing several nanoclays. *Polymer Composites* 29, 782–790.
- Mural, P.K.S., Mohanty, S., Nayak, S.K., Anbudayanidhi, S., 2011. Polypropylene/high impact polystyrene blend nanocomposites obtained from E-waste: evaluation of mechanical, thermal and morphological properties. *International Journal of Plastics Technology* 50, 1–15.
- Oromiehie, A., Mamizadeh, A., 2004. Recycling PET beverage bottles and improving properties. *Polymer International* 53, 728–732.
- Pegoretti, A., Kolarik, J., Peroni, C., Migliaresi, C., 2004. Recycled poly (ethylene terephthalate)/layered silicate nanocomposites: morphology and tensile mechanical properties. *Polymer* 45, 2751–2759.
- Rahimi, A., Shokrolahi, P., 2001. Application of inorganic polymeric materials: I. Polysiloxanes. *International Journal of Inorganic Materials* 3, 843–847.
- Ramezani-Dakhal, H., Garmabi, H., 2010. A systematic study on notched impact strength of super-toughened polyamide 6 nanocomposites using response surface methodology. *Journal of Applied Polymer Science* 118, 969–979.
- Rana, H.T., Gupta, R.K., GangaRao, H.V.S., Sridhar, L., 2005. Measurement of moisture diffusivity through layered-silicate nanocomposites. *AIChE Journal* 51, 3249–3256.
- Sadat-Shojai, M., Bakhshandeh, G.R., 2010. Recycling of PVC wastes: a review. *Polymer degradation and stability* 96, 404–415.
- Salmiaton, A., Garforth, A., 2007. Waste catalysts for waste polymer. *Waste Management* 27, 1891–1896.
- Salmiaton, A., Garforth, A., 2011. Multiple use of waste catalysts with and without regeneration for waste polymer cracking. *Waste Management* 31, 1139–1145.
- Santana, R.M.C., Manrich, S., 2003. Morphology and mechanical properties of polypropylene/high-impact polystyrene blends from postconsumer plastic waste. *Journal of Applied Polymer Science* 88, 2861–2867.
- Shabani, I., Haddadi-Asl, V., Seyedjafari, E., Babaeijandaghi, F., Soleimani, M., 2009. Improved infiltration of stem cells on electrospun nanofibers. *Biochemical and Biophysical Research Communications* 382, 129–133.
- Shabani, I., Haddadi-Asl, V., Soleimani, M., Seyedjafari, E., Babaeijandaghi, F., Ahmadbeigi, N., 2011a. Enhanced infiltration and biomineralization of stem cells on collagen-grafted three-dimensional nanofibers. *Tissue Engineering Part A* 17, 1209–1218.
- Shabani, I., Hasani-Sadrabadi, M.M., Haddadi-Asl, V., Soleimani, M., 2011b. Nanofiber-based polyelectrolytes as novel membranes for fuel cell applications. *Journal of Membrane Science* 368, 233–240.
- Shabani, I., Haddadi-Asl, V., Seyedjafari, E., Soleimani, M., 2012. Cellular infiltration on nanofibrous scaffolds using a modified electrospinning technique. *Biochemical and Biophysical Research Communications* 423, 50–54.
- Shahabadi, S., Garmabi, H., 0000. Response surface analysis of structural, mechanical, and permeability properties of polyethylene/Na<sup>+</sup>-montmorillonite composites, prepared by slurry-fed melt intercalation. *eXPRESS. Polymer Letters* 6, 657–671.
- Shi, G., He, L.J., Chen, C.Z., Liu, J.F., Liu, Q.Z., Chen, H.Y., 2011. A novel nanocomposite based on recycled poly (ethylene terephthalate)/ABS blends and nano-SiO<sub>2</sub>. *Advanced Materials Research* 150, 857–860.
- Simoneit, B.R.T., Medeiros, P.M., Didyk, B.M., 2005. Combustion products of plastics as indicators for refuse burning in the atmosphere. *Environmental Science & Technology* 39, 6961–6970.
- Taurino, R., Pozzi, P., Zanasi, T., 2010. Facile characterization of polymer fractions from waste electrical and electronic equipment (WEEE) for mechanical recycling. *Waste Management* 30, 2601–2607.
- Tri Phuong, N., Gilbert, V., Chuong, B., 2008. Preparation of recycled polypropylene/organophilic modified layered silicates nanocomposites part I: the recycling process of polypropylene and the mechanical properties of recycled polypropylene/organoclay nanocomposites. *Journal of Reinforced Plastics and Composites* 27, 1983–2000.
- Xie, W., Gao, Z., Pan, W.P., Hunter, D., Singh, A., Vaia, R., 2001. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chemistry of Materials* 13, 2979–2990.
- Xu, H., Kuo, S.W., Lee, J.S., Chang, F.C., 2002. Preparations, thermal properties, and Tg increase mechanism of inorganic/organic hybrid polymers based on polyhedral oligomeric silsesquioxanes. *Macromolecules* 35, 8788–8793.
- Yoo, Y., Kim, S.S., Won, J.C., Choi, K.Y., Lee, J.H., 2004. Enhancement of the thermal stability, mechanical properties and morphologies of recycled PVC/clay nanocomposites. *Polymer Bulletin* 52, 373–380.
- Zare, Y., Garmabi, H., 2012a. Analysis of tensile modulus of PP/nanoclay/CaCO<sub>3</sub> ternary nanocomposite using composite theories. *Journal of Applied Polymer Science* 123, 2309–2319.
- Zare, Y., Garmabi, H., 2012b. Nonisothermal crystallization and melting behavior of PP/nanoclay/CaCO<sub>3</sub> ternary nanocomposite. *Journal of Applied Polymer Science* 124, 1225–1233.
- Zare, Y., Garmabi, H., Sharif, F., 2011. Optimization of mechanical properties of PP/Nanoclay/CaCO<sub>3</sub> ternary nanocomposite using response surface methodology. *Journal of Applied Polymer Science* 122, 3188–3200.
- Zhang, S.D., Ban, Q., Huang, H.X., Li, Y.Z., 2009a. Modified recycled glass fiber reinforced flame retardant PBT with improved mechanical properties by nanoparticles. *The 5th ISFR, Chengdu, China*, pp. 171–177.
- Zhang, Y., Broekhuis, A.A., Picchioni, F., 2009b. Thermally self-healing polymeric materials: the next step to recycling thermoset polymers? *Macromolecules* 42, 1906–1912.