

Mechanical, Thermal and Viscoelastic Properties of Polymer Composites Reinforced with Various Nanomaterials



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1 Introduction

Nanotechnology has attracted a considerable attention in science community due to the growing demand to develop high-performance materials for medical, sensors, computing, packaging, textiles, automotive, membrane-based separation, water purification, etc. to make our lives more comfortable. Various nanomaterials such as carbon nanotubes, graphite, metal oxide nanoparticles, clay nanoparticles, and nanocellulose have been extensively investigated due to their good physical, antimicrobial, electrical, thermal, chemical and mechanical properties. In recent years, nanomaterials have been used in applications that require elevated

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mechanical performance such as polymer nanocomposites as a reinforcing element. Polymer nanocomposite is a combination of the polymer matrix and nanomaterials with one, two and/or three dimensions.

Polymers are widely used in various applications due to their low cost, flexibility and easy processing. However, they have inherited some drawbacks such as low tensile properties and poor fracture toughness which limits their applications [20]. Therefore, to address these drawbacks nanomaterials have to be compounded with the polymer matrix. To develop polymer nanocomposites with the required properties depends on the filler properties and dispersion of the filler within the polymer matrix. For instance, to formulate polymer nanocomposites with high conductivity, carbon nanotubes should be used as filler due to its high conductivity [4]. However, it is widely accepted that poor dispersibility causes agglomeration of filler which led to poor interfacial adhesion between a filler and polymer matrix and therefore results in the poor mechanical performance of the resultant material [20]. To improve the dispersion of fillers in a polymer matrix, modification of either filler or polymer should be considered to alter the functional groups of the materials in order to achieve a good interaction between polymer and filler which enhances properties of the resultant materials [95, 96].

Many researchers have investigated the effect of nanomaterials on the properties of polymer nanocomposites [14, 87–89, 93, 94]. However, many studies indicated that the incorporation of nanomaterials enhanced the properties of the resultant polymer nanocomposites [90–92, 101]. For example, [67] reported that the incorporation of nanocellulose enhanced tensile and thermal properties of polyvinyl alcohol (PVA) nanocomposites. It was also widely noticed that the increase in loading showed a positive effect on mechanical properties of nanocomposites.

This book chapter reviews the effect of nanomaterials on the properties of polymer nanocomposites. It is also highlighting the hybridization of fillers and studied their effect on the properties of nanocomposites. Lastly, this chapter highlights the incorporation of nanomaterials in biopolymers and investigated their properties.

2 Mechanical Properties of Nanocomposites

2.1 Mechanical Properties of Polymer Reinforced with Cellulose-Based Nanofillers

Cellulose-based nanofillers are categorized into cellulose nanocrystals (CNCs) and cellulose nanofibres (CNFs). CNFs consist of crystalline and amorphous region whereas CNCs consist of the only crystalline region. In addition, CNFs are web-shaped [58] bundles stabilized by hydrogen bonds while CNCs are rod-like shaped [75]. The diameters of both CNFs and CNCs are in nanoscale and their lengths in microscale [77]. It was also reported that the tensile strength and modulus of CNCs were 14.3–28.6 and 143 GPa, respectively [19]. In addition, CNCs have a

low elongation at break, high aspect ratio, and large surface area. CNFs have similar characteristics with CNCs.

Due to the aforementioned extraordinary properties of cellulose-based nanofillers, they have attracted a considerable attention in polymer nanocomposites field as suitable reinforcement using low loading amount. The study reported by Chen et al. [25] revealed that the addition of 10 wt% of CNCs extracted from pea hull fiber in pea starch polymer enhanced tensile strength and elongation at break of the pea starch nanocomposites due to their high aspect ratio. The authors added that the strong adhesion between the two materials led to the improvement of mechanical properties of the resultant nanocomposites. Similar observations were reported in the case of CNFs [13, 45, 48, 49]. In addition, [49] indicated that the increase in CNFs loading in polylactic acid (PLA) led to the enhancement of tensile strength and modulus but, elongation at break was reduced. This was attributed to the good mechanical properties of CNFs and the interaction between CNFs and PLA. In contrast, [47] reported that no significant alterations in tensile properties were observed in melt-spun PLA reinforced with CNCs.

