Thermal Properties of Sustainable Thermoplastics Nanocomposites Containing Nanofillers and Its Recycling Perspective

Pooja Takkalkar, Sabzoi Nizamuddin, Gregory Griffin and Nhol Kao

1 Introduction

Commercialized fuel-based polymers have created immense adverse effects on the environment due to their non-renewable nature and emission of greenhouse gases, particularly carbon dioxide (CO_2) [1]. Pollution created by conventional polymers has risen to dangerous extents, predominantly in developing nations. These polymers, being non-biodegradable, are resistant to microbial degradation and hence they accrue in the surroundings. Furthermore, increases in oil prices have aided in stimulating interest in biodegradable polymers. Eco-friendly polymers were first introduced in the 1980s [2]. Over the past two decades, bio-based polymers have attracted considerable attention, mainly because of two major limitations with the use of conventional polymers. Firstly, the environmental pollution created by the increased reliance on fossil fuels and secondly the fact that the source of these petroleum-based polymers is limited and exhaustible [3].

Polymer nanocomposites are new engineering materials in which nanofillers [4], with at least one dimension less than 100 nm, are dispersed in a polymer to improve its properties [5–7]. Based on the appropriate application and final properties desired of the nanocomposite, the type and concentration of nanofiller can be studied. Nanocomposites possess more advanced properties than that of micro-composites as the incorporated nanofiller has a better aspect ratio and surface area. Biodegradable nanocomposites are considered more advantageous because they are light in weight, transparent, and have better mechanical, thermal and barrier properties than that of conventional composites, even at a very low concentration of nanofiller [8].

Nanocomposites have improved properties than the constituent polymers itself [9, 10]. The efficient dispersion of nanofiller in the polymer indicates that there is an

P. Takkalkar · S. Nizamuddin · G. Griffin · N. Kao (✉)
School of Engineering, RMIT University, Melbourne, Vict 3001, Australia
e-mail: nhol.kao@rmit.edu.au

increased interfacial interaction among the constituents [11]. Although the biodegradable polymers are environmentally friendly, their properties are inferior to conventional polymers; hence, nanocomposites with biodegradable polymers have been investigated to seek improved properties. The area of nanocomposites with biodegradable polymers has gained attention in the last two decades. A number of bio-based polymer matrices have been studied after incorporating organic and inorganic fillers to enhance their properties. The biodegradable polymers used as a matrix in preparation of nanocomposites are polybutyl succinate, polylactic acid, cellulose, starch, alginate, soy protein isolate, plant oil based polymers, polyhydroxy alkanoate and epoxies [12]. The properties which are aimed to be improved in these biodegradable nanocomposites include their thermal, mechanical, barrier, rheological and crystalline properties while maintaining their biodegradability. Depending on the particular application of these nanocomposites the appropriate nanofiller can be selected. The nanofillers are classified based on their source, shape, aspect ratio and crystallinity. Although the research in this area and the applications of biodegradable nanocomposites is in its infancy, it is expected to be enormous in future years.

The overall properties of the polymer nanocomposites are largely affected by-

   i. Compatibility and interactions between the polymer matrix and nanofiller
  ii. Nanofiller shape and aspect ratio
 iii. Dispersion of nanofiller within the polymer matrix
 iv. Modifications on the surface of nanofiller (if any).

This chapter provides a description of the thermal properties of sustainable thermoplastic nanocomposites; its recycling perspective is also considered.

2 Sustainable Thermoplastic Nanocomposite

Polymer scientists have shown increased interest towards developing various environmental friendly polymer nanocomposites which can potentially reduce the dependency on conventional polymers. These sustainable thermoplastic nanocomposites deserve attention as they aid in resolving concerns on issues such as the emission of greenhouse gases, depletion of fossil fuels and pollution [12]. Thermoplastic polymers are preferred over thermoset polymers due to various advantages such as low processing cost, design flexibility and easier moulding of complex parts [13]. Simple moulding techniques such as extrusion or injection moulding are widely used for fabrication of such types of composites.

The polymer matrix plays an important part for the performance of a polymer nanocomposite. In addition, the dispersion of fibers in the composite is also one of the crucial parameters for achieving the consistency of the product. Further, the properties of fibers, fibre-matrix interface and aspect ratio of fibres also govern the properties of nanocomposites [13]. The performance and properties of

thermoplastic composites are also influenced by process parameters [14]. It is reported by Takase and Shiraishi [15] that tensile strength of polypropylene/wood composite changed non-linearly with mixing temperature, mixing rate and time. The dispersion of fibers and fiber length should be optimized in order to enhance the properties of the composite. It is important that a uniform dispersion of nanomaterial within the polymer should be carried out [16]. Several dispersion methods for thermoplastic polymers have been reported in the literature, but the easiest method is blending in a minimax injection moulder's crucible [17], where the rotary cylinder is used for mixing the polymer melt with fiber addition by hand.

The concept of combining nanomaterials as filler and polymer as a matrix in order to form different forms of nanocomposites has been gaining much recognition by researchers [18–28]. Nanomaterials such as nanotubes and nanoclays provide great potential for fabrication of a variety of different forms of composites, coatings, adhesives and sealant materials with specific properties. These nanoparticles can be successfully utilized as a filler in thermoplastic polymers in order to improve the mechanical, physical and thermal properties of the polymer.

