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ABSTRACT

Recycling process seems to be the most efficient way to reduce ecological impacts of used polymers. Nevertheless, the properties of the recycled PP polymer are proved to be insufficient during its reuse, particularly with regard to its thermo-mechanical and rheological behaviors. The incorporation of nanoparticles as fillers into polymer matrix seems to be one of the most successful solutions to upgrade recycled PP polymer. This paper presents an overview on the application of different nanofillers such as clay, calcium carbonate ($CaCO_3$), Silica (SiO_2), Zinc Oxide (ZnO), carbon black (CB), carbon nanotubes (CNT), antioxidizers and others into recycled PP matrix. Literature works on the effects of nanofillers on obtained nanocomposites are extensively studied. The first section deals with PP recycling and its impact on thermal, mechanical and rheological properties of the polymer. Then, the second part summarizes recent studies on the effects of nanoparticles incorporation on thermo-mechanical and rheological properties of recycled PP. Finally, recyclability of PP-based nanocomposites is discussed.
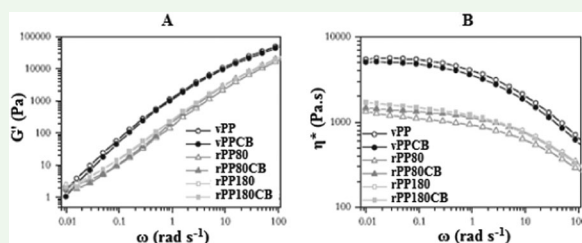
1. Introduction

Polypropylene (PP) polymer is widely used in several applications, such as automotive components, aerospace, laboratory equipments, plastic parts, food packaging, geotextiles and containers. Because of its wide consumption, each year, millions of tons of polypropylene are released back into the environment. One of the methods to reduce negative environmental impacts consists of reusing PP wastes throughout a recycling process to produce new products with low production cost. However, some main problem with PP recycling is degradation of polymer during extrusion which leads to degradation of the properties of the final product.

As is well known, we can achieve considerable enhancement of mechanical, thermal, optical and barrier properties by incorporation of nanofillers (with low content) into polymer matrix (1). 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 (2). The enhanced properties are provided without any increase in density and cost or reduction of the light transmission properties of the base polymers.

Therfore, nanofillers could be used to increase the properties of waste polymers. Furthermore, the quantitative analysis of interfacial adhesion, in prepared nanocomposites from waste polymers, showed a strong interfacial adhesion between the nanoparticles and waste polymers and justified the recycling of polymers via the incorporation of nanoparticles (3). In the last few years, many researchers have used nanofillers to recycle waste PP polymers (4–18). These studies investigating polymer recycling via the incorporation of nanofillers with improved nanocomposites' properties are reported in Table 1.

Table 1. Nanofillers mixed with recycled PP and improved nanocomposites' properties.

Nanofiller	Improved properties	References
Clay	Mechanical, thermal and rheological	(4,5)
Montmorillonite (MMT)	Mechanical and gas barrier	(6,7)
Calcium Carbonate (CaCO3)	Hardness and impact strength	(8,9)
Carbon nanotubes (CNTs)	Thermal stability and tensile strength	(10,11)
Zinc Oxide (ZnO)	Rheological and photodegradation	(12,13)
Silica (SiO2)	Thermal and electrical conductivity	(14,15)
Boehmite Alumina(BAL)	Mechanical and thermal	(16,17)
Graphene (GN)	Mechanical and electrical	(18)

There are three common methods used to enhance polymers with nanofillers to produce nanocomposites: melt compounding, *in situ* polymerization and the solvent method. Melt compounding – or processing – of the nanofillers into polymer is done simultaneously when the polymer is being processed through an extruder, injection molder, or other processing machines. With *in situ* polymerization, the nanofiller is added directly to the liquid monomer during the polymerization stage. Using the solution method, nanoparticles are added to a polymer solution using solvents such as toluene, chloroform and acetonitrile to integrate the polymer and nanofiller molecules. Since the use of solvents is not environmentally friendly, melt processing and *in situ* polymerization are the most widely used methods of nanocomposite production (19).

In this review, a comprehensive study of literature works on the application of nanofillers in the recycling process of PP polymers is carried out which can help researchers and industrials in their potential works.

2. Polypropylene recycling

There are several techniques for recycling of waste polymers including mechanical, chemical and thermal recycling (20).
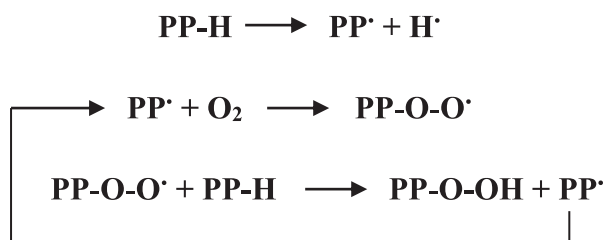
Mechanical recycling process is a physical method, in which the plastic wastes will be converted into flakes or granulates of appropriate quality for manufacturing, where they would be melted by extrusion to make new products. In general, the mechanical recycling process consists of contaminants removal, grinding into flakes and pellets, washing, drying and melting (21).

Chemical recycling process consists of converting the polymer into monomer or other basic chemicals by chemical reactions. Then, these monomers may be reused for polymerizations into new plastics to produce other related polymeric products. Condensation polymers like polyethylene terephthalate (PET) or Nylon, can undergo different chemolysis reactions (hydrolysis, alcoholysis, acidolysis and glycolysis) to produce mainly the monomers from which they have been produced or other oligomers. In contrast, vinyl polymers, such as polyolefins (polypropylene PP and polyethylene PE) cannot be degraded with simple chemicals to their monomers due to the random scission of the C–C bonds. Two main chemical recycling routes are the thermal and catalytic degradation of these polyolefins (22).

Thermal recycling consists of breaking down the chemical structure of the polymer at high temperatures in the absence of sufficient oxygen for combustion. Thermal recycling can be applied to all types of polymers. When reasonably pure compounds can be recovered, they can be used as raw products, whereas when the products are a complex mixture and separation is difficult, products are often used as fuel. Degradation can cause some deterioration effects such as a decrease in molecular weight, branching formation of chemical groups, etc., and the new material created from the recycled plastic can have reduced physical properties (23,24).

From an ecological point of view, mechanical recycling is the ideal solution for the valorization of plastics especially polypropylene. However, the main problems in the recycling of PP arise from the easy degradability of this polymer during processing and recycling operations. Heat and mechanical stress strongly modify the structure and the morphology and thus the characteristics of polypropylene. Although the degradation behavior is common to all polymeric materials, the effects of thermomechanical degradation on PP are dramatic because of the tertiary carbon present in the chain of this polymer. The degradation of PP occurs through the following series of reactions describing its oxidative degradation:

$$PP\text{-}H \longrightarrow PP^{\bullet} + H^{\bullet}$$

$$PP^{\bullet} + O_2 \longrightarrow PP\text{-}O\text{-}O^{\bullet}$$

$$PP\text{-}O\text{-}O^{\bullet} + PP\text{-}H \longrightarrow PP\text{-}O\text{-}OH + PP^{\bullet}$$

The degradation kinetics depends on many factors, in particular the type and level of the external stresses and morphological characteristics of the polymer (molecular weight, crystallinity, etc.). Finally, oxygenated groups, formed during oxidative degradation, act as catalysts of the reactions, accelerating the degradation rate. The main effects of the degradation phenomena on the PP structure are the decrease of the molecular weight,

change of the molecular weight distribution (MWD) and formation of oxygenated functional groups. Hence, the properties of the recycled polymer (rheological, mechanical, etc.) are strongly altered as a result of changes in structure and morphology (25).