The hydrophilic nature of cellulose-based nanofillers led to poor interaction between nanofillers and the hydrophobic polymer matrix. Hence, the surface modification of these materials is crucial to improving their hydrophobicity, dispersion, and interaction between them and the polymer matrix. The incorporation of acetylated CNCs up to 4.5 wt% resulted in an overall increase in tensile strength and modulus as well as elongation at break. The further increase above that resulted in a decrease in tensile properties. This can be explained by the fact that when loading was less than 4.5 wt%, the distance between CNCs was big and therefore the interaction was weak to form percolation network. However, at higher loadings, a decrease in tensile properties was observed due to agglomeration [114]. On the other hand, [13], reported that the enhancement of tensile properties in thermoplastic starch (TPS) reinforced with unmodified CNFs was due to the formation of hydrogen-bonded nanofibres network, entanglement and strong interfacial adhesion between TPS and CNFs. The authors also reported that tensile properties of TPS reinforced with acetylated CNFs were lower than those of unmodified CNFs reinforced TPS. This was attributed to the lack of fibers-to fibers and fibers-to-polymer matrix interactions due to the surface hydrophobicity in modified CNFs.

2.2 Mechanical Properties of Polymer Nanocomposites Reinforced with Carbonaceous Nanofillers

Carbonaceous nanofillers such as carbon nanotubes (CNTs) and graphite have exhibited extraordinary tensile strength and modulus, electrical properties, large surface area, high aspect ratio and low density. Given these extraordinary properties, CNTs can be regarded as ideal candidates for reinforcement in polymer nanocomposites to enhance the mechanical properties, thermal conductivity and electrical properties of the resultant polymer nanocomposites. Considering the

properties of CNTs, [20] developed epoxy nanocomposites reinforced with multi-wall carbon nanotubes (MWNTs). The results suggested that the incorporation of pristine MWNTs in epoxy led to a slight increase in tensile modulus but decrease tensile strength. However, incorporation of functionalized MWNTs with polystyrene sulfonate (PSS) and poly(4-amino styrene) (PAS) in epoxy resulted in an increase in both tensile modulus and strength. Similar findings were also reported by Mashhadzadeh et al. [69]. It was also reported that the addition of CNTs in high-density polyethylene (HDPE) resulted in the improvement of its hardness [35]. In contrast, other authors reported that the addition of carbonaceous fillers without modification in polymer matrix results in improvement of tensile properties [4, 74, 109, 111]. Moreover, it is worth noting that the increase in filler loading enhanced mechanical properties of the resultant polymer nanocomposites [4]. In addition, the addition of carbonaceous nanofillers in polymer matrix induce the electrical properties of nanocomposites [50]. Lopez-manchado et al. [63] investigated the effect of thermal reduced graphene oxide on the mechanical properties of plasticized natural rubber with dodecyltrimethylammonium bromide (DTAB). The addition of thermal reduced graphene oxide enhanced the stiffness of plasticised natural rubber.

Numerous researchers have investigated the effect of loading of carbonaceous nanofillers in polymer matrices [2, 50]. For instance, [50] investigated the effect of large aspect ratios and exceptional high mechanical strength MWNTs loading on the mechanical properties of acrylonitrile butadiene styrene. Both tensile strength and modulus increased with increase in loading but, in the case of tensile strength it increased up to 7 wt% and decreased with further increase in loading. The enhancement of mechanical properties was due to the uniform dispersion of MWNTs throughout the polymer matrix. Above 7 wt% loading, the agglomeration of MWNTs was clearly observed which could be the reason for the decline in the tensile strength of the nanocomposites. On the other hand, elongation at break decreased with an increase in loading. In addition, the addition of MWNTs at different loading also improved the electrical conductivity. Liao et al. [60] tested the impact strength of polypropylene (PP) nanocomposites reinforced with MWNTs and hydroxyapatite designed for bone implants. The authors reported in their extensively investigated study that the impact strength of PP reinforced with hydroxyapatite decreases with increasing hydroxyapatite loading. However, the incorporation of MWNTs in PP nanocomposites reinforced with hydroxyapatite enhanced the impact strength due to their flexibility and large strain to failure. Also, it was reported that the inclusion of MWNTs increases the degree of crystallinity of PP nanocomposites which lead to the enhancement of tensile properties and impact strength. Younesi et al. [116] investigated flexural behaviour of low-density polyethylene (LDPE) reinforced with single wall carbon nanotubes (SWNTs) and wood flour. The addition of SWNTs and the modification of LDPE with maleic anhydride enhanced the flexural modulus. However, the flexural modulus increased with increasing loading (1–3 wt%) of SWNTs. The enhancement of flexural properties was due to the high aspect ratio of SWNTs. It was also reported that SWNTs were well dispersed in the polymer and therefore improved the interfacial adhesion between polymer and SWNTs which result in improvement of flexural properties. Furthermore, impact strength also improved when SWNTs were added.