In this context, polylactide (PLA) has been leading among other thermoplastic polymers due to its inherent advantages like good mechanical strength, renewability, biocompatibility, and biodegradability. It is a versatile polymer made from agricultural raw materials, which are fermented into lactic acid. Then, this lactide acid is ring-opening polymerized through cyclic dilactone (lactide) to the desired polylactic acid. The polymer is altered through different means, which improves the thermal stability of the polymer and decreases the residual amount of monomers [29]. The thermal stability of the polylactic acid also can be improved by reinforcing it with fibers. The thermal properties are essential characteristics to understand the behaviour of the raw material and the final product [30]. Therefore, the thermal properties of various thermoplastic nanocomposites have been elaborated in detail in the following sections.

3 Thermal Properties of Sustainable Nanocomposites Based on Types of Sustainable Polymers

3.1 Polylactic Acid (PLA) Based Nanocomposites

PLA is a thermoplastic biodegradable polymer derived from corn. Although it is a biodegradable polymer, its properties need to be optimized to make it suitable for commercial packaging applications. Polylactic acid nanocomposites with improved properties by incorporation of cellulose nanofibers (CNFs) were prepared by Frone et al. [31]. CNFs were obtained using the most commonly used acid hydrolysis method. Microcrystalline cellulose (MCC) with particle size 20 μm was hydrolysed to form CNF with diameter 11–44 nm. These CNF were further surface treated to

form silanized (CNFS) after that, both the CNF and the CNFS were added in PLA at 2.5 wt% of each nanofiller were melt blended to form the nanocomposites. The effect of treated and untreated CNFs on nucleation characteristics of PLA was determined through differential scanning calorimetry (DSC) analysis. There was no substantial change in T_g, owing to the presence of nanofiller at very low concentrations. The PLA nanocomposite with CNF as nanofiller showed higher crystallinity due to the better nucleating effect created by CNF. In comparison, due to the better dispersion and adhesion of CNFS with PLA, the crystallinity was reduced as compared to CNF. Overall the degree of crystallinity was improved for PLA with both nanofillers, however, the effect was more pronounced with CNF nanofiller [31].

A similar study on cellulose nanocrystals (CNC) and silylated CNC (SCNC) in PLA was reported in the literature [32]. The authors prepared the nanocomposite with 1 and 2 wt% of each type of nanofiller through solvent casting with chloroform as a solvent. The samples with 1 and 2 wt% of CNC were labelled as PLLA-CNC-1 and PLLA-CNC-2, respectively and the samples with a similar concentration of SCNC were coded as PLLA-SCNC-1 and PLLA-SCNC-2, respectively. As expected, the bulk of the measurements showed there was no change in the melting temperature of all the nanocomposites, at around 171 °C. The degree of crystallinity (X_c) was determined using the enthalpy data from DSC. The X_c values were higher than pure PLA (14.3%) for all the nanocomposites. The X_c values were improved slightly for PLLA-CNC nanocomposites and they increased with filler loadings. Conversely, in the case of PLLA-SCNC nanocomposites, the X_c values were almost doubled, but decreased slightly with the increase in SCNC loading. The highest crystallinity was achieved for PLLA-SCNC-1 (30.4%). This was attributed to the improvement in nucleation effect triggered by homogeneous dispersion of the nanofiller within the PLLA matrix [32].

A recent study described the improvement in properties of PLA based nanocomposites with starch nanocrystals (SNC) as nanofillers at three different loadings of SNC- 1, 3 and 5 wt% [33]. The nanocomposites were prepared by solvent casting and evaporation techniques. The square-shaped SNC nanofiller used in this study was derived from acid hydrolysis of waxy maize starch, which consists of 99% amylopectin. The thermal properties of these nanocomposites were studied by means of TGA and MDSC. The TGA study revealed that all the nanocomposites were stable to process in the commercial processing range of polymers (25–240 °C). The MDSC results indicated a slightly higher degree of crystallinity for PLA-SNC-3 wt% but with further increase in the concentration of SNC, it declined. Also, a decline in the cold crystallization temperature was detected for all the nanocomposites. These changes were attributed to the enhanced nucleation effect created by crystalline SNC. Beyond the 3 wt% of SNC, the nanofillers had a tendency to aggregate and declines in thermal and rheological properties were observed. Similar results were reported for PLA and acetylated microcrystalline cellulose (Ac-MCC) based nanocomposites [34]. The optimum concentration obtained through rheological percolation threshold was at 2.5 wt% of Ac-MCC.

PLA nanocomposite with nanographite platelets (NGP) was prepared by melt blending at 180 °C [35, 36]. The concentration of NGP in PLA was varied from 1

to 10 wt%. The influence of NGP loading on thermal and crystallization properties was studied via MDSC. The NGP was unable to exhibit any nucleating effect or improve the overall crystallinity and thermal properties of the nanocomposites. However, a comparatively higher crystallinity and fusion enthalpy were noticed for nanocomposite with 5 wt% NGP. The researchers concluded that the melt compounding method alone is not sufficient to obtain a well-dispersed nanocomposite. A similar study was reported by the same group of authors [36], however, a melt intercalation and mixing technique were used to fabricate the PLA-NGP nanocomposites. In this study, the MDSC results showed that the melting temperature and glass transition temperatures were unaffected by the presence of NGPs, though the crystallisation temperature and degree of crystallinity were increased up to 5 wt% loading of NGP.

