# 3 Recycled Polymers: Properties and Applications

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## 3.1 Introduction

The total production of plastics is currently more than 230 million tonnes/year, which will increase to 400 million tonnes in 2020, based on a very conservative growth rate of about 5% per year [1, 2]. The increasing consumption of polymer products, in various fields, generates a large quantity of waste materials, which equates to more than 12% of the urban solid waste stream [3]. Therefore, the world is confronting a crisis, due to the generation of huge amounts of plastic waste by industries and householders; hence, an increasing attempt has been made to cope with waste polymers, due to environmental, economic and petroleum concerns.

The old-style methods, such as combustion of waste polymers or burying underground, lead to negative influences on the environment *via* the formation of dust, fumes and toxic gases or the pollution of underground water and other resources. It seems that the recycling process is the best technique to treat waste polymer products. Recycling is generally achieved *via* a series of processing operations performed on plastics to produce secondary materials or energy [4, 5]. To date, a number of scientists and industrialists have tried in this field to evaluate the feasibility of recycling processes.

The recycling rate of different polymers varies, but, an overall recycling rate of 8% or 2.4 million tonnes was reported in 2010 [6]. Various technological processes for the recycling of waste polymers include mechanical recycling, chemical or feedstock recycling and energy recovery [7–9]. Mechanical recycling is a relatively simple and common method in plastics industries. It is a preferable method when adequate quantities of homogenous and separated waste can be provided [10, 11]. A conventional mechanical recycling process includes the separation, grinding and feeding of ground products, using suitable equipment, producing a secondary material which has not undergone any changes in the chemical nature of the material. It is clear that mechanical recycling is limited due to the downcycling effects and difficulties of obtaining sufficiently clean and homogenous wastes. Chemical or feedstock recycling

involves the preparation of low molecular weight materials from recycled polyvinyl chloride (rPVC) *via* chemical treatment [12–14]. Chemical recycling is considered to be a complementary method to mechanical recycling and is now an attractive field of research.

The energy recovery technique is also a method which can be applied to dispose of rPVC, *via* incineration, when it contains a large amount of impurities or combustible solids. However, simple recycling to produce secondary products cannot solve the problems of plastic waste. Many types of plastics cannot be easily separated or processed together, and the products containing mixed recycled materials show poor mechanical properties and thus, limited applications [15]. For example, one stray polyvinyl chloride (PVC) bottle in a melt of 10,000 polyethylene terephthalate (PET) bottles can cause the deterioration of the whole batch of PET bottles, as they are difficult to identify from each other. Therefore, manufacturers determine plastic types using the numerical coding system generated by the Society of Plastics Industry in the 1980s for ease of separation [6]. **Table 3.1** displays the identification codes and some household applications of the most commonly used polymers. However, plastic pipes, toys, household items and other products do not fit into the coding system. Moreover, it was reported that the polymer structure is degraded after several processing cycles, which causes weaker mechanical properties compared with a virgin polymer [16, 17]. The recycling of PVC from waste is given in the next section as an example in this field.

| Table 3.1 Identification codes and some household applications of the most consumed polymers | | |
|---|---|---|
| Polymer | Identification code | Applications |
| PET | 1 | Fizzy drink bottles and waterproof packaging |
| HDPE | 2 | Milk, oil and detergent bottles, toys and plastic bags |
| PVC | 3 | Food trays, cling film, liners and blister packages |
| LDPE | 4 | Carrier bags, bin liners, shrink wrap and garment bags |
| PP | 5 | Bags, bottle tops, carpets and household components |
| PS | 6 | Foams, plastic cutlery and packaging for electronic goods |
| HDPE: High-density polyethylene LDPE: Low-density polyethylene PP: Polypropylene PS: Polystyrene | | |

## 3.2 Polyvinyl Chloride Recycling

Since about half of PVC products are considered long-life items, i.e., with a lifespan of about 30–40 years, a substantial increase in rPVC production is expected in the near future. The material and chemical recycling of rPVC may be an appropriate solution to the problems of environmental pollution from landfilling or incineration of such waste. On a worldwide level, demand for PVC exceeds about 35 million tonnes/year; it is rated second, in terms of volume, after polyethylene (PE) in the plastics industry [18]. Because of the particular properties of PVC, i.e., low cost and high performance, combined with the wide range of products that can be obtained from different processing techniques, PVC has become a widespread polymer. PVC can be processed into a wide variety of products, such as packaging for food, textile, cleansing and medical materials, as well as beverage packaging bottles as short-life products. In addition, PVC is used for long-life products such as pipes, cable insulation, window frames, floors coverings, roofing sheets and so on. Recently, the rapid growth of rPVC has gained increasing importance in scientific and industrial communities.