Incarnato et al. (26) have studied the effect of repetitive recycling operations on the rheological and mechanical properties of virgin PP (vPP). They have shown that the polymer viscosity decreases with the increase of the recycling operations (Figure 1) and this effect is more evident in the low-frequency region (high solicitation duration). This was explained by the decrease of the molecular weight (MW) of the PP after recycling and a narrowing of MWD of the polymer.

In order to study the effect of recycling operations on the mechanical properties of vPP, Jansson et al. (27) have examined PP polymers using a simulated recycling test procedure consisting of repeated cycles of extrusion and accelerated thermo-oxidative aging. Figure 2 shows the extruded/aged series where PP was first extruded 10 times, and then aged for a longer period of time. They depicted that the elongation slowly decreased upon extrusion. On the subsequent aging, step 11, the elongation dropped considerably. After multiple steps, the elongation at break was only 5%.

In an other work, Aurrekoetxea et al. (28) have found that elastic modulus (E) increases with the number of recycling steps, while elongation at break (εb) and fracture toughness (K$_{IC}$) decrease (Figure 3). Through thermo-mechanical analyses, these authors have confirmed that the increase in elastic modulus of recycled PP (rPP) seems to be correlated with the higher degree of crystallinity. In fact, a crystalline material is significantly stiffer than the equivalent plastic in its amorphous condition (29). Indeed, at room temperature, the amorphous phase of the PP is above the glass transition temperature (Tg), and the crystalline region is
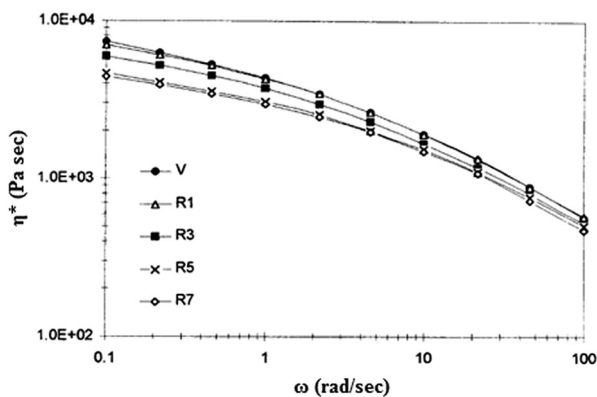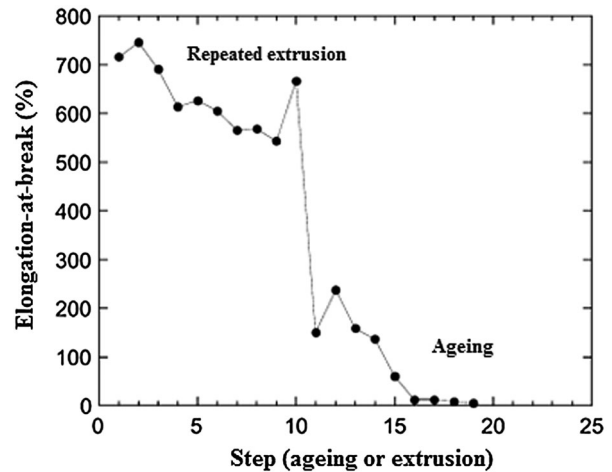

Figure 2. Elongation at break of PP after repeated extrusion followed by aging (27).

below its melting point (Tm), so the higher the crystallinity is, the higher material's strength is. The lower elongation at break is attributed to the decrease in the molecular weight. Fracture toughness also decreases for the recycled materials due to the higher yield stress and the lower tie-molecule density (30). Therefore, lower molecular weight inserts more chain ends into the structure, resulting in fewer chains completely integrated into the crystal to sustain stress during tensile loading, causing failure at lower elongation (31).

The effect of the recycling process on thermal properties of PP was investigated by Phuong et al. (32). Authors have shown that onset crystallization temperature (Tc) increases as a function of the number of extrusion cycles. They also observed that the melting point (Tm) decreases in comparison with virgin PP one (Figure 4). The difference between the temperature of fusion for the virgin and recycled polypropylenes and the lowest value is attributed to the decrease in the molecular weight resulting from the degradation. It should be remembered that for a lower molecular weight, there corresponds a higher mobility resulting in a higher crystallinity, but the resulting crystals will have more imperfections. As mentioned before, such imperfections are mainly due to the formation of free radicals during rupture of the molecular chains.

On the other hand, the effect of recycling operations on thermal properties of an impact PP copolymer was investigated by Elloumi et al. (33). They determined that both melting enthalpy and crystallization degree increase with the number of recycling operations. This increase can be explained by the fact that lower molecular weight macromolecules react as nucleating agents allowing polymer chains to fold and build more and more crystal structures. Indeed, it showed that the

Figure 1. Flow curves of virgin and recycled polypropylene at T = 240°C (26).
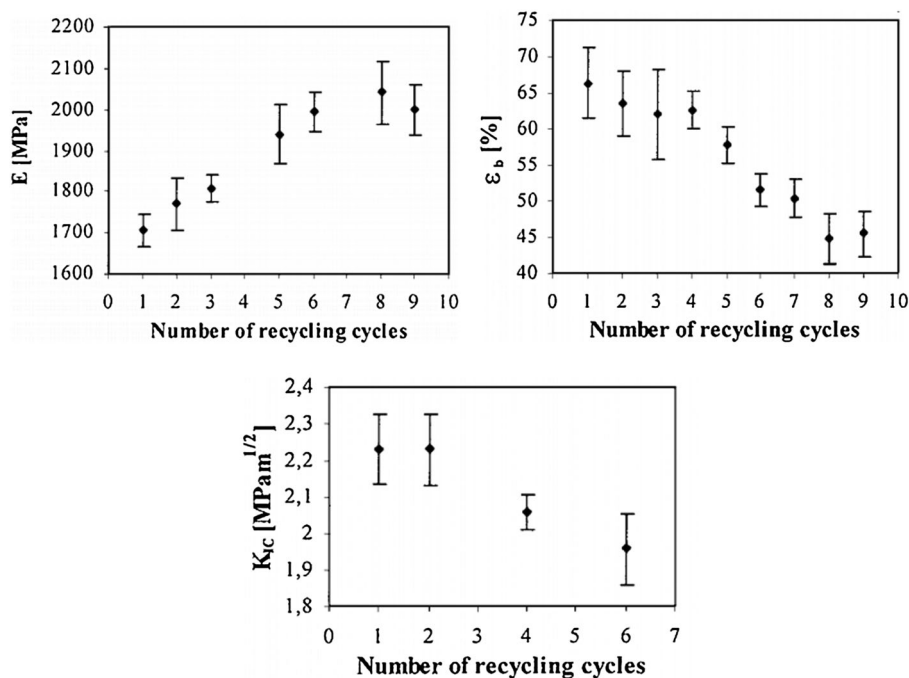
Figure 3. Elastic modulus (E), elongation at break (εb) and fracture toughness (K_{IC}) as a function of the number of recycling cycle (*28*).
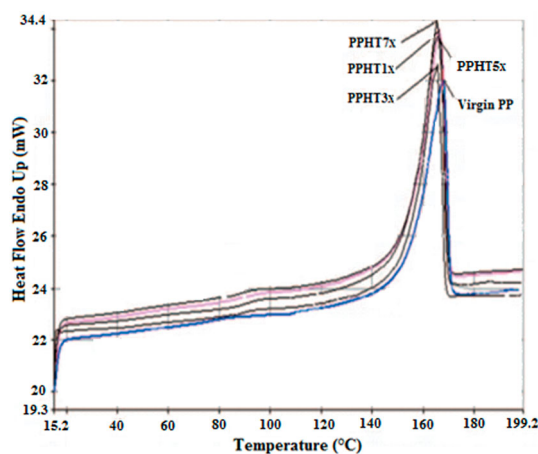
crystal content increase with recycling operations (Table 2) which is attributed to the recrystallization of the molecule segments released by the scission of macromolecules with repeated injections. Nevertheless, no significant evolution of the crystallization temperature of PP is observed which is not in accordance with the work of Aurrekoetxa (*28*).