3.2 Thermoplastic Starch (TPS)

There is an environmental demand to create biodegradable plastics which have adequate properties and can replace commercial plastics. Nanocomposites prepared from starch as a matrix have great potential as they are available in abundance and are renewable. To overcome some of the inherent limitations of starch such as limited gas barrier properties, low heat distortion temperature and brittleness; polysaccharide nanofiller such as cellulose or starch nanocrystals can be incorporated in thermoplastic starch. The addition of biodegradable nanofiller not only improves the properties of the biodegradable polymer but maintains their biodegradability as well. Kaushik et al. [37] prepared biodegradable nanocomposites with thermoplastic starch as nanocomposite and cellulose nanofibers (CNFs) as nanofiller, at three different loadings of CNF, 5, 10 and 15 wt% by solution casting method. The CNFs reported in their study were extracted from wheat straw through a combination of steam explosion, chemical treatments (involving alkali and acid hydrolysis and bleaching) and mechanical treatments (homogenization). Morphological, structural, mechanical, thermal and moisture retention properties of the prepared nanocomposites were studied. The nano-dimensions of CNFs were measured through TEM, which showed fiber diameter in the range of 10–60 nm with a tendency to agglomerate. There was a significant improvement in the mechanical property of the nanocomposite with increase in CNF concentration; this was noted as a linear increase in tensile strength and modulus of the nanocomposite. The barrier property improved until a loading of 10 wt% and declined after a further increase in CNF concentration. This was credited to agglomeration of CNF fibers within the nanocomposite. The thermal properties of nanocomposites were studied through TGA and DSC. The thermal property study indicates the interaction between glycerol and CNF. The TGA results showed no change in onset degradation temperature until a concentration of CNF-10 wt% was reached, beyond that
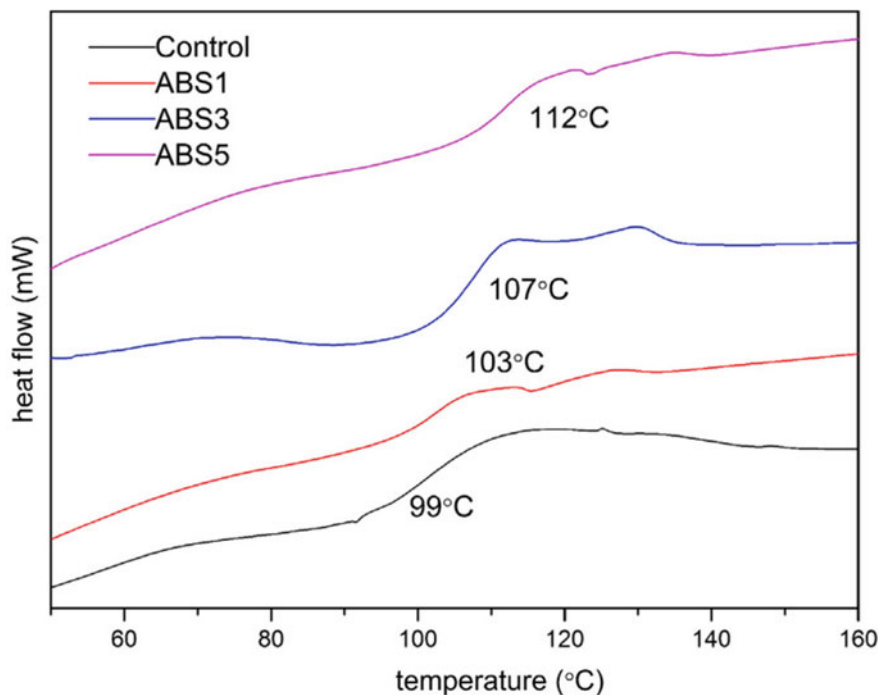
Fig. 1 DSC curves for Acrylonitrile butadiene styrene and Acrylonitrile butadiene styrene/ organ-montmorillonite nanocomposite at 1, 3 and 5 wt% loading of nanofiller. Reprinted from Ref. Weng, Wang [54] with permission from Elsevier

the onset degradation temperature reduced when compared to pure starch. They presented two possible causes for this reduction- (i) the reduced flexibility of branched amylopectin hindered by nanocrystalline cellulose and (ii) accumulation of the plasticizer (glycerol) on the CNF surface [37].

Cao et al. [38] reported similar properties of solvent cast plasticized starch (PS) based nanocomposite with different concentrations of cellulose nanocrystals derived from flax fiber (FCNs). PS was reinforced with FCN at six different loadings 5, 10, 15, 20, 25, 30 wt% of FCN. The thermal properties of the prepared nanocomposites were recorded through DSC analysis. They focussed the thermal analysis on the changes in glass transition temperature (T_g). T_g was associated with two phases; T_{g1}—glycerol rich phase (−80 to −50 °C) and T_{g2}—starch-rich phase (30–60 °C). The T_{g1} remained unaffected by the presence of FCNs, however, the T_{g2} kept increasing as the FCN loadings were increased. This was ascribed to the high interaction of FCNs with PS at the interface which hinders the molecular mobility of PS chains.