Despite all the advantages of recycling, only a very small amount of PVC waste is now recycled worldwide. The current method is to send plastic waste to landfill in many developing countries, and only less than 1% of the total amount is recycled [19]. Moreover, European countries and the USA faced with a similar problem, and the major portion of plastic waste is either landfilled or incinerated with other municipal solid waste. However, the recycling rates of PVC have enhanced in the USA and European countries since the 1980s, when many new recycling programmes were developed. Vinyl 2010, as a volunteer commitment, was arranged in Europe in 2000 to reduce the environmental impact of PVC production, decrease waste, encourage responsible use of additives, and improve collection and recycling [18]. Vinyl 2010 reported that about 195,000 tonnes of PVC was recycled in 2008, which shows a 30% increment compared with the recycling level in 2007. The PVC waste which was recycled in 2008 was only 2.5% of PVC consumption in Europe. **Figure 3.1** shows the tonnage of rPVC in Europe from 2003 to 2008. This illustration clearly indicates the rapid increase in the rate of recycling in the last decade. Among European countries, Germany has the highest number of recyclers in Europe, which is globally regarded as the most advanced country for PVC recycling.

Additionally, the recycling of plastics usually requires a suitable separation method in which plastic materials in the mixed solid wastes are separated into a homogeneous stream. A homogeneous plastic material demonstrates better properties, which results in the wider application of recycled products. In other words, the incompatibility of different polymer wastes leads to problematic processing and poorer mechanical-physical properties of the obtained materials.
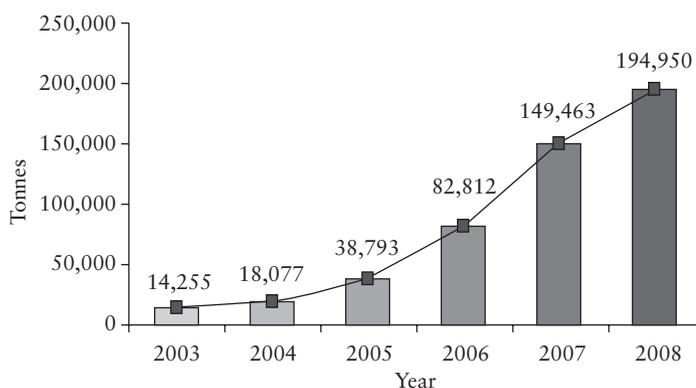
**Figure 3.1** The tonnage of rPVC in Europe from 2003 to 2008. Reproduced with permission from M. Sadat-Shojai and G-R. Bakhshandeh, *Polymer Degradation and Stability*, 2011, **96**, 404. ©2011, Elsevier [18]

Although the separation of PVC from mixed plastic waste is necessary, a high quality and generally acceptable automatic segregation of PVC is not yet available. Therefore, the recycled products fabricated from an imperfect separation process cannot compete with the virgin polymer in most cases. Hence, many researchers have attempted to provide economic and reliable separation methods, in which PVC can be separated from various waste mixtures. Generally, the sorting methods can be mostly categorised into three groups: macro, micro and molecular separations [20]. Macro sorting involves separating plastic based on a whole product, i.e., using visual sensing. Micro separation refers to the sorting of chipped or granulated polymers, which includes primary processing into uniform pieces, such as size or density, and then separation. In addition, molecular separation includes the selective dissolving of various plastics in solvents and the subsequent reclaiming of dissolved constituents. Although a number of methods have been suggested for PVC waste separation, few of them have been used in practice.

A simple method, such as the macro sorting technique, is the separation of PVC materials from plastic wastes *via* hand sorting [21]. A study on PVC bottles in a mixed plastic recycling programme demonstrated that manual separation is about 80% accurate in the identification of PVC bottles; therefore, manual separation is an expensive and uneconomic method. Research has also been conducted to offer suitable fully automated separation methods without manual intervention. Recent systems for automated sorting depend on the responses to differing environments, such as specific gravity change, visual recognition and dissolution in a solvent [18]. These methods can separate plastic types to a certain extent.

## 3.3 Application of Nanofillers

### *3.3.1 Overview*

One of the simplest methods to recycle waste plastics seems to be the application of nanofillers, i.e., the development of nanocomposites. As is well known, we can achieve a considerable enhancement of mechanical, thermal, optical and barrier properties using a low content of nanofillers [22–28]. The addition of nanofillers generally increases the overall performance of polymers and is attributed to the high specific surface area of nanoparticles which can significantly increase the interfacial interactions between the polymer and filler [29–34]. The enhanced properties are provided without any increase in density and cost or reduction of the light transmission properties of the base polymers. In addition, nanofillers can increase the melt strength and viscosity of waste polymers. Furthermore, the quantitative analysis of interfacial adhesion, in prepared nanocomposites from waste polymers, justified the recycling of polymers *via* the incorporation of nanoparticles [35]. The interfacial bonding was evaluated using various models to determine the tensile properties of composites; the calculated parameters showed a strong interfacial adhesion between the nanoparticles and waste polymers.

Many researchers have used nanofillers to recycle waste polymers and the studies investigating polymer recycling *via* the incorporation of nanofillers are presented in **Table 3.2**. They are extensively discussed in the following sections.