2.2.1 Mechanical Properties of Biopolymers Reinforced with Carbonaceous Fillers

Much research is focusing on the development of biobased and biodegradable products due to their eco-friendliness, sustainability, and biodegradability. Biopolymers are among the materials that have been extensively investigated. Biopolymers which are widely studied include polylactic PLA, TPS, poly(hydroxybutyrate-co-hydroxyvalerate) PHBV, poly(butylene succinate) (PBS), polysaccharides and proteins. Like any other material, biopolymers have inherited some drawbacks such as moisture absorption, difficulty in processability and low properties in comparison to traditional petroleum-based polymers. To address these drawbacks, biopolymers are blended with other polymers or reinforced with stiffer nanofillers. For instance, [97] reported that the addition of 1 wt% CNTs in PHBV reduced water uptake

Table 1 Biopolymers reinforced with carbonaceous nanofillers

Biodegradable polymer	Filler	Publication year	References
Larch lignocellulose	MWNTs	2017	Huang et al. [46]
Poly(butylene succinate-co-adipate) (PBSA)	Halloysite nanotube	2016	Chiu [27]
Polycaprolactone (PCL)	MWNTs	2010	Sanchez-garcia et al. [97]
Hydroxyapatite	MWNTs	2017	Khan et al. [52]
PBSA/maleated polyethylene blend	Halloysite nanotube	2017	Chiu [28]
Poly(lactic-co-glycolic acid)	Carboxylation MWNTs	2011	Lin et al. [61]
Epoxidized natural rubber	MWNTs	2018	Krainoi et al. [55]
Poly lactide/poly(ϵ -caprolactone)	Thermally exfoliated graphene oxide (GO)	2018	Botlhoko et al. [17]
Poly(3-hydroxyalkanoate)	Grafted MWNTs	2015	Mangeon et al. [68]
PLA	Kenaf fibre/ MWNTs	2017	Chen et al. [22]
Poly(l-lactide) (PLLA)/poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)) blend	MWNTs	2017	Gao et al. [38]
TPS	Oxidized MWNTs	2013	Cheng et al. [26]
PLA	CNT	2016	Wang et al. [112]

whereas at increased CNTs loading an increase in water uptake was observed. Similar results were observed in the case of PHBV reinforced with carbon nanofibres. Other studies that investigated the mechanical properties of biopolymers reinforced with carbonaceous nanofillers are summarized in Table 1.

Incorporation of carbonaceous nanofillers into biodegradable polymers improves the mechanical properties of the resultant polymer nanocomposites [55, 97]. For example, the incorporation of MWNTs in epoxidized natural rubber nanocomposites led to enhancement of mechanical properties as shown in Fig. 1.

It was also reported that mechanical properties of epoxidized natural rubber nanocomposites increased with increasing MWNTs loading. It was seen that at 5 wt% MWNTs loading reinforced epoxidized had the highest tensile strength, further increase in loading above 5 wt% MWNTs led to a decrease in tensile strength while modulus was constantly improving. The decrease in tensile strength after 5 wt% MWNTs could be due to CNTs aggregation in the polymer matrix. Conversely, the elongation at break decreased with MWNTs loading [55]. Similar results were reported by Wang et al. [112], in their case they discovered that 3 wt% CNTs loading was the optimum and further increase in CNTs loading led to decrease in tensile properties.

Other researchers [18, 26, 61, 68] incorporated functionalized carbonaceous nanofillers in biopolymers to further enhance mechanical properties of the nanocomposites. Lin et al. [61] incorporated carboxylated MWNTs in poly (lactic-co-glycolic acid) for bone tissue engineering. Morphological properties indicated that the treatment shortened the length of CNTs which tend to avoid agglomeration. This led to enhancement of tensile properties of the resultant nanocomposites by nearly three-fold in comparison to the virgin polymer and by nearly two-fold in comparison to those of polymer reinforced with untreated MWNTs. In addition, functionalized MWNTs based nanocomposites degrade faster than both unfunctionalized MWNTs based nanocomposites and virgin polymer. Similar results were observed in the case of PHBV reinforced with 3 wt% grafted CNTs [68]. In contrast, the addition of functionalized graphene oxide in polylactide/poly(ϵ -caprolactone) blend led to the decrease in tensile properties. However, tensile properties slightly improved with the increase in loading.