3.3 Polycaprolactone (PCL)

Performance improvement of biocompatible polymers like polycaprolactone (PCL) by adding nanofillers like clay or nanocellulose is studied widely. PCL based nanocomposites were fabricated with unmodified cellulose nanowhiskers (CNWr) and poly-ester grafted cellulose nanowhiskers (CNWr-g-PCL) at three different concentrations of each nanofiller- 2, 4 and 8 wt% in PCL matrix [39]. The CNWr were obtained through alkaline and acid hydrolysis of ramie fibers. Finally, the nanocomposites were prepared by melt blending PCL and the nanofillers at 120 °C. There was no significant change in the melting and crystallisation characteristics of the nanocomposites with CNWr as nanofiller. The crystallization temperature increased slightly with the increase in the concentration of CNWr-g-PCL. The grafted nanofiller largely improved the thermo-mechanical properties of the prepared nanocomposite. A similar study of melt blended PCL nanocomposites was reported previously [40].

3.4 Polyamide/Clay Nanocomposites

In the last decade, the number of investigations about the thermal degradation of clay-based nanocomposites has increased markedly due to the importance of this property for polymers production. In particular, clay-based nanocomposites polymers have drawn more interest recently [41]. The nanofillers are added into polymers as they have a potential to improve the thermal properties, particularly increasing the flame or chemical resistance characteristics, enhance the bulk clarity and ionic conductivity as well as decrease the moisture, hydrocarbons or gases permeability [42]. However, the problem of polymers thermal degradation in nanocomposites is still an obstacle to produce anti-thermal degradation polymers. This is due to the high temperature used in the preparation process of the clay-nanocomposites. Normally, degradation of the clay-based-polymers occurs if the temperature used in the preparation is higher than the stable temperature of the organic material used to reinforce the polymer [42]. Therefore, different materials have been used to advance the thermal and the mechanical properties of polymer products. For example, clay modified with cationic surfactants, specifically quaternary ammonium-organic surfactants, dispersed at the nanoscale into the polymer to improve the mechanical compatibility and increase the interlayer spacing of the clay and, hence, decrease the forces between the single platelets and thus aid exfoliation [41].

Morgan et al. (2002) have successfully formed a clay-catalysed-carbonaceous-char and reinforced char by clay polystyrene nanocomposites. They stated that the enforcement of the char by clay has decreased the flammability of the nanocomposites of polystyrene [43]. In this case, the mass fraction of clay loading, 5%, was

the optimal percentage amount to be loaded for improving the heat release rates among the 0, 2, 5, 10% mass fractions used in this study [43].

3.5 *Polypropylene/Layered Silicates Nanocomposites*

Polymer nanocomposites, compared to traditional composites, show a dramatic transformation in various properties at low loadings of nanofillers such as graphite nanoplatelets, carbon nanotubes, and nanosilicate layers [44]. The performance of these nanofillers is highly dependent on the uniform dispersion of the nanofillers and strong interactions at the interface between the polymer matrix and nanofillers. The graphene nanosheets, which is structurally similar to silicate layers and chemically analogous to carbon nanotubes [45], are considered as the most promising nanofiller in order to improve the barrier, mechanical as well as thermal properties. In spite of great potential of graphene nanofiller, the good dispersion is still a challenge for the effective reinforcement of polymers, specifically in nonpolar polymers such as polypropylene. Trokeson et al. [45, 46] fabricated fully-exfoliated polypropylene/graphite nanocomposites through a solid-state shear pulverization method. It was noticed that 2.5 wt% loading of graphite exhibited a 100% increase in Young's modulus and around 60% improvement in yield strength compared to pure polypropylene. Miltner et al. [47] successfully incorporated carbon nanotubes in polypropylene latex by sonication for fabrication of very well-dispersed polypropylene/carbon nanotubes nanocomposites.

Graphene-based polypropylene nanocomposite with improved mechanical and thermal properties were successfully fabricated by previous researchers [44]. An eco-friendly technique was utilized for preparation of polymer nanocomposite with well-dispersed graphene sheets within the polymer matrix, through coating graphene with polypropylene latex, and then melt-blending coated graphene with polypropylene matrix. It was observed that yield strength and Young's modulus of polypropylene were improved up to 75% and 74% respectively at 0.042% loading of graphene. It was reported that the thermal properties were improved after addition of graphene. For instance, the glass transition temperature was increased by 2.5 °C at 0.041% loading of graphene. Similarly, the thermal oxidative stability was also enhanced significantly up to 26 °C at 0.42% loading of graphene. Mounir et al. [48] synthesized graphene/polypropylene nanocomposite through melt mixing and investigated the effect of graphene loading on propylene characteristics (thermal properties). It was observed that an increase in graphene loading resulted in a significant improvement of mechanical and thermal properties of polypropylene. Further, graphene showed a significant effect on thermal stability of neat polypropylene and its composite. It was reported that the thermal degradation temperature of both the neat polypropylene and polypropylene/graphene nanocomposite occurs as a single step process with maximum degradation temperature of 460 °C. An increase in thermal stability of polypropylene after graphene

loading, at initial degradation stage, was observed which was attributed to the hindered diffusion of volatile decomposition products within the nanocomposites and is highly dependent upon the interaction between chains of nanosheets and the polymer.