### *3.3.2 Nanocomposites from Recycled Polyethylene Terephthalate*

It was reported that a higher content of OMMT provided greater stiffness and tensile strength [36, 37]. Basilia and co-workers [38] also found that 5 wt% of synthesised Philippine organically modified sodium montmorillonite (Na-MMT) caused the best improvement of tensile properties. Furthermore, the optimised values of strength and toughness were taken at 2.5 wt% of OMMT, instead of 5 wt% [39]. An optimal OMMT (DK2) content of 3 wt% was observed for the tensile strength of both recycled polyethylene terephthalate (rPET) and virgin polyethylene terephthalate (vPET) nanocomposites [40]. In addition, all samples prepared from rPET presented higher tensile properties, compared with vPET. At low shear frequencies, the samples containing 3 and 5 wt% of OMMT demonstrated a higher storage modulus, while more Newtonian behaviour was shown in the samples containing an OMMT concentration of lower than 5 wt%. As a result, the highest level of stiffness and strength can be obtained at a larger content of nanoclay, while the optimised level of strength and toughness is provided at a lower nanoclay content (about 2 wt%). Generally, reduced chain mobility, as a result of the mechanical involvement of chains with nanoclay layers, decreases the toughness.

| Table 3.2 Recent studies on nanocomposites from waste polymers | | |
|---|---|---|
| **Waste polymer** | **Nanofiller** | **References** |
| PET | Nanoclays | [36–46] |
| | $Si_3N_4$ | [47] |
| PET/rubber | OMMT | [48] |
| PET/PMMA | OMMT | [49] |
| PET/ABS | $SiO_2$ | [50] |
| PET/PEN | MWCNT | [51] |
| PP | OMMT | [52, 53] |
| | $CaCO_3$ | [54] |
| | CNT | [55] |
| PP/PE | OMMT | [56] |
| PP/HIPS | OMMT | [57] |
| PE | Nanoclays | [58, 59] |
| HDPE | Graphene | [60] |
| HDPE/baggase | OMMT | [61] |
| PE | Nano-fly ash | [62] |
| PVC | OMMT | [63] |
| PVC/PP | $CaCO_3$ | [64] |
| PS | OMMT | [65, 66] |
| Expanded polystyrene | $TiO_2$ | [67] |
| PMMA | OMMT | [68] |
| PBT/glass fibre | $SiO_2$, MMT, mica | [69] |
| PC | OMMT | [70] |
| PC/ABS | OMMT | [71] |
| Polycaprolactone-based thermoplastic polyurethane | OMMT | [72] |
| Rubber from tyres | CNT | [73] |
| ABS: Acrylonitrile-butadiene-styrene<br>CNT:  Carbon nanotube(s)<br>HIPS: High impact polystyrene<br>MMT:  Modified montmorillonite<br>MWCNT: Multiwalled carbon nanotube(s)<br>OMMT:  Organically modified montmorillonite<br>PBT:  Polybutylene terephthalate<br>PC: Polycarbonate<br>PEN:  Polyethylene naphthalate<br>PMMA: Polymethyl methacrylate<br>Reproduced with permission from Y. Zare, *Waste Management*, 2013, **33**, 598.<br>©2013, Elsevier [3] | | |

The mechanical properties of an rPET/OMMT nanocomposite are shown in **Figure 3.2** from [45]. By increasing the OMMT content up to 1 wt%, the yield strength and ultimate strength of the nanocomposite improved by 17 and 27%, respectively. Additionally, the incorporation of OMMT into the rPET resulted in a significant increase of the modulus, which was well described by Mori–Tanaka, and solution of Eshleby at low MMT content. Also, the prepared nanocomposite exhibited reduced creep, which could be predicted by the power law equation for long-term creep.

The incorporation of 5 wt% of a different OMMT in rPET was evaluated [41]. To get a well-exfoliated structure, the surface polarities of the polymer matrix and OMMT should be matched [74, 75]. The ammonium cations in Cloisite 30B, 10A and 25A are more polar, while those in Cloisite 6A, 15A and 20A, containing two long alkyl groups, are nonpolar. Hence, Cloisite 30B, 10A and 25A revealed a strong interaction with PET chains. In these samples, the maximum level of delamination was found in samples containing Cloisite 25A and 30B.
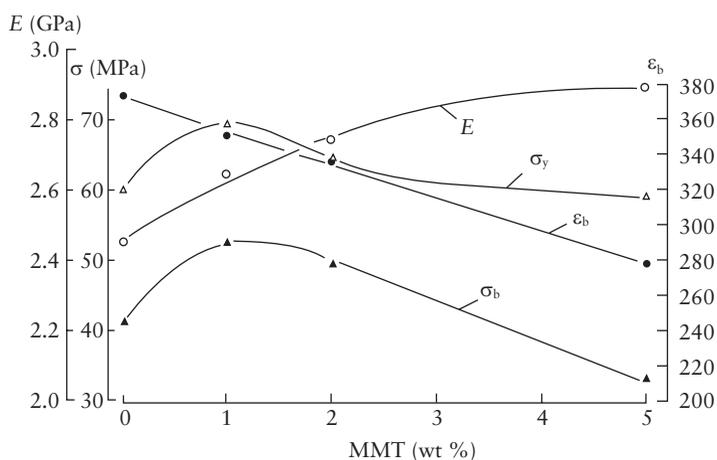


**Figure 3.2** Yield strength ($\sigma_y$), ultimate tensile strength ($\sigma_b$), ultimate deformation ($\varepsilon_b$) and elastic modulus ($E$) of rPET/OMMT nanocomposites at different concentrations of OMMT. Reproduced with permission from R. Merijs Meri, J. Zicans, R. Maksimovs, T. Ivanova, M. Kalnins, R. Berzina and G. Japins, *Composite Structures*, 2014, **111**, 453. ©2014, Elsevier [45]

Moreover, the observations confirmed that the Cloisite 25A nanoparticles were better dispersed in the rPET matrix, compared with nonmodified natural MMT

(Cloisite Na$^+$) [36, 44]. Cloisite 25A which has long alkyl side groups could offer better tensile properties. However, both nanoclays had a beneficial effect on the dimensional stability of rPET. Finally, it seems that the Cloisite 25A type of OMMT induced better properties in the rPET nanocomposites.