In their work, Da Costa et al. (*34*) showed (as illustrated on Figure 5) that the increase in recycling cycles number and extrusion temperature leads to an increase in the crystallinity of PP polymer.

To minimize the effect of recycling, stabilizers, like antioxidants, can be added to the PP polymers. These additives improve the thermal stability, which has the

effect of slowing the oxidation phenomena during the mechanical recycling process. The addition of antioxidants thus makes it possible to avoid, even partially, the degradation of the macromolecules, which limits the loss of the mechanical and thermal properties of the polymers.

Marrone and La Mantia study (*35*) demonstrated that in the presence of stabilizers the elongation at break decreases from 700% to 543% after 5 cycles of recycling, whereas without stabilizers, it dramatically decreases to 20%. However, the addition of these stabilizers constitutes an additional cost in the recycling chain and depends on the further processing route (extrusion, injection molding, etc.) and the end-use of the recycled material (*36,37*).

3. Effects of nanoparticles incorporation on recycled PP

In this section, we will give an overview about several works on the enhancement of recycled PP properties through the adjunction of nanofillers to PP matrix.

Figure 4. DSC thermograms of virgin and recycled PPHT (*32*).

Table 2. Thermal characteristics of recycled PP samples (*33*).

Recycling number	ΔHc (J/g)	ΔHm (J/g)	Tm (°C)	Tc (°C)	X (%)
0	67.1	67.3	166.3	123.0	32.2
1	69.0	69.3	166.5	121.8	33.3
2	70.6	71.7	168.6	122.0	34.4
3	71.0	72.4	167.1	122.4	34.6
4	75.7	78.4	167.4	122.0	37.5
5	77.5	79.6	165.5	123.1	38.0
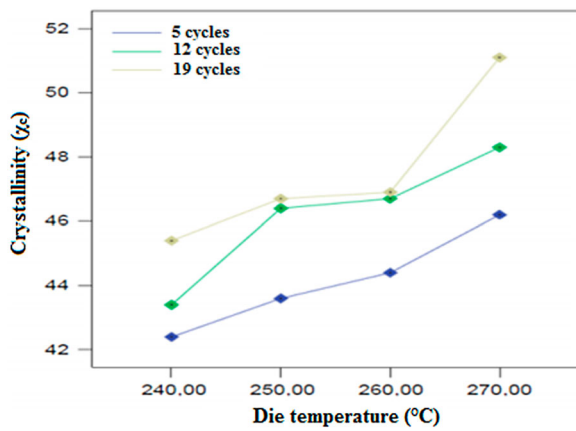
Figure 5. Variation of crystallinity (Xc) with die temperature and cycles of extrusion of rPP (*34*).

Discussed results are limited to most-used nanoparticles, such as montmorillonites (or clays), carbon black (CB), carbon nanotubes (CNT), Shrimp Shell (SS), calcium carbonate ($CaCO_3$), Silica (SiO_2), Graphene (GN), Boehmite alumina (BAL), Ethylene–Octene Rubber (EOR), Zinc Oxide (ZnO) and graphite (C).

3.1. Impact on mechanical properties

Husin et al. (*38*) studied graphene (GN) nanoparticles' performance in improving mechanical properties of recycled polypropylene with crosslinked polyaniline (PANI) prepared via ultrasound extrusion. Their results of tensile tests showed that the improvement in both tensile strength and elastic modulus (Figure 6) was observed in rPP/PANI/GN nanocomposites at 1.5 and 2 phr (parts per hundred rubber) of GN loading. The improvements obtained for the mechanical properties are attributed to the stiffness of the platelets and effective stress transfer between rPP matrix and GN. They also stated that the uniform dispersion of GN in the matrix at these filler concentrations is thought to be responsible for the enhancement of tensile properties.

In their works, Yuan et al. (*39*) and Dong et al. (*40*) concluded that with 4% clay content, tensile modulus is 0.83 GPa, while for 10% clay percentage, it becomes 2.66 GPa. In fact, the increase of clay content limits the mobility of the polymer chains so that tensile modulus is improved. In addition, increasing the clay content increases the shear forces which leads to platelet exfoliation in the matrix.

Later on, Khanjanzadeh et al. (*41*) showed that the tensile strength and Young modulus of rPP increased with the addition of nanoclay (NC) from 0 to 3% by weight (Figure 7).
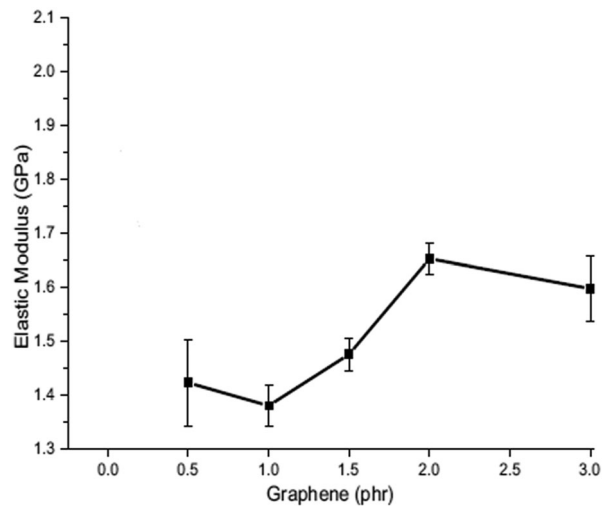

Figure 6. Elastic modulus of rPP/GN nanocomposites (*38*).

The maximum of improvements in tensile strength (20.3%) and modulus (15.6%) was achieved when 3 wt% of nanoclay was incorporated into PP matrix. The increased tensile properties up to 3 wt% nanoclay content may be attributed to the high aspect ratio of stiff silicate layers in the polymer matrix that results in a higher extent of interaction with the polymer chains and good interfacial adhesion between the nanoclay particles and the rPP matrix, so that the mobility of polymer chains is restricted under loading (*42,43*). Similar results were obtained in the case of PP/clay nanocomposites by Mohan et al. (*44*). Also, the tensile modulus (Young's modulus) of PP/clay nanocomposites reached 2.6 GPa in the work of Dong et al. (*40*).