4 Thermal Properties of Sustainable Nanocomposites Based on Various Thermal Properties

4.1 Thermogravimetric/Differential Thermogravimetric Analysis (TGA/DTG)

TGA is an important method used to examine thermal decomposition behaviour of polymeric materials for high-temperature applications [49]. In TGA, the weight loss of a substance is monitored as a function with time or temperature. The weight loss is due to the generation of the volatile product post-degradation. The thermal properties are essential characteristics to understand the behaviour of the raw material and the final product [30]. The thermal stability of any polymer matrix can be improved by adding a small number of nano additives/nanofillers [40]. Wang et al. [50] noticed that thermal stability of Acrylonitrile butadiene styrene was improved by 5% of organ-montmorillonite.

Alemdar and Sain [51] synthesized wheat straw nanofiber/thermoplastic starch polymer nanocomposite and studied the thermal behaviour of neat polymer and nanocomposite at 5% loading of the nanofiber. It was observed that the degradation temperature for both the neat polymer matrix and nanocomposite is similar but less than that of each individual component. Similar behaviour for degradation temperature of thermoplastic starch and thermoplastic starch/lignocellulosic fiber composite was observed in the study conducted by Averous and Boquillon [52]. Yuan et al. [53] reported the effect of multiwall carbon nanotubes on thermal stability of polyamide 12. It was found that there were two stages of decomposition for neat polyamide 12 at 443 and 462 °C respectively. The addition of carbon nanotube at 1% loading stabilized the polymer matrix against first degradation stage; this is due to the carbon nanotube network capturing thermal radicals and transferring the thermal energy effectively between the polymer chains and carbon nanotube thus avoiding chemical decomposition of the polyamide 12. Similar enhancement in thermal stability of nanocomposite was detected by Weng et al. [54]. They concluded that the addition of nanofiller in the polymer increased the thermal stability by acting as a superior insulator or barrier to the volatiles produced during degradation. In addition, the onset temperature moved slightly to a higher temperature than that of pure matrix confirming that the thermal stability was improved by the reinforcement using nanofiller. Bera and Maji [55] prepared graphene oxide/polyurethane and reduced graphene oxide/polyurethane nanocomposites and measured their thermal properties with the help of TGA and DSC to

understand the effect of nanofillers on the thermal properties of end product-nanocomposite. The results suggest that both the neat polyurethane and nanocomposites represented a two-stage thermal degradation pattern which corresponds to the degradation of hard and soft segments. Further, it was reported that the neat polyurethane was thermally stable up to 300 °C and the degradation of the soft segment for raw polyurethane occurred in the range of 300–405 °C, while degradation of the hard segment took place after 405 °C. The initial degradation temperature and T_{max} for graphene oxide/polyurethane nanocomposite at 0.10% loading of graphene oxide were increased by 6 and 8 °C; for reduced graphene oxide/polyurethane at 0.10% loading of reduced graphene oxide initial degradation temperature and T_{max} increased by 5 and 6 °C, respectively. Based on these findings, it was concluded that the graphene oxide provides more thermal stability than reduced graphene oxide at the same loading. An increase in thermal stability by addition of graphene oxide or reduced graphene oxide nanofillers is attributed to the physicochemical interaction between nanofiller and polyurethane, which leads to restricted motion of the polyurethane chains [56]. Furthermore, the volatiles produced during decomposition also remain in the material due to the high barrier properties of nanocomposite compared to raw polyurethane. Their findings were in agreement to literature in which a similar effect of nanofiller on thermal stability of nanocomposite is reported [57].

Arrieta, Fortunati [58] studied the thermal properties of binary and ternary nanocomposite films. The binary system involved neat PLA incorporated with unmodified and surface modified CNC, coded as PLA-CNC and PLA-CNCs, respectively. The ternary system consisted of PLA-PHB-CNC (PHB refers to poly (hydroxybutyrate)) and PLA-PHB-CNCs. The key observation was that the neat PLA and PLA-CNC had a single degradation step while the PLA-CNCs had dual degradation step. The first degradation step of PLA-CNC takes place at temperatures lower than the main degradation step, which might be associated with surfactant loss.