Additionally, the two-step modification of Na-MMT with 1,2-dimethyl-3-octadecyl-1 H-imidazol-3-ium chloride (MMT-IM) and then with [3-(glycidyloxy)propyl] trimethoxysilane (MMT-IME) was performed [42]. The modifications led to the considerable enhancement of the Young's modulus of rPET, especially by MMT-IME. Moreover, the rPET/MMT-IME nanocomposite introduced a larger melt viscosity and storage modulus compared with the MMT-IM system. Although the neat matrix showed Newtonian behaviour over the whole range of shear rates, the addition of modified nanoclays increased the complex viscosity at low shear rates. The enhanced melt viscosity and elasticity of rPET nanocomposites at higher shear rates can be applied in extrusion, injection and blow moulding technologies.

Kracalik and co-workers [43] also silanisated a commercial OMMT, such as Cloisite 25A, 10A and 30B. The modification of Cloisite 25A increased the homogeneity of silicate layers in rPET, while the additional modification of Cloisite 10A and 30B resulted in decreased levels of both the delamination structure and melt viscosity. The silanisation of Cloisite 10A and 30B created a significant loss of melt strength, due to the higher water retention of silicate layers as well as the chemical reactions between the organic groups of the modifier. In addition, the prepared samples showed a shear thinning behaviour, produced by the disruption of network structures and orientation of nanoparticles in the flow.

Some authors have blended waste PET with different polymers and nanofillers. Yesil [51] studied the properties of rPET/PEN/MWCNT with two types of functional elastomers including a terpolymer of ethylene-ethyl acrylate-maleic anhydride (E-EA-MAH) and a terpolymer of ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) to improve the miscibility between rPET and PEN. Both elastomers enhanced the miscibility between rPET and PEN, as shown by thermomechanical tests. The morphological images showed that the samples containing E-EA-MAH exhibited better elastomer phase dispersion with smaller domain sizes, which demonstrated better mechanical properties than those containing E-MA-GMA. The addition of MWCNT improved the mechanical properties of the samples containing each type of elastomer. Also, the samples prepared with E-MA-GMA exhibited higher electrical conductivity values, compared with those containing E-EA-MAH, due to differences in the selective distribution of CNT particles between the polymer phases in the samples.

Kerboua and co-workers [49] also studied a blend of rPET and virgin PMMA with OMMT. It was observed that 2 wt% of Nanofil2 OMMT significantly changed the

blend morphology. An increase in OMMT loading from 2 to 5 wt% considerably reduced the particle size, while it became impossible to distinguish the dispersed PMMA domains at higher OMMT loadings; hence demonstrating the strong interfacial activity exerted by the nanoclay in this polymer pair. Also, the addition of OMMT enhanced the strength, modulus, viscosity and dynamic storage at low frequencies.

Shi and co-workers [50] also incorporated $SiO_2$ nanoparticles in an rPET/ABS/ acrylonitrile-acrylic-styrene copolymer (AES) blend. The uniform dispersion of nanoparticles [1 part per hundred matrix parts (phr)] in rPET/ABS was illustrated, in which the $SiO_2$ nanoparticles were mainly distributed in the rPET phase. The rPET/ ABS/AES blends did not act as a tough polymer, but a substantial improvement of impact and tensile strength was obtained when using $SiO_2$ nanoparticles. As discussed, the simultaneous addition of nanofillers and other polymers (virgin or recycled) to rPET can be an efficient technique for the improvement of rPET properties.

Zahedi and co-workers [46] carried out the alcoholysis of rPET using industrial products, as a new method. In this process, rPET was partially depolymerised using excess ethylene glycol (EG) in the presence of manganese acetate, which acted as a transesterification catalyst in the manufacture PET oligomers. Moreover, the influences of reaction time, EG/PET molar ratio, catalyst concentrations and particle size of rPET on the partial glycolysis reaction were investigated based on the Box-Behnken method of experimental design. The optimal conditions to synthesise the PET oligomer (with a melting point of about 180 ºC) for a 2 h glycolysis reaction time were an EG/PET molar ratio of 2, no catalyst and using PET granules. Maleated PET, as a compatibiliser for preparing PET nanocomposites, was then produced *via* a reaction between a maleic anhydride (MA)/phthalic anhydride mixture and optimised PET oligomers. Hence, the melt mixing of maleated PET with organoclay produced a good dispersion of layered silicate in the maleated PET matrix. Moreover, the extent of depolymerisation was enhanced upon increasing the EG/PET molar ratio, the amount of catalyst and reaction time.