Nevertheless, with further increase in NC loading from 3 to 5 wt%, a decrease in the tensile strength and Young's modulus of the rPP/clay nanocomposites was observed. This can be explained by the fact that the nanoclay was dispersed more uniformly through the polypropylene at low concentrations (under 5 wt%) to increase the surface attraction between the filler and the polymer matrix (*45,46*). The decrease in mechanical properties with increased clay loading up 3% can be attributed to the agglomeration of the nanoclay, resulting in induced local stress concentration in the nanocomposites and reduction in the clay aspect ratio, thereby reducing the contact surface area between the organoclay and the polymer matrix and formation of agglomerated clay tactoids (*47,48*).

Generally, the improvement of tensile properties is obtained in detriment to that of the impact strength. Therefore, Khanjanzadeh et al. (*41*) showed that the impact strength of the rPP composites decreased with the incorporation of nanoclay (Figure 8). This can be explained by the stiffening of polymer chains and
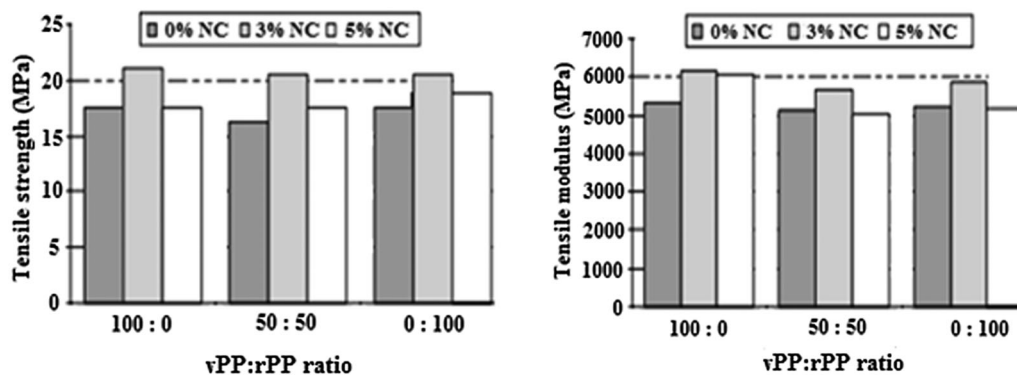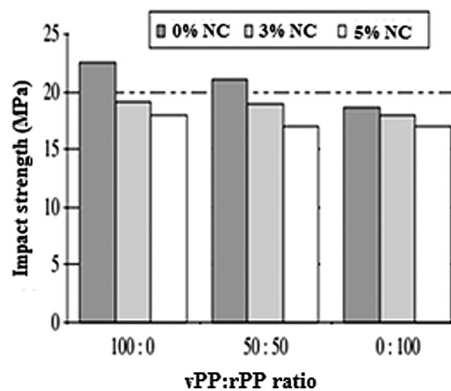
Figure 7. Effects of nanoclay (NC) content on tensile modulus and tensile strength (*41*).

agglomeration of clay particles, which results in absorbing less impact energy. Besides the formation of clay agglomeration at higher nanoclay content, the presence of unexfoliated aggregates and structural voids can reduce the impact strength (*49,50*).

Mohamad et al. (*51*) showed that Shrimp Shell (SS) filler addition decreases the impact strength in rPP significantly (Figure 9). However, the impact strength of rPP/SS composites slightly improves when the filler content is increased. This indicates that the positive contribution of SS to increase toughness in recycled PP composites. Furthermore, it is found that nanocomposites with fine SS consistently show higher impact strength than those with coarse SS. This indicates that the smaller particle size improves the interfacial bonding between the matrix and filler.

Similar results were obtained from the works of Santosa et al. (*52*). In fact, they found that the impact strength is equal to 19.12 kJ/m² for 3% of clay content and 14.37 kJ/m² with 5% clay content. This can be explained, as previously mentioned, by the agglomeration of the clay particles at higher contents.

Indeed, the formation of agglomerates affects the structural stability of nanocomposites, then harms the

absorption of the impact energy and favors crack propagation in the interface. To overcome this problem, some studies have shown that the use of an impact modifier agent improves impact resistance of nanocomposites (*53,54*). The use of an elastomer creates a balance between impact resistance and rigidity.

Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure. They are shaped as long cylinders of covalently bonded carbon atoms, which possess extraordinary electronic, mechanical and thermal properties. CNT has emerged as the most promising nanofiller for polymer composites.

Recently, Gao et al. (*55*) studied rPP/CNT nanocomposites with different CNT fraction prepared by the melting blend method. With increasing CNT content, tensile strength and elongation at break increase firstly and then decrease. When CNT content is 3%, tensile strength and elongation at break are 34.71 MPa and 27%, respectively. The improvement in the tensile properties arises from several factors. CNT particles promote the crystallization of rPP and the crystallites strengthen the composites. Also, CNT nanofillers are well dispersed in the matrix, allowing a more uniform load distribution. In addition, the interaction between the PP chains and CNT enables a more efficient load transfer from the matrix to the nanotubes.

Figure 8. Effect of nanoclay content on notched impact strength (*41*).
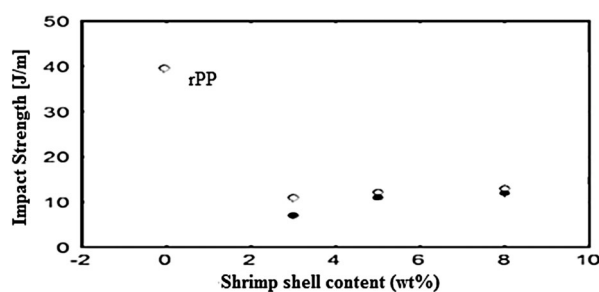
Figure 9. Relation between SS content and impact strength for rPP/fine SS (open diamonds) and rPP/coarse SS (closed diamonds) nanocomposites (*51*).

3.2. Effect on thermal characteristics

Thermal properties of recycled polypropylene nanocomposites are influenced by several characteristic parameters such as the fillers content, the type of surfactant and the elaboration process. In this section, we will give an overview on results of several studies on the enhancement of thermal properties of rPP.

Elloumi et al. (*33*) have shown that no differences of melting and crystallization temperatures can be observed between vPP and rPP reinforced with $CaCO_3$ nanoparticles. On the other hand, these authors indicated that the presence of nanosized $CaCO_3$ in PP matrix has a significant effect to increase crystalline domains. A small decrease in the crystal content of recycled blends, compared with that of virgin blends, is observed up to 10% of fillers content. This was attributed to the effect of the nanoparticles that restrict molecular movements and hinder the packing of molecule segments. When the filler content is 20%, an increase in the crystal content of the rPP, compared to vPP nanocomposite, is observed (Table 3). This could be explained by the nanofiller–matrix interactions and blend morphologies enhancing the interfacial adhesion (*56*).

In the same focus, few years later, Hadi et al. (*57*) studied the effect of $CaCO_3$ nanofillers on crystallinity and thermal conductivity of virgin PP and waste PP. According to their X-Ray Diffraction (XRD) patterns (Figure 10), the nanocomposites show sharp and highly intense peaks while waste PP shows less intense peaks. This may be due to the development of crystallinity in the polymer. The crystallinity increases with $CaCO_3$ content increasing; this is due to $CaCO_3$ nanoparticules filling the hole and orienting the chain so the crystallinity increases.