A global research is now moving towards hybridizing two or more fillers to enhance the performance of the material for diversified applications [22, 60, 116]. Chen et al. [22] fabricated PLA nanocomposites reinforced with a combined functionalized kenaf fibres and MWNTs by melt mixing and compression moulding techniques. They reported that tensile properties of the resultant nanocomposites increased due to the interfacial interaction between modified kenaf fibres by 3-glycidoxypropyltrimethoxysilane and PLA which improved the stress transfer and thus, lead to increase in tensile properties. Impact strength results were correlating well with those of tensile properties. The authors reported that the enhancement of impact strength was attributed to the structure of cellulose which tolerates higher deformation under impact.

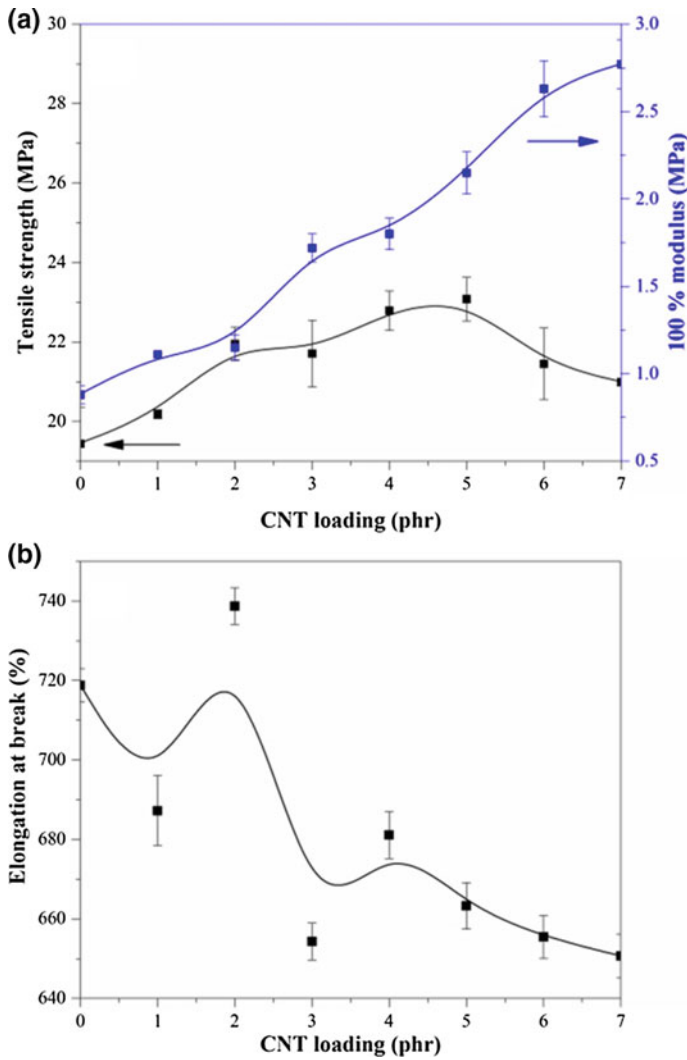


Fig. 1 Tensile strength and modulus of epoxidized natural rubber and their nanocomposites (a) and elongation at break of epoxidized natural rubber and their nanocomposites [55], copyright with the permission from Elsevier

2.3 Mechanical Properties of Polymer Reinforced with Nanoclays

In recent years, nanoclays have received considerable attention as reinforcing element in polymer nanocomposites due to their extraordinary properties such as high mechanical properties, large surface area and high aspect ratio, good thermal,

optical, magnetic and electrical properties. Other properties of nanoclays include environmental friendliness, abundantly available and non-toxic which make them suitable for food packaging applications. Most recent, nanoclays have been utilized to develop active packaging materials with improved tensile strength, modulus, and elongation at break. It was also reported in the same study that the incorporation of nanoclays reduced the diffusion of water vapour across the polymer matrix [85].