### 3.3.3 Nanocomposites from Recycled Polypropylene

Cengiz [53] studied a recycled polypropylene (rPP)/organoclay nanocomposite containing ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) and polypropylene-grafted-maleic anhydride (PP-*g*-MA) compatibilisers. The rPP/ Cloisite 15A nanocomposite provided the highest improvement in mechanical properties. PP-*g*-MA was indicated as a better compatibiliser and furthermore, the improvement of both tensile and impact properties were better at a compatibiliser to clay ratio of 3. In addition, a significant enhancement of dispersion level as well

as mechanical properties was observed at the extrusion temperature of 180 °C and screw speed of 350 rpm.

Also, it was found that the nanoclay loading of 4 wt% and PP-*g*-MA content of 20 wt% led the best impact and tensile strength [52]. Furthermore, the addition of PP-*g*-MA did not improve the nanocomposite performance due to a portion of PP-*g*-MA dispersing in the matrix, which disturbs the homogeneity of the nanocomposite.

The effect of $CaCO_3$ nanoparticles on virgin PP and rPP was studied by Elloumi and co-workers [54]. A nonuniform dispersion of nanoparticles in the matrix was shown. Also, the reduction of ductility by $CaCO_3$ nanoparticles indicated a decrease in the matrix deformation, attributed to the introduction of mechanical stresses by nondeformable particles

In addition, Long and co-workers [55] prepared an rPP/CNT nanocomposite by melt mixing, in which the tensile strength and elongation at break increased with increasing CNT content up to 3 wt%. However, a downturn in mechanical properties occurred at 5 wt% of CNT, due to the presence of small bundles of CNT in these samples. Moreover, the thermal degradation of the nanocomposite shifted to higher temperatures as the content of CNT increased. In addition, the additional mass loss was stopped as the temperature of the rPP/CNT nanocomposite was raised from 700 to 1,000 °C.

In one study, rPP and recycled polyethylene (rPE) were blended with two compatibilisers, polyethylene-grafted-maleic anhydride (PE-*g*-MA) and ethylene propylene diene monomer (EPDM) copolymer, and OMMT [56]. Scanning electron microscopy (SEM) micrographs showed that the blend with EPDM exhibited a better compatibilisation than PE-*g*-MA. The presence of OMMT caused an increase of the storage modulus and loss modulus; additionally, OMMT improved the thermal stability.

Mural and co-workers [57] also optimised the mechanical properties of an rPP and recycled high impact polystyrene (rHIPS) blend at a composition of 70/30 wt%. Consequently, this composition was mixed with a styrene-ethylene-butylene-styrene (SEBS) block copolymer triblock copolymer and Cloisite 20A OMMT. Using X-ray diffraction, the samples containing 3 wt% of nanoclay were found to lack the characteristic nanoclay peak, which indicated the mixed intercalated and exfoliated clay layers where the intercalated layers were further pushed toward the interphase [76]. The incorporation of a compatibiliser and nanoclay also improved the thermal stability of the PP/HIPS blend. SEBS and nanoclay performed as an interfacial compatibiliser, which led to the reduction in particle size of rHIPS and the promotion of interfacial adhesion.

The optimised conditions for the preparation of rPP nanocomposites are briefly expressed in **Table 3.3**. The low content of different nanofillers such as OMMT, CaCO₃ and CNT has a positive effect on rPP, and the PP-*g*-MA compatibiliser leads to a large improvement of performance. In addition, the nanofiller improved the blend of two waste polymers, especially in the presence of a compatibiliser, by enhancing the interfacial adhesion.

| Table 3.3 Optimised conditions for rPP nanocomposites | | |
|---|---|---|
| Parameter | Optimal condition | References |
| Nanofiller level | 4 wt% of nanoclay | [52] |
| | 2 wt% of Cloisite 15A | [53] |
| | 3 wt% of CaCO₃ | [54] |
| | 3 wt% of CNT | [55] |
| Compatibiliser content | 20 wt% of PP-*g*-MA | [52] |
| | Compatibiliser to organoclay ratio of three | [53] |
| Process condition | 180 ºC and 350 rpm | [53] |
| Optimisation of PP/HIPS | 70/30 wt% of blend with 3 wt% of nanoclay and 5 wt% of SEBS compatibiliser | [57] |
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### 3.3.4 Nanocomposites from Recycled Polyethylene

Satapathy and co-workers [62] used three different methods to prepare the rPE/nano-fly ash (NFA) composites. They applied the following techniques: i) modification of the rPE matrix by first grafting with MA and then preparing the composite; ii) preparing rPE composites and subjecting them to electron beam irradiation and iii) subjecting the NFA to electron beam radiation first and then preparing the rPE composites. It was observed that the composite prepared using method ii gave the best physical, thermal, mechanical and ageing properties. The dynamic mechanical properties showed that the storage modulus reached the highest value for the irradiated nanocomposites. The results also indicated that the nanocomposites act as excellent stress absorbers, which prevented crack propagation and enhanced the properties upon irradiation with an electron beam.