They found also that the values of thermal conductivity increased with the nanoparticle concentration and crystallinity level increasing. The vPP and rPP polymers show a significant and clear difference for thermal conductivity up to 3% of CaCO3; after that, the convergence occurs gradually up to 10% by weight (Figure 11). This fact can be attributed to the intrinsic thermal conductivity of both nanoparticles and their large surface area which even at lower loadings of nanofillers they are still effective to transfer heat through the samples; at a higher volume fraction, this effect becomes stronger.

In their work, Juan et al. (*58*) studied the effect of Silica Sol (KSol) nanoparticules on the thermal and crystallization behavior of isotactic PP (iPP). Their DSC cooling thermograms clearly showed that the addition of KSol and 2,2′-methylene-bis (4,6-di-tert-butylphenol) phosphate (MDBP-POOH)-modified Silica Sol (PKSol)

Table 3. DSC results for vPP and rPP nanocomposites (*41*).

Sample	Tm_2 (°C)	Tc (°C)	ΔHc (J/g)	ΔHm_2 (J/g)	Xc (%)
vPP	166.4	121.8	69.1	69.3	33
vPP/3%NCC	167.4	121.9	73.8	75.1	36
vPP/10%NCC	167.4	122.2	78.4	82.1	39
vPP/20%NCC	167.7	122.4	83.5	84.2	40
rPP	166.2	122.6	77.5	78.1	37
rPP/3%NCC	166.2	122.7	77.2	66.5	32
rPP/10%NCC	167.1	121.3	69.2	72.2	34
rPP/20%NCC	165.8	122.7	87.5	86.5	41

could increase the crystallization temperature of iPP, from 116.4°C to 118.8°C and 120.81°C, respectively. However, MDBP-POOH alone had little effect on crystallization capacity and even led to a slight decrease of Tc (115.9°C). The results demonstrated that although metal salts of organic phosphate showed good nucleation activity on PP polymer, organic phosphate itself had nearly no obvious effect on the crystallization behavior of iPP. Furthermore, the highest crystallinity Xc (50%) was observed in iPP with 0.2 wt% of PKSol and the addition of MDBP-POOH and KSol led to a relatively small increase of crystallinity of iPP nanocomposites (Table 4).

Furthermore, in the studies of Ataeefard et al. (*59*) and Zare (*60*), a dramatic decrease in the crystallization temperature Tc was remarked. In fact, for a clay content equal to 4%, Tc is equal to 127° C. While, with 10% clay content, Tc declined to 116°C. This may be explained by the addition of clay nanoparticles which act as nucleating agents.

In the research of Zhang et al. (*61*), the authors showed that the melting temperature of PP/clay nanocomposites prepared with 15 Å clay particles modified by an intercalating ammonium ion base is greater than melting temperature of PP/clay nanocomposite prepared with Na montmorillonite particles modified by an intercalator amine base.

In their work, Brachet et al. (*62*) studied the modification of rPP thermal properties by addition of elastomer ethylene–octene rubber (EOR) nanoparticules. Their DSC results showed a small increase of Tm between raw rPP and rPP/EOR nanocomposites from 159.6°C to 160°C. They also estimated that rPP contains a small fraction of PE polymer. The presence of this fraction is either through impurities or within the different PP copolymers used for packaging materials (*63*).

Jarugala et al. (*64*) have studied the influence of Boehmite alumina nanoparticles content on the thermal properties of rPP using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It was found that BAL significantly altered the crystallization temperature and the degree of crystallization of rPP polymer (Table 5).
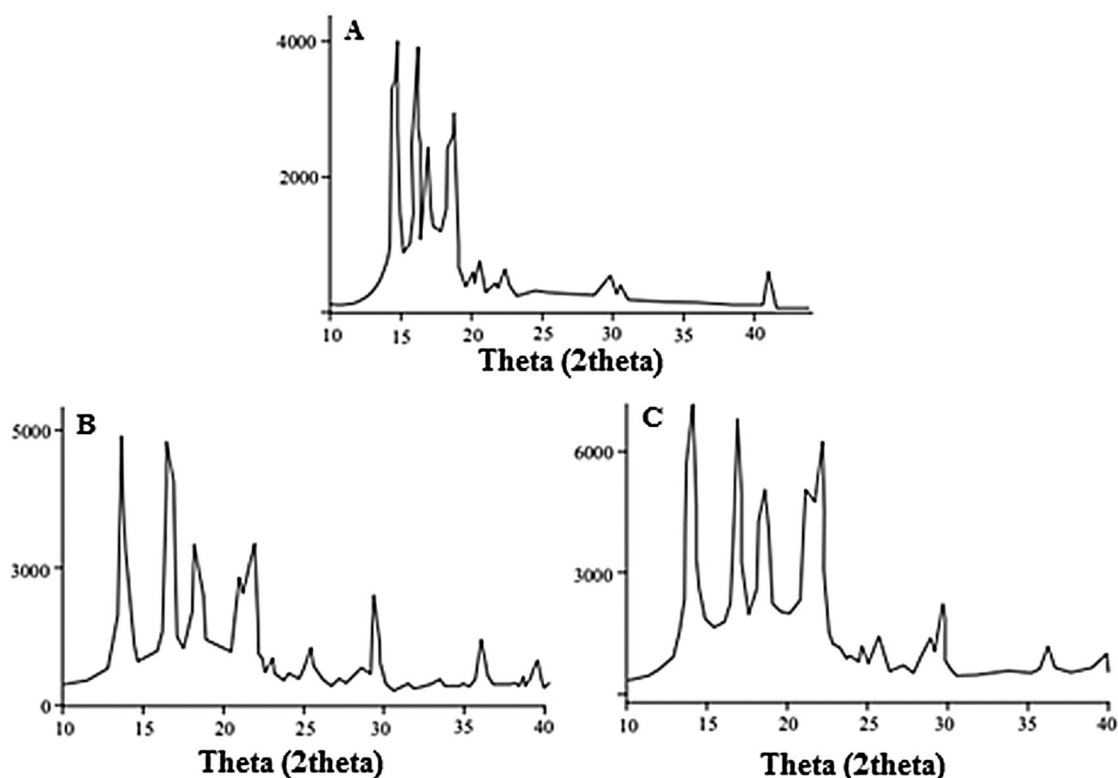
Figure 10. XRD patterns for: (A) waste PP, (B) 5% $CaCO_3$, (C) 10% $CaCO_3$ (*57*).

Other authors as Patnaik et al. (*65*) indicate that the melting temperature of PP shifted to higher values with increasing BAL content. Therefore, the addition of nanofillers enhanced the thermal stability of recycled PP. In cooling scan (Figure 12), it can be observed that the crystallization temperature (Tc) of the nanocomposites is higher than that of raw rPP.

Similar trends were observed by Zhang et al. (*66*) for rPP polymer reinforced with clay nanoparticules. According to DSC thermograms, these authors showed that increasing the clay content decreases the melting point of the nanocomposite compared to raw polypropylene

(Figure 13). This can be explained by the introduction of polypropylene grafted with Maleic Anhydride (PP-g-MA) as compatibilizer, which has a lower melting point, which affects the mobility of macromolecular chains by increasing the interaction between the clay and the matrix.