Montmorillonite, bentonite, and sepiolite are the most commonly used nanoclays and they were successfully applied in various polymer nanocomposite systems as nanofillers. These materials are hydrophilic in nature which makes them miscible with hydrophilic polymer matrices. In the case of hydrophobic polymeric matrices, the miscibility of nanoclays and matrix can be achieved by modifying nanoclays by exchanging interlayer of cationic galleries of silicate layer with organic component [86]. Shah et al. [100] reported a study on organoclays modified with quaternary ammonium substituents. They reported that the d-spacing, interlayer spacing and hydrophobicity (parameters that determine compatibility between nanoclays and polymer matrix) of nanoclays increased with increasing chain length and benzyl substituents which result in an increase in exfoliation. This study also discovered that the incorporation of organoclays enhances tensile strength and modulus, flexural strength, hardness and elongation at break of the resultant nanocomposites. However, the incorporation of organoclays showed an inverse effect on impact strength.

Other critical issues affecting mechanical properties of nanocomposites reinforced with nanoclays are higher phase separation and particles aggregation in a polymer matrix which should be prevented to achieve proper reinforce effect of nanoclays. These shortcomings can be mitigated by modifying nanoclays. In one study, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) revealed that the addition of pristine nanoclays in polymer matrix resulted to disordered structures which indicate poor dispersion of nanoclays in the polymer matrix. On the other hand, nanocomposites reinforced with organoclays displayed some fine exfoliated and individual un-exfoliated layers of clay and therefore dispersion of clay in polymer matrix was evident [100]. Malkappa et al. [66] reported that the surface roughness increases with increasing in organoclays loading while; agglomeration was evident and became more visible when organoclays loading was increasing as shown in Fig. 2. Also, tensile strength and modulus increased with increasing organoclays loading whereas elongation at break showed inversely effect. Similar observations were evident in Alcântara et al. [6] study, they also reported that water resistance, biocompatibility, and biodegradation were improved when fibrous nanoclays were incorporated in polysaccharides. In another study, it was reported that tensile strength and modulus (as shown in Fig. 3) of biopolymer blends reinforced with expanded organoclay (EOC) increased linearly with increasing nanoclays loading. However, elongation at break was inversely proportional to nanoclays loading [76].

Recently, [72] fabricated PP/LDPE blends reinforced with organoclays by twin screw extruder and injection moulding and investigated their effect on mechanical properties. They discovered that the impact strength of PP decreased after blending

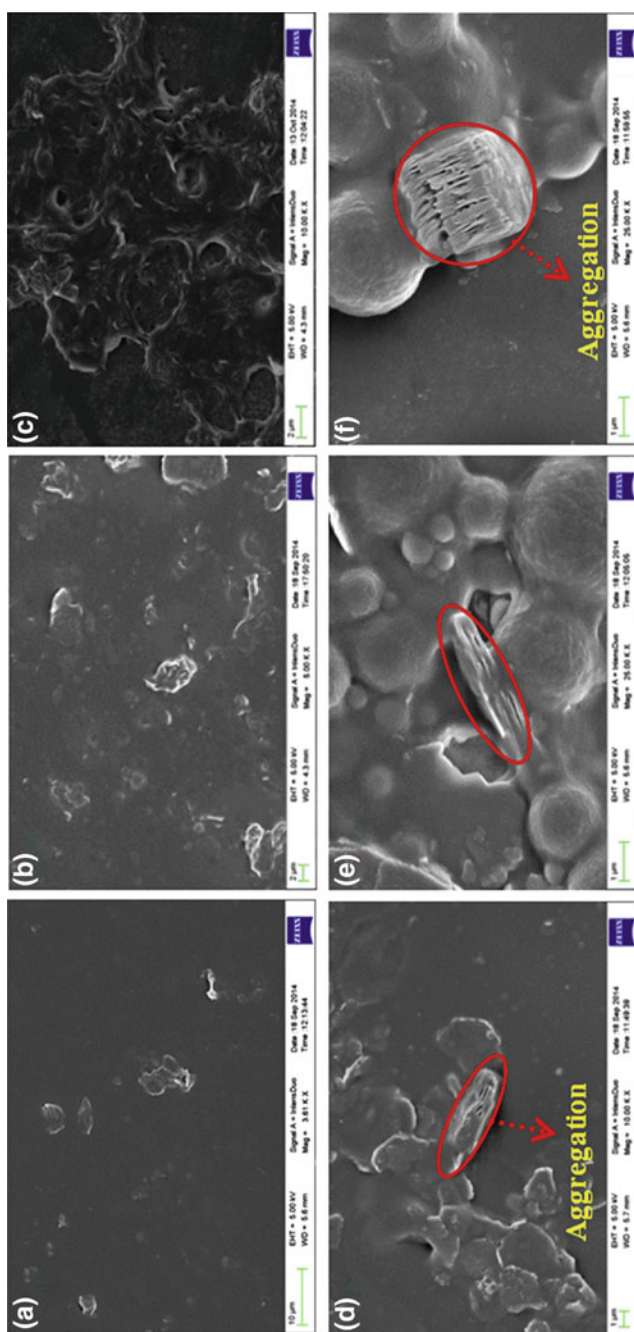
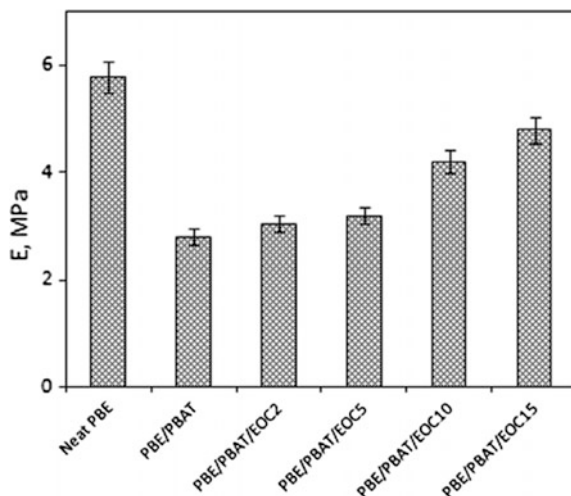