Lei and co-workers [58] used both PE-*g*-MA and titanate for the compatibilisation of recycled high-density polyethylene (rHDPE) with nanoclay. Both compatibilisers

were successful, but the best results for mechanical properties were obtained at an equivalent content of nanoclay and PE-*g*-MA of 1 wt%. The addition of 2.5 wt% of PE-*g*-MA increased the temperature and rate of crystallisation along with the degree of crystallinity, while the absence of a compatibiliser had a negative effect on these parameters. Moreover, completely exfoliated OMMT platelets were exhibited in the samples produced using the two-step blending method.

Reddy [60] reported that a large improvement of rHDPE properties is obtained upon the addition of a small amount of graphene due to the separation of a single graphene sheet to 1 nm. Graphene has been shown to exert a positive effect on the tensile modulus of rHDPE. It was stated that as little as 0.25 wt% of graphene improved the tensile modulus, dielectric constant (k) and thermal conductivity in an rHDPE nanocomposite. Additionally, the properties improved to a greater degree upon increasing the graphene content.

Hill and co-workers [59] also studied the improvement of mechanical properties of rHDPE through the addition of MMT and bentonite types of nanoclay and cellulose fibre. They found that Cloisite 20A is the most compatible clay for this system, due to its nature. Similarly, it was revealed that bentonite could compete with Cloisite 20A clay in the imparted mechanical properties. For all clay types, an increase in modulus was observed upon the addition of 1 vol% of nanoclay. However, only Cloisite 20A improved the modulus upon the addition of more nanoclay. In the hybrid system containing both nanoclay and cellulose, the effective stiffening and strengthening were provided by nanoclay and cellulose, respectively.

The most favourable conditions for obtaining optimised rHDPE nanocomposites are detailed in **Table 3.4**. It is concluded that only a slight content of nanofillers is enough to increase the rHDPE properties.

| Table 3.4 The most favourable conditions to fabricate rHDPE nanocomposites | | |
|---|---|---|
| Parameter | Optimal condition | References |
| Nanofiller content | 1 wt% of nanoclay | [58] |
| | Cloisite 25A | [59] |
| | Higher content of graphene (maximum 8 wt% was reported) | [60] |
| Compatibiliser | 1 wt% of PE-*g*-MA | [58] |
| | PE-*g*-MA especially at higher clay loadings | [59] |
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### 3.3.5 Nanocomposites from Recycled Polyvinyl Chloride

Andricic and co-workers [64] mixed both virgin PVC and CaCO$_3$ nanoparticles into a waste laminate containing PVC, CaCO$_3$ and PP. The SEM images illustrated the agglomeration of the nanofiller due to the differences in polarity of the polymer and nanofiller, as well as insufficient dispersion during the mixing process. The CaCO$_3$ filler created a new interlayer between the two polymer phases which improved their compatibility. PVC and PP could not be efficiently recycled without some compatibility improvement. The mechanical properties of the samples with a smaller PP content improved as the filler content increased, while the mechanical properties reached their maxima at about 6 wt% of CaCO$_3$ in the samples containing a higher PP content.

Moreover, rPVC/clay nanocomposites were prepared using modified MMT (Cloisite 30B) [63]. The fully exfoliated clay layers were depicted throughout the rPVC matrix. The mechanical properties of the nanocomposite increased for various clay contents, i.e., 1, 3, 5 and 10 wt%. Moreover, the thermal decomposition behaviour of the nanocomposite was enhanced upon the addition of nanoclay. It was also found that the storage modulus of the nanocomposite containing 10 wt% of nanoclay was 11 times greater than that of neat rPVC at 55 °C. In addition, the coefficient of thermal expansion reduced upon the addition of OMMT.

### 3.3.6 Nanocomposites from Other Waste Polymers

A superabsorbent nanocomposite based on partially neutralised acrylic acid, recycled PS foam and Na-MMT was prepared *via* emulsion polymerisation [65]. The results indicated that the acrylic acid monomer had successfully grafted onto the PS chains and the layers of Na-MMT were exfoliated after copolymerisation. Moreover, the addition of Na-MMT not only improved the thermal stability of the samples, but also increased the content and rate of water absorbency.

In addition, the recycled expanded polystyrene and TiO$_2$ were mixed *via* the solution method [67]; the transmission electron microscopy images indicated that the nanocomposites had an average particle size of 6–12 nm. The nanocomposite samples had greater polymer stability and higher discoloration efficiency for aqueous methylene blue solutions, due to the incorporation of TiO$_2$ nanoparticles.

The addition of small amounts of commercial organoclays (Cloisite 15A and 30B) to recycled polycarbonate (rPC) was evaluated [70]. The results showed that the effect of the nanoclays on polymer degradation during the fabrication process depends on the amount of clay and the chemical nature of the organic modification. It was demonstrated that when small amounts of the appropriate clay are used, polymer

degradation is minimised and an improvement of some properties is achieved. In addition, thermogravimetric analysis curves indicate that the organoclays delay the degradation of PC chains at high temperatures and also cause more charring at the end of the experiment.