According to TGA analysis, these authors indicated that the addition of nanofillers enhanced the thermal stability of the rPP nanocomposites. As observed in the thermograms (Figure 14), we can conclude that rPP nanocomposites are more thermally stable than pure
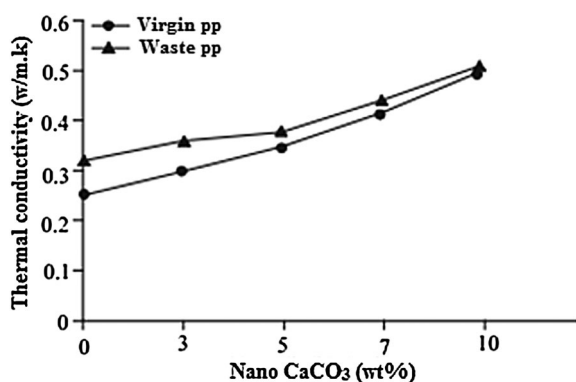
Figure 11. Thermal conductivity of virgin and waste PP at different $CaCO_3$ concentrations (*57*).

Table 4. DSC results of iPP/Silica Sol nanocomposites (*58*).

Sample	ΔHm (j.g^{-1})	Tm (°C)	Tc (°C)	Xc (%)
iPP	82.77	160.9	116.35	39.60
iPP/MDBP-POOH	87.47	163.98	115.78	41.9
iPP/KSol	98.63	162.01	118.78	47.2
iPP/PKSol	104.2	162.15	120.81	50.0

Note: ΔHm – melting enthalpy.

Table 5. DSC analysis of rPP/BAL nanocomposites (*64*).

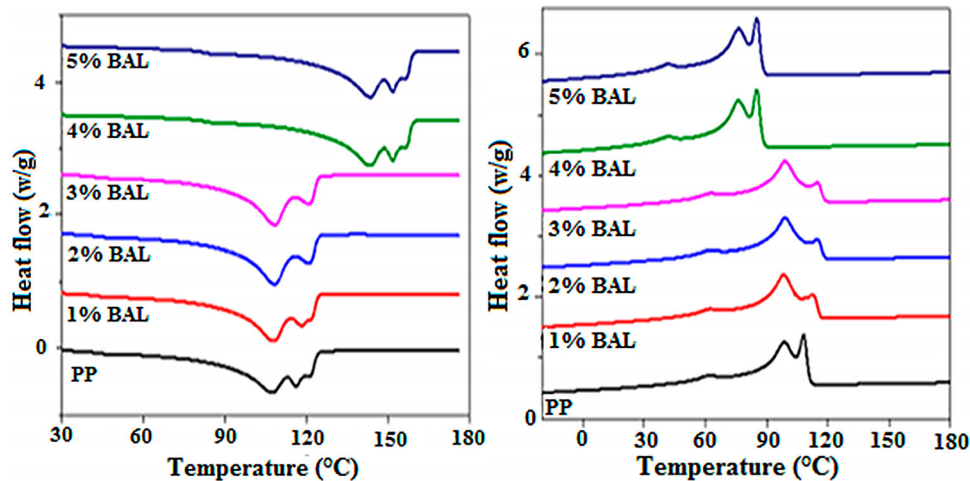|	Tm (°c)	Tc (°C)	ΔHm (w/g)	Xc (%)
rPP	107	98	78.3	41.7
rPP/1%BAL	108	98.2	79.6	45.0
rPP/2%BAL	108	98.7	84.1	47.8
rPP/3%BAL	109	99.3	83.7	45.3
rPP/4%BAL	133	76.3	81.1	42.7
rPP/5%BAL	132	76.2	82.5	43.6

Figure 12. DSC analysis of rPP/BAL nanocomposites (*65*).

rPP. The enhancement of thermal stability of the rPP/BAL nanocomposites can be attributed to their higher degree of crystallinity (*67,68*).

According to thermogravimetric analysis, E. Hamid (*69*) showed that the addition of an amount of 3% by weight of organophilic montmorillonite (MMT) makes the polypropylene more stable thermally. In fact, starting from a temperature of 375° C, the pure polypropylene degrades completely, while the PP/MMT nanocomposites lost only 23–26% of their initial mass.

Dong et al. (*70*) stated in their work that by incorporating 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-immobilized silica nanoparticles (5 wt.%) into polypropylene matrix, the thermal oxidative stability of PP exhibited an improvement of 62°C for the half weight loss temperature (antioxidative effect of DOPO-immobilized nanoparticules). Based on the results, they speculated that DOPO-immobilized silica nanoparticles could inhibit the degradation of polypropylene and catalyze the formation of carbonaceous char on the surface. Thus, thermal stability was significantly improved.
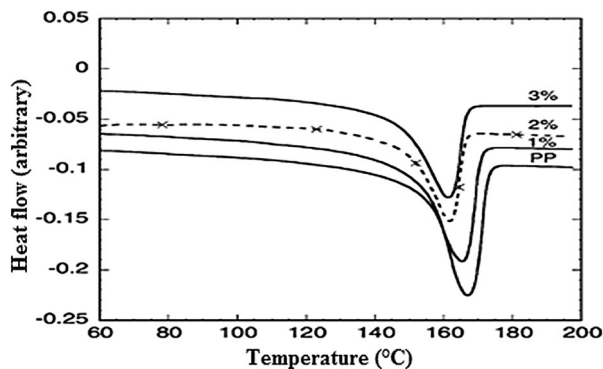
3.3. Enhancement of rheological properties

Rheological analysis allows identifying the flow behavior of plastic polymer during its transformation in the molten state (*71*). The principle of this technique is to put the sample under linear or sinusoidal deformation, at a shear rate or at a given frequency, and record the resulting response of the material. One advantage of the rheological analysis is that it takes into account the overall microstructure of the nanocomposite, and the rheological behavior of the material is significant at a time of global dispersion of nanofiller in the matrix, and the matrix itself. So, when using this technique, we need to separate the phenomena in the matrix and the effects induced by the interaction of nanofillers within the matrix (*72*).

Nizar et al. (*73*) have studied the influences of Zinc Oxide nanoparticles on the rheological behavior of rPP. They found that the viscosity increasing with the ZnO nanoparticles percentage increasing, because the interaction between nanoparticles and the chains of waste PP polymer may increase the viscosity and reduce the flexibility of chains movement. The increasing of viscosity
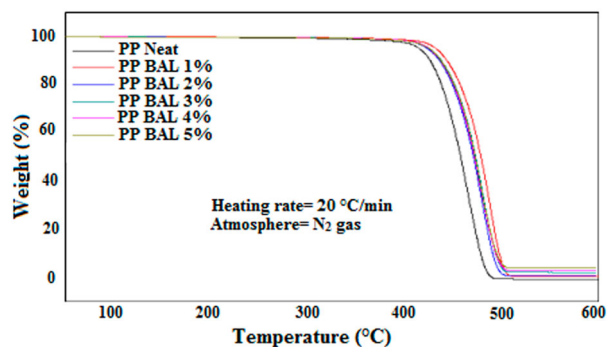

Figure 13. DSC thermograms of PP/clay nanocomposites with various clay contents (*66*).

Figure 14. TGA analysis of rPP/BAL nanocomposites (*65*).

was confirmed with the Melt Flow Rate (MFR) decrease (Figure 15).