Fig. 2 Field emission electron microscopy (FESEM) images of: **a** water dispersible polyurethane (WDPUs)/Cloisite-30B-1 wt%, **b** WDPUs/Cloisite-30B-3 wt%, **c** WDPUs/Cloisite-30B-5 wt%, **d** WDPUs/OKao-3 wt% and **f** WDPUs/OKao-5 wt% [66], copyright with the permission from Elsevier

Fig. 3 tensile modulus of neat Natureplast PBE 003 (PBE), PBE/PBAT blend and its nanocomposites reinforced with expanded organoclay (EOC) [54], copyright with the permission from Elsevier



it with 20 wt% LDPE due to poor compatibility between the two polymers. However, the addition of organoclays in the blend led to the deterioration of impact strength which could be due to the restriction of chain mobility. In the same study, they investigated the effect of organoclays on tensile strength, tensile modulus, and elongation at break of polymer blends. The values of tensile strength, tensile modulus, and elongation of the blend were intermediates in comparison to those of neat polymers. The incorporation of organoclays in polymer blends enhanced tensile modulus and elongation at break while tensile strength was deteriorating. Moreover, a similar trend was also observed when the combination of organoclays and the compatibilizers were added to the blend. The highest elongation at break was observed when the combination of organoclays and the compatibilizers were added to the blend this was due to the miscibility of the materials. This indicates that nanoclays were well dispersed in the blend and the interaction between them and both polymers in the blend was improved.

Numerous researchers have reported the effect of hybrid of nanoclays together with other nanofillers such as metal oxide nanoparticles, nanotubes and natural fibres on the mechanical properties of nanocomposites [1, 9, 23, 51, 81, 117]. For instance, [23] reported that the incorporation of fillers (organoclays and rice husk) in recycled HDPE and polyethylene terephthalate (PET) blend enhanced the mechanical performance of nanocomposites. They suggested that the improvement of tensile properties could be due to the presence of organoclays which might carry much load and the fact that clay is stiffer than polymer matrix. The further enhancement was observed when compatibilizers were incorporated in polymer matrix reinforced with organoclays and rice husk. These results were in agreement with the results reported by other researchers [1, 9, 33] and they also reported that the mechanical performance was further improved when natural fibers were alkali treated. Other researchers [51, 117] investigated the effect of hybrid of nanoclays

and metal oxide nanoparticles (zinc and silver) on mechanical properties of nanocomposites. They reported that incorporation of nanoparticles enhanced the tensile strength and modulus. In addition, the inclusion of nanoparticles reduced water vapour permeability but, increased water content and density. Moreover, the inclusion of nanoparticles improved the antibacterial activity against Gram-positive *S. aureus*, Gram-negative *E. Coli*, and foodborne pathogens.

2.3.1 Mechanical Properties of Biopolymers Reinforced with Nanoclays

In recent years, nanocomposites from biopolymers reinforced with nanoclays have been extensively studied due to their low toxicity