Mahanta and co-workers [71] prepared a blend of rPC, recycled acrylonitrile-butadiene-styrene (rABS) and nanoclay, Cloisite 30B or Cloisite 15A. The blend was compatibilised with both PP-*g*-MA and solid epoxy resin. The mechanical properties of the rABS/rPC blend without a compatibiliser decreased in comparison to neat matrices. However, upon the addition of 5 wt% of a PP-*g*-MA compatibiliser, the mechanical properties improved. Similarly, further addition of the epoxy led to a synergistic behaviour in mechanical performance, particularly the modulus and tensile strength. Also, a greater improvement of the modulus was achieved in the rPC-rich blend by simultaneously adding two nanoclays. The thermal stability of the blends compatibilised with PP-*g*-MA and epoxy exhibited positive thermal properties.

Martin and co-workers [68] also studied the nanocomposites of recycled PMMA with both natural and organically modified MMT. They reported that the tensile modulus increased upon increasing the content of both nanoclays, which resulted in nanocomposites with attractive mechanical, transparency and thermal properties.

Moreover, Zhang and co-workers [69] improved the mechanical properties of recycled glass fibre reinforced flame retardant PBT with three types of nanoparticles including $SiO_2$, OMMT and mica. A strong adhesion, which acts as an effective bridge to pass the stress to the nanoparticles, was provided in these nanocomposites. The addition of OMMT caused a reduction of impact strength, due to a reduction in chain mobility. In addition, the heat distortion temperature increased upon the addition of $SiO_2$ and mica. Furthermore, the nanoparticles did not significantly affect the electrical and flame retardant properties.

The effect of CNT on the mechanical and electrical properties of waste rubber from wet tyres was investigated [73]. The SEM images (**Figure 3.3**) showed that the aspect ratio of the neat CNT ($\alpha = 83$) decreased during the fabrication process with recycled rubber ($\alpha = 68$), perhaps due to the destruction of CNT during the process. The results indicated that the toughness and fracture energy of the recycled rubber monotonically increased as a result of CNT addition. Moreover, the modulus of nanocomposites increased by 28 times when using 5 wt% of CNT. The cyclic stress-strain measurements also indicated that the hysteresis and dissipation energy decreased upon increasing the cycle number and increased as a function of the CNT concentration. Moreover, the addition of CNT to the recycled rubber improved the electrical conductivity by more than two orders.
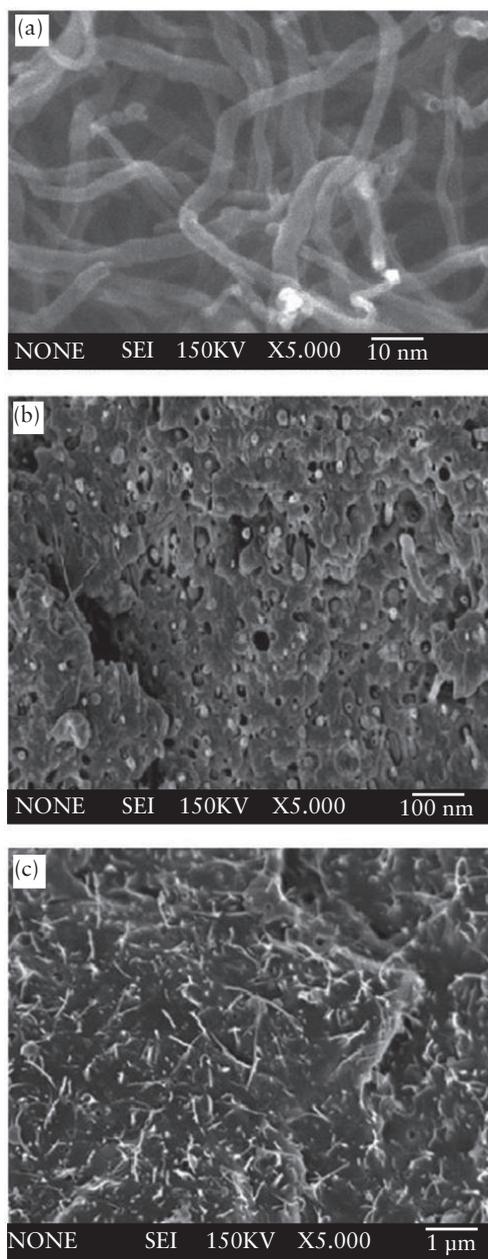
**Figure 3.3** SEM images of a) CNT; b) waste rubber/1 wt% CNT; and c) waste rubber/5 wt% CNT samples. Reproduced with permission from W.E. Mahmoud, E. El-Mossalamy and H. Arafa, *Journal of Applied Polymer Science*, 2011, **121**, 502. ©2011, Wiley [73]

In addition, recycled polycaprolactone-based thermoplastic polyurethane (rPTPU) was mixed with different commercial organoclays (Cloisite 10A, 15A and 30B) [72]. The nature of the OMMT organomodifier strongly influenced the properties of the nanocomposites. Among different nanoclays, Cloisite 30B exhibited a strong polar interaction with the rPTPU matrix, which facilitated the intercalation of clay platelets and the formation of the delaminated nanocomposite. The results also showed that the melt flow index (MFI) and mechanical properties of rPTPU deteriorate with increasing mastication time. Additionally, OMMT slightly reduced the tensile properties and MFI, but accelerated the hydrolytic degradation process. Moreover, the degradation of rPTPU nanocomposites containing organoclays of higher hydrophilicity proceeded faster than those with a hydrophobic nature.