Hadi and Mohamed (*74*) studied the effect of silica nanoparticules incorporation on rheological behavior of post-consumer PP. Their results show that the MFR value increases with the nanoparticules content increasing. The SiO2 nanofillers increase the free volume and the Brownian motion of the chains. This produces decreasing in shear viscosity and increasing in the flow rate (Figure 16). The flexible and ductile structure of PP polymer chains is obtained due to the reduction in shear viscosity. The viscosity is proportional to the density and molecular weight of polymer. The results of viscosity show that the viscosity decreases with the MFR increasing, due to the scission of the chains during the melting processes.

In order to analyze the influence of nanofillers on rheo-mechanical properties of recycled PP, Darchan Kumar et al. (*75*) added Silica and graphite nanoparticules to rPP matrix. They have noticed that the tensile modulus of rPP/Silica/graphite composites was increased drastically from 3149 MPa when compared to rPP 1657 MPa, but percentage elongation reduced drastically from 12.33% to 3.722% when compared with rPP because the graphite has more carbon content and makes the material more brittle, hence reduce in the % elongation. Flexural strength of rPP/Silica/graphite composites showed improvement from 1650 to 2539.403 Mpa. The improvement in the flexural is because of the addition of silica. On the other hand, there is an improvement in hardness from 65 shoreD to 95 shoreD, because the presence of graphite makes the material harder. They also, have noticed that the rPP/Silica/graphite composites have a slight decrease in compression value when compared to raw PP.

Elloumi et al. (*33*) studied the evolution of storage modulus versus frequency for virgin and recycled PP polymers and their related nanocomposites with 3% of nano $CaCO_3$ fillers. The authors have shown that addition of $CaCO_3$ to polymer melt shows an increase in the storage modulus G′ (Figure 17). They concluded that a better dispersion and distribution of nanofillers is obtained in a recycled matrix at low contents which have a significant influence on rheological behavior.

Hong et al. (*76*) showed that the storage modulus G′ and the viscosity increase by incorporating clay particules, but begin to decrease when increasing the concentration of PP-g-MA (used as a compatibilizing agent). This decrease may be explained by the fact that the molecular weight of the PP is lowered by PP-g-MA. While, Lertwimolnun and Vergnes (*77*) have shown that the elastic modulus undergoes a very rapid increase when the concentration of PP-g-MA compatibilizer varies between 5% and 25%.

Carbon black is a material produced by the incomplete combustion of heavy petroleum products. CB particles could also be used as nanofillers to enhance polymer nanocomposites' properties. Incorporation of CB nanofillers into virgin PP matrix improves thermal stability (*78,79*), flammability (*80*), mechanical strength (*81*), electric conductivity (*82*) and rheological behavior (*83*) of resulting CB/PP nanocomposite.

Recently, Luijsterburg et al. (*84*) showed that the addition of carbon black (CB) nanofiller to virgin and recycled isotactic PP polymers improves their mechanical and rheological performances. Indeed, the stiffness can be improved by a factor 10 to over 11 GPa, while the tensile strength can be improved by a factor 15 to over 385 MPa. The viscoelastic data are presented on Figure 18. The addition of carbon black nanoparticules to the materials results in a more or less equal complex viscosity η*. Also incorporation of CB changes the absolute value of G′ to some extent, but does not influence the trend.

4. Recyclability of PP-based nanocomposites

Nanoparticles are produced with complex and high cost processes in terms of money and energy. So, the recyclability of polymer/nanofiller nanocomposites is of great interest. Unfortunately, from literature analysis, it is
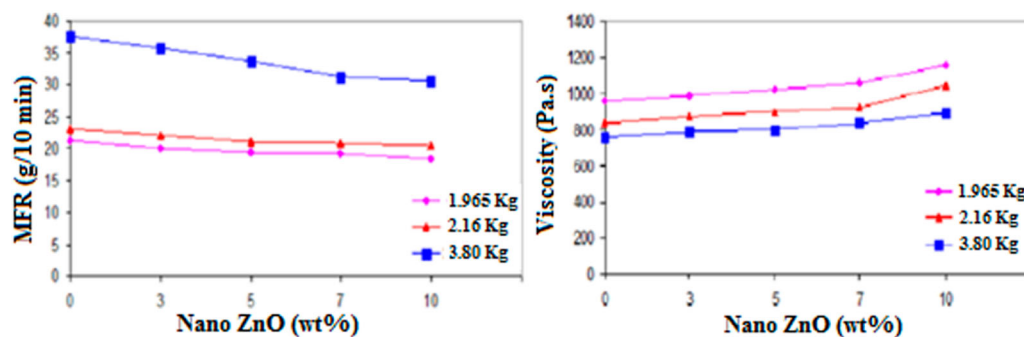
Figure 15. Viscosity and MFR of rPP/ZnO nanocomposites with different loads at 230°C (*73*).
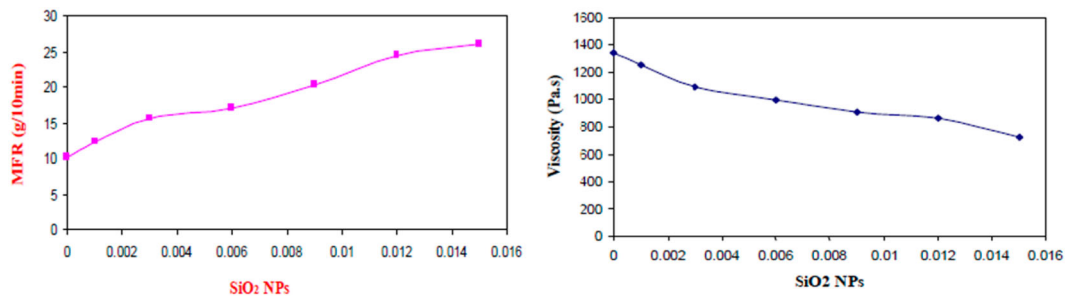
Figure 16. MFR and viscosity behaviors of PP at different SiO2 nanoparticules (NPs) content (*74*).

obvious that recycling of polymer nanocomposites, upon the end of their life cycle, has attracted so far less attention than its production. Some limited studies of nanocomposite recycling have been done, and bulk of the work in recycling of PP polymer-based nanomaterials has been primarily focused on nanoclay (montmorillonite) reinforcements.

In their work, Touati et al. (*85*) studied the effects of different processing times (mixing time) on the structure and properties of organo-modified montmorillonite (OMMT)/PP nanocomposites. These authors found that the initial storage modulus (G′) of the nanocomposites, which was highly improved in presence of PP-g-MA, seems to be less affected by reprocessing cycles at very low frequencies exhibiting a quasi-plateau compared to pristine PP/OMMT. In contrast, the complex viscosity was found to decrease for the whole samples indicating that the main effect of reprocessing was a decrease in the molecular weight. Moreover, the thermal and mechanical properties of the nanocomposites were significantly reduced after the first cycle; nevertheless, they remained almost unchanged during recycling. No change in the chemical structure was observed in the FT-IR spectra for both the nanocomposites after four cycles.

Few years later, Delva et al. (*86*) analyzed the effect of multiple extrusions on the properties of OMMT/Polypropylene nanocomposites. The results showed an improved intercalation of the OMMT clay in the first few extrusions, thus improving the mechanical properties. Increasing the processing steps furthermore leads to a decrease in elastic modulus and impact strength, which was attributed to a reduction in matrix-nanofiller interaction, most probably caused by organoclay degradation as shown by thermogravimetric analysis (TGA).