4.2   Differential Scanning Calorimetry (DSC)

DSC provides important data such as the heat capacity (ΔC_p) assigned to the polymer matrix, heat enthalpy (ΔH_m) assigned to the nanofiller, glass transition temperature (T_g), and the melting temperature (T_m). The addition of nanofiller in polymer matrix helps to improve the DSC results. It is reported in the literature [54] that the glass transition temperature (T_g) was improved with the loading of the nanofiller. It is reported that the T_g of a neat ABS polymer was 99 °C, which increased to 103, 107 and 112 °C at 1, 3 and 5% loading of nanofiller as shown in Fig. 1. According to Yu et al. [59], the DSC results showed that the PLA used in their study had a T_g around 57.7 °C and T_m of 149.1 °C. The T_g for neat PLA was observed at 57.7 °C, with an increase in loading of starch nanocrystals (StN) to grafted PCL (StN-g-PCL) it reduced to 47.8 °C for 5 wt% filler and eventually, it disappeared for higher loadings. This was ascribed to the increased

flexibility of the PLA chains during the melting process of the PCL. The fabrication of nanocomposites, with PLA as a matrix, and 1 and 3%wt of unmodified (CNC) and surfactant-modified (s-CNC) cellulose nanocrystals as fillers, using solvent casting technique was reported by Fortunati et al. [60]. There is no significant change in the T_g as reported in the previous literature on PLA based nanocomposites. Conversely, a reduction in T_g values was detected in the PLA 1 s-CNC system (about 15 °C), though a less intense signal, which was hard to perceive, was recorded for the PLA 3 s-CNC nanocomposite. This effect may be credited to the presence of the surfactant that acts as a plasticizer of the polymer, decreasing the glass transition temperature.

The raw polyurethane did not have a sharp melting point (T_m) for the hard segment [61] due to its lower percentage i.e. 23%. Therefore, the T_m of second heating was considered as true T_m because the impurities in polymer get melted in first heating, therefore, the T_m of neat polymer or nanocomposites takes place in the second heating [55]. On the other hand, Gabr et al. [62] found that the addition of nanoclay as a nanofiller does not have any effect on T_m. They found that the T_m of both the neat polymer and nanocomposite was 165 °C as confirmed by the DSC heating curve of neat polypropylene and polypropylene/nanoclay composite as shown in Fig. 2b. Yu et al. [59] noticed that the neat PLA has a single sharp melting peak at 149.1 °C, however, dual peaks were observed for nanocomposites which were assigned to the presence of PCL. The dual peaks are indicative of the presence of interfacial layers based on the interactions between PLA, PCL, and StN. Gabr et al. [62] synthesized a polypropylene/organoclay nanocomposite up to 5% and studied the DSC analysis of both the raw polypropylene and nanocomposite as shown in Fig. 2a. The results revealed that crystallization peak temperature of neat polypropylene was 121.1 °C, which increased to 123.4 °C at 5% loading of nanoclay filler. An increase in crystallization peak temperature by the addition of organoclay is assumed to be due to the layers of organoclay acting as effective nucleating agents for crystallization of polypropylene. Due to the interaction between layers of organoclay and polypropylene, organoclay layers absorb molecule segments of polypropylene and some of the polypropylene is immobilized and
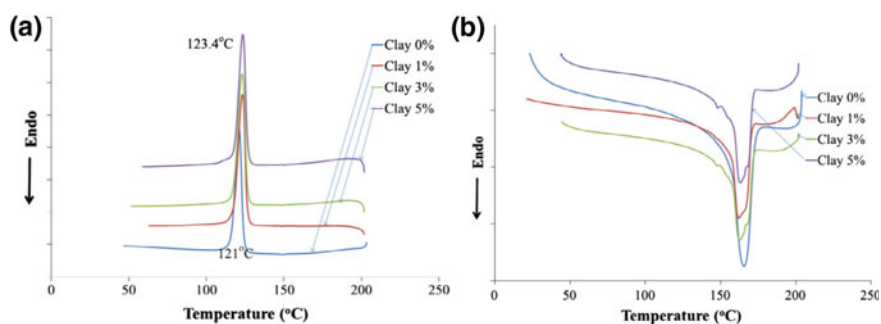

Fig. 2 **a** and **b** Cooling and heating curves for DSC of neat polypropylene and polypropylene/organoclay nanocomposite. Reprinted from Ref. Gabr, Okumura [62] with permission from Elsevier

this immobilization of polypropylene molecules helps in the crystallization of polypropylene. An increase in crystallization temperature by the addition of nanofillers in the polymer matrix was reported by Mingliang and Demin [63].

Robles, Urruzola [64] reported six different nanocomposites based on PLA and surface modified cellulose nanofibres and cellulose nanocrystals, obtained from blue agave bagasse. The nanocomposites were developed using a Haake Minilab twin-screw extruder with an L/D ratio of 24:1 at 170 °C. Two different surface modifications were done in order to modify the hydrophilic character of the nanofillers. The surface treatment was done using 3aminopropyl triethoxysilane and dodecanoyl chloride for cellulose nanofibers and cellulose nanocrystals, respectively. An improvement in crystallization of the PLA chains was noted with an increase in the loading of nanoreinforcement, without altering the overall crystallinity of the PLA matrix. The slight deviation in the T_c and the rise in the enthalpy of melting are ascribed to the good nucleation of the nanocellulose filler (fiber and crystals). This enables the PLA chains to flow freely around the crystals whilst maintaining a stable melting temperature.