### 3.3.7 Evaluation of Interfacial Adhesion by Modelling Mechanical Properties

The experimentally measured tensile modulus and strength of various nanocomposites from waste polymers were fitted to micromechanics models to evaluate the interfacial adhesion [35]. **Table 3.5** shows the studied samples and the calculated parameters. As noted in **Table 3.5**, the 'a' adhesion parameter, using the Nicolais–Narkis model [77, 78], was 0.59 for the PP/CaCO$_3$ nanocomposite, which is lower than 1.21 and demonstrates good interfacial adhesion between rPP and the CaCO$_3$ nanofiller. Moreover, smaller 'a' values were calculated using the Kunori–Geil model [79], which means less stress concentration and good interfacial adhesion in the nanocomposites from waste polymers. Also, the same trend of calculations was observed using the Piggott–Leidner model [80], where a low 'a' parameter, indicating strong interfacial adhesion, was obtained for reported samples.

Additionally, the obtained values of the 'B' adhesion parameter using the Pukanszky model [81, 82] varied from a minimum of 1.74 to a maximum of 21.45 for the studied samples. These findings confirmed that the nanofillers introduce a better interfacial interaction to the recycled polymers. Moreover, the calculated 'ζ' (adhesion) using the Sato–Furukawa model [83, 84] were lower than zero. Since a better modulus is achieved by inferior 'ζ' values, the calculated 'ζ' data indicated that the small content of nanofillers introduce a significantly improved modulus in the nanocomposites from waste polymers. In conclusion, the performed analysis confirmed that the nanofillers can yield considerable interfacial interaction with waste polymers. As known, the greatest advantages of nanocomposites, such as modulus and strength, are produced *via* perfect interfacial adhesion between the nanoparticles and waste polymer matrices.

Table 3.5 Calculated interfacial parameters from different models

| No. | Sample | a (Nicolais–Narkis) | a (Kunori–Geil) | a (Piggot–Leidner) | B (Pukanszky) | ζ (Sato–Furukawa) | References |
|-----|--------|---------------------|-----------------|--------------------|----------------|--------------------|------------|
| 1 | PET/clay | – | -17.63 | -23.28 | 21.45 | -2.5 | [37] |
| 2 | PET/clay | – | -4.75 | -6.83 | 8.48 | -18 | [38] |
| 3 | PET/clay | – | -3.27 | -3.8 | 6.9 | -4 | [40] |
| 4 | PP/clay | – | -10.77 | -15.67 | 15.6 | – | [52] |
| 5 | PP/clay | – | -1.49 | -1.52 | 4.91 | – | [53] |
| 6 | PP/CNT | – | -4.35 | -7.13 | 9.3 | – | [55] |
| 7 | PP/CaCO$_3$ | 0.59 | 1.52 | 1.48 | 1.74 | – | [54] |
| 8 | HDPE/clay | – | 1.61 | 1.61 | 1.76 | – | [58] |

## 3.4 Conclusions and Future Trends

The recycling technique, i.e., a series of processing operations carried out on waste, is the best way to produce secondary materials from waste polymer products. A simple and efficient method to recycle waste plastics is the application of nanofillers and the development of new nanocomposites with improved properties compared with waste polymers.

As extensively discussed, the application of nanofillers such as MMT (preferably OMMT), $CaCO_3$, CNT, $SiO_2$ and so on can be an effectual technique for recycling waste polymers, composites and blends. The goods prepared through the addition of nanoparticles to waste polymers can exhibit unexpectedly improved properties, low weight, ease of processing and low cost which are not simultaneously found in other manufactured products. Nanofillers can compensate for the shortcomings of waste polymers and thus, result in the improvement of mechanical, thermal, optical and barrier properties using a low content of nanofillers. It was also indicated that a suitable compatibiliser can significantly improve the interfacial interactions and produce a recycled product with efficient characteristics.

With the objective of a successful and economical recycling process in which the recycled polymer has largely acceptable properties, considerable effort must be made to encompass all the aspects of recycling in future studies to enhance the competitiveness of these systems. The first step could be the improvement of interfacial adhesion in prepared nanocomposites to achieve better physical and mechanical properties from recycled polymer wastes. Many procedures such as compatibilisation, functionalisation and surface modification could be developed in the future. Furthermore, the addition of effective nanofillers including available nanofillers or a combination of nanofillers will provide further progress and new opportunities in these systems. In addition, the development of fabrication techniques and also, the optimisation of available methods such as melt mixing should be performed, due to its important role in the final properties of recycled products.

The recycling operation of polymers could be increasingly carried out by other approaches: the development of methods and equipment for the separation of waste plastics; improvement of the available methods or development of new techniques for recycling plastic wastes; new ideas for the recycling of mixed polymer wastes and development of novel energy-recovery procedures. Furthermore, future studies must also consider all features of effective waste management. They must calculate the cost and energy requirements for any recycling process to determine the net benefits of recycling from an economical approach.

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