In another work, Majka et al. (*87*) investigated the possibility to recover reusable MMT nanoparticles by pyrolysis of polypropylene/MMT nanocomposites. They found that polymer nanocomposites can be successfully pyrolyzed (at 500°C), providing a solid product, which retains some of the properties of the initial organoclay, and can be easily used once again as a nanofiller.

Zhang et al. (*88*) studied the effects of recycling on the properties of carbon nanotube filled polypropylene
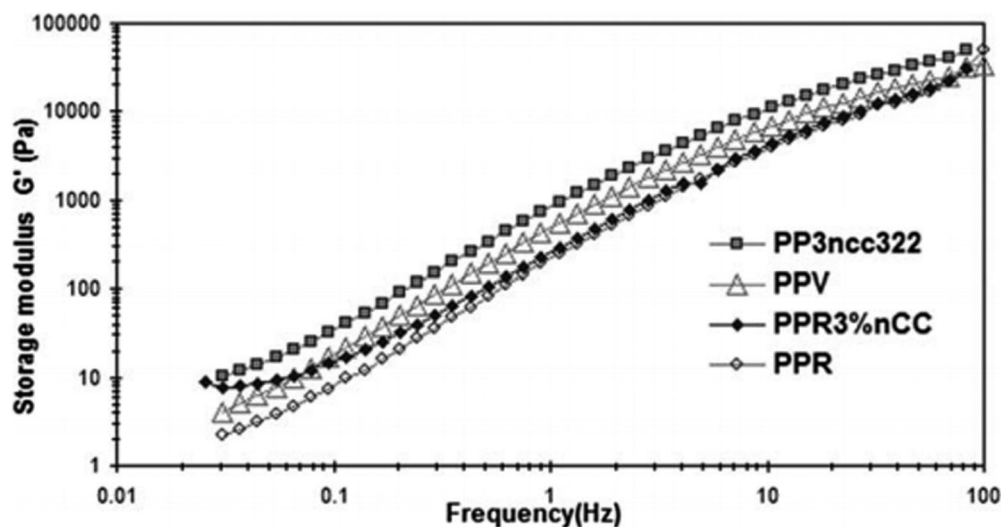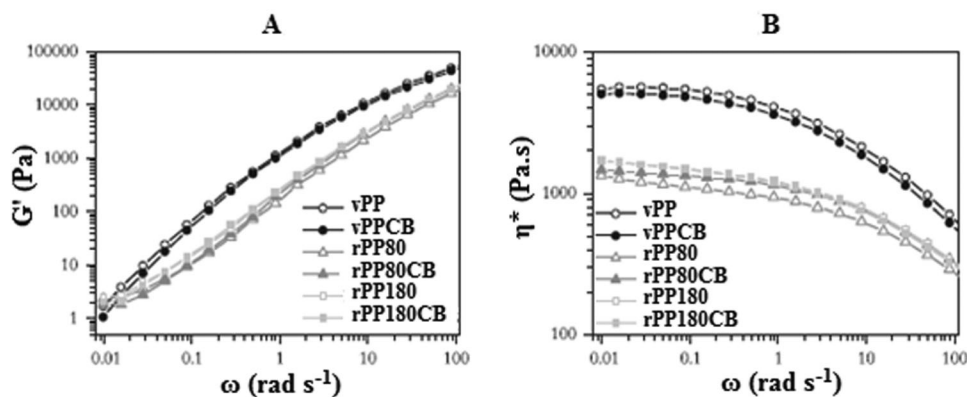

Figure 17. Storage modulus of recycled PP and virgin PP nanocomposites with 3% of $CaCO_3$ (*33*).

Figure 18. (A) Storage modulus, (B) complex viscosity of recycled and virgin PP polymers and their CB reinforced nanocomposites (84).

nanocomposites. They found that the CNT-filled PP materials showed an increase in toughness with recycling (Figure 19). DSC analysis showed that this was due to changes in the crystallization behavior of CNT-filled PP materials with recycling. They conclude that the addition of CNT to PP matrix increases the resistance to degradation of the PP. This offers potential for addition of CNT for the purpose of improving recycling resistance. Moreover, this is positive for sustainability and reuse of these materials for companies producing products with CNT-filled PP, as there is little loss in properties with recycling. Scrap from the manufacturing process may be incorporated/reused without significant loss in tensile properties. However, recycling should be performed under proper exposure controls because grinding generates high exposures to nanoparticles and CNT-containing respirable fibers.

Dorigato et al. (89) investigated the influence of the time under processing conditions on the microstructure and thermo-mechanical properties of polypropylene matrix compounded with a given amount (2 vol %) of both untreated (hydrophilic) and surface-treated (hydrophobic) fumed silica nanoparticles. They found that chain scission reactions induced by thermal processing caused a remarkable decrease of the melt viscosity of both PP matrix and nanocomposites, but the degradative effect was significantly hindered by the presence of silica nanoparticles. It was observed that the size of nanofiller aggregates noticeably decreased as the compounding time increased, especially when hydrophobic silica nanofiller was considered. While the melting temperature seemed to be unaffected by the processing time, a remarkable embrittlement of the samples was observed for prolonged compounding times.

5. Conclusion

In addition to the environmental concern, recycling of PP derives its driving force from the increasing value and applications of virgin and modified PP. As described in the first sections, many scientific findings have been made in the field of PP recycling. Particular focus in this study was given to the methods used to enhance properties of recycled PP.

The study of the recycling effect on different properties of virgin PP shows that recycling process affects mechanical, thermal and rheological properties. The main effect of recycling is the lowering of the melt viscosity, which is attributed to molecular weight decrease. Recycled PP exhibits greater crystallization rate, higher crystallinity and equilibrium melting temperature than those measured for vPP. On the other hand, elastic modulus and yield stress increase after recycling. However, elongation at break and fracture toughness decrease.

Thus, to minimize the effect of recycling, nanofillers can be added to recycled polypropylenes. The study of based rPP nanocomposites shows that incorporation of low content of nanoparticles improves mechanical properties, thermal stability and rheological behavior.
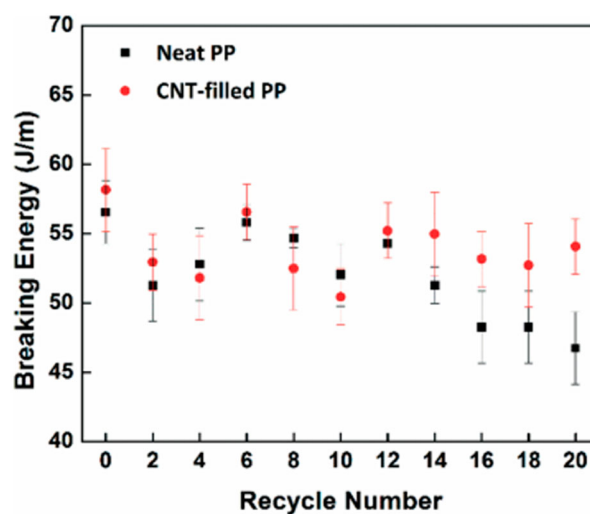
Figure 19. Izod impact resistance of recycled neat PP and CNT-filled PP (88).

Literature information about the economic and environmental impacts of polymer nanocomposites recycling is scarce and this research axis could be a challenge for the next few years to academics and industrials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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