4.3 Thermal Conductivity

Thermoplastic polymers have a wide range of applications to act as electrical and thermal insulators. To enhance the thermal and electrical conductivity of these polymers, it is suggested to add any nanofiller to obtain a nanocomposite, which has potential to overcome the limitations of these polymers in electrical and thermal applications [53]. Polymeric nanocomposites have the potential for utilization in a variety of thermal applications such as heat exchange and electronics thermal management. It is reported that the thermal conductivity of polymers can be enhanced significantly by reinforcement with small amounts of nanomaterials [65]. For example, single-wall carbon nanotube have thermal conductivity over 3000 W/m K; it is estimated by simulation that this value can be as high as around 6000 W/m K [66]. Another study reported that a factor of 250 enhancements in thermal conductivity was observed at 10% loading of multiwalled-carbon nanotubes [67, 68]. A number of studies have been conducted for improving the thermal conductivity of polymers by incorporating different amount of loadings of different types of nanomaterials in a polymer matrix.

Yuan et al. [53] prepared two different nanocomposites by incorporating carbon nanotube as a nanofiller in two different thermoplastic polymers i.e. polyamide 12 and polyurethane and investigated the effect of nanofiller on thermal conductivity. It was reported that the thermal conductivity was improved significantly by reinforcing 0–1% of carbon nanotube into the polymer matrix for both the polymers as shown in Fig. 3. Patton et al. [69] prepared vapour grown carbon nanofiber/epoxy nanocomposite and measured the thermal conductivity of pure resin and nanocomposite. It was found that the thermal conductivity of pure resin was 0.26 W/m K, which improved to 0.8 W/m K at 40 vol.% of carbon nanofiber. The
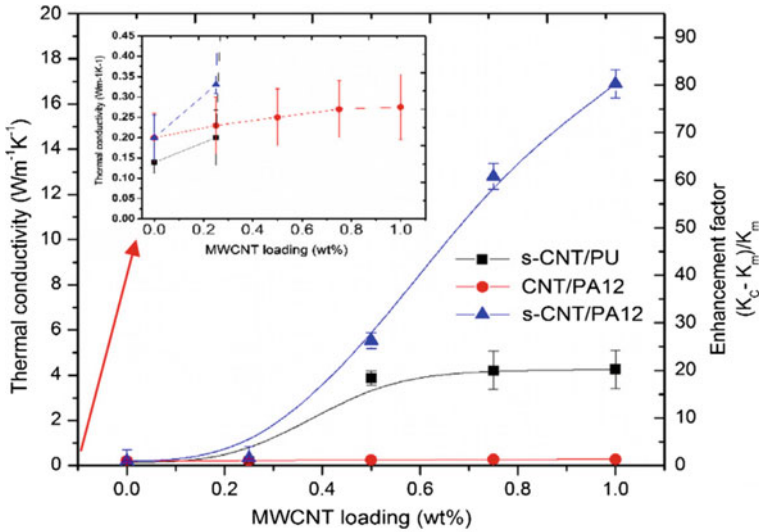
Fig. 3 Thermal conductivities of carbon nanotube/polyamide and carbon nanotube/polyurethane with 0–1% loading of carbon nanotube as a nanofiller. Reprinted from Ref. Yuan, Bai [53] with permission from Elsevier

small increment in thermal conductivity of nanocomposite was ascribed to the difficulty in transmitting thermal energy from fiber to fiber. Lafdi and Matzek produced 20% carbon nanofiber/epoxy resin and measured the thermal conductivity and observed a rise in thermal conductivity from 0.2 W/m K of neat resin to 2.8 W/m K of nanocomposite [70].

It is reported in the literature that the thermal conductivity depends on the temperature [71]. They fabricated polypropylene/single wall carbon nanotube and studied the dependence of thermal properties of both the neat polymer and nanocomposite on temperature. The research found that both the neat polypropylene and polypropylene/carbon nanotube nanocomposite showed a decreasing thermal conductivity with increasing temperature at lower temperatures but this trend reversed at higher temperatures—refer to Fig. 4. Further, the temperature dependence of thermal conductivity of both the raw polymer and nanocomposite can be modelled by bicubic regression polynomials. Also, the thermal conductivity increases with an increase in the amount of loading of nanofiller.

5 Recycling Perspective

In the past few years, considerable effort has been devoted globally to extend the applications of sustainable thermoplastic materials by conferring on them advanced properties through mixing and blending them with various nanofillers.
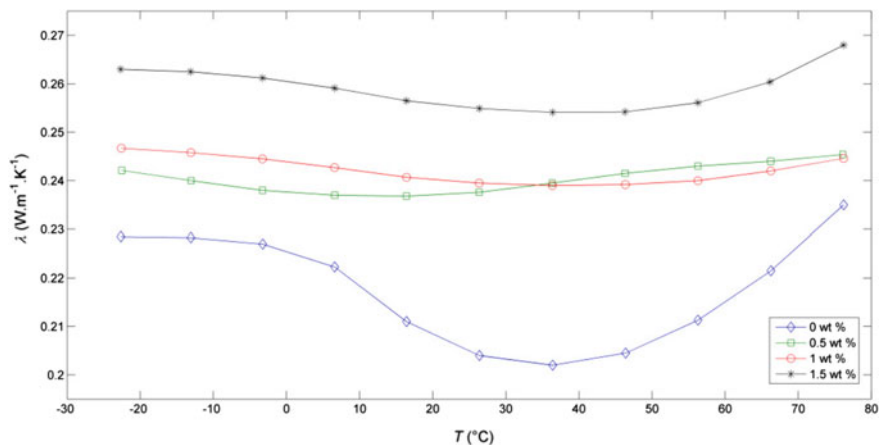
Fig. 4 Temperature dependence of thermal conductivity of pure polypropylene and nanocomposite. Reprinted from Ref. Ivan, Pavol [71] with permission from Elsevier

Thermoplastic polymers like polyolefins, polyamide, polyesters, and styrene polymers are the most representative commodity polymers for cost-efficient manufacturing techniques, outstanding thermo-mechanical properties and good compatibility with the environment, together with easy recycling. The thermal features of thermoplastics nanocomposites plays an important role in deciding its recyclability properties. Sustainable nanocomposites are considered the polymeric materials of this era and are used with organic or inorganic nanofillers with size usually of 1–100 nm. In particular, the higher surface area of the nanofillers than their counterparts allows efficient interfacial interaction with the polymer. The unique properties of the biodegradable nanofillers enhance the overall performance of the polymer matrix. These thermoplastics nanocomposites have a wide variety of applications due to their good thermal and mechanical properties as well as durability in the area of optoelectronic and chemiresistor devices, temperature sensors, linear polarizers, polymeric matrices, catalytic and other chemical sensors, functional materials, polyolefins, polyesters and polyamides. The current total production of plastics is very high and will continue to increase. Hence, due to the creation of huge quantities of plastic waste by industrial manufacturers and householders, the world is confronting a crisis in concerns to environmental, economic and petroleum affects of such production.

Old-style methods of disposal of plastics have negative influences on the environment, for instance, the combustion of unwanted polymers in the form of fumes and toxic gases as well as waste to underground water. The recycling practice is the best method to treat waste polymers and recycling commonly involves processing plastics to produce energy [72]. The overall recycling rate is 2.4 million tonnes for different polymers. Different technological processes have been reported for recycling of polymers such as chemical or feedstock recycling with energy recovery and mechanical recycling [73]. In plastic industries,

mechanical recycling is a relatively simple and common method and is also preferable for adequate quantities of homogenous and separated wastes [74]. The conventional mechanical recycling process includes the separation, grinding and producing another material without changing its chemical nature; therefore, mechanical recycling is limited. Low molecular weight materials can be produced by chemical or thermal treatment during feedstock recycling [75], which is an attractive method to substitute for mechanical recycling. The energy recovery techniques mainly applies to plastic disposal wastes via incineration, which also contains a large number of combustible solids. After melting, a stray polyvinyl chloride (PVC) bottle within 10,000 polyethylene terephthalate (PET) bottles can cause the deterioration of the whole batch of PET bottles due to separation difficulties. Therefore, the Society of plastics industry passed the numerical coding system act in the 1980s for ease of separation to determine plastic types. Therefore, these material and chemical recycling of plastic is an appropriate solution to the problems of environmental pollution from various wastes on a worldwide industry level. This can be achieved by using a wide range of different processing techniques with low-cost parameters and has gained increasing importance in the scientific and industrial communities for thermoplastics nanocomposites. Among European countries, Germany has the highest number of recyclers and is globally regarded as the most advanced country for PVC/plastic recycling. The recycling of these polymers usually requires a suitable separation method in which polymer/plastic materials in the mixed solid wastes are separated into a homogeneous stream, which allows a wide range of applications from the recycling perspective.

A simple method is a separation technique of general polymers from plastic wastes is via hand sorting. The application of low content nanofillers is one of the widest and well-known methods to add value to recycled waste plastics to produce thermoplastic nanocomposites, which enhance the thermal stability as well as mechanical properties [76]. The surface area, strength, and viscosity of polymers increase with the addition of nanofiller, which affects interfacial interactions between the polymer and filler [77] and ultimately it increases the performance. The interfacial interactions improve the tensile properties of composites. Titanium dioxide was also incorporated via solution method to improve polymer stability of recycled plastic as well as discolouration resistance [78]. The addition of small organoclays also allows a change in chemical nature of polymer to enhance the recyclability of the polymer [79]. In this way, degradation is minimized with an improvement of some properties. Thus the recycling process involves different new developments and separation techniques for waste polymers with novel energy-recovery procedures for effective cost management.

6   Conclusion

The concept of combining nanomaterials as filler with polymer as a matrix in order to form different forms of nanocomposites has been gaining much recognition these days by researchers. The nanomaterials such as nanotubes and nanoclays provide great potential for fabrication of a variety of different forms of composites, coatings, adhesives and sealant materials with specific properties. Incorporating small quantity of nano additives/nanofillers tends to affect the thermal characteristics of the polymer matrix. Both the initial degradation temperature and T_{max} values for nanocomposites are greater than the neat polymer due to the presence of nanofiller in the nanocomposite. The thermal conductivity highly depends upon the temperature and is well-modelled by bicubic regression polynomials.

Recycling is the best way to treat and minimize waste polymer products and is achieved using various processes on plastics. Different technological processes have been reported for recycling of polymers such as chemical or feedstock recycling with energy recovery, and mechanical recycling. The recycling process involves new development and separation techniques for waste polymers with novel energy-recovery procedures for effective cost management from an economical standpoint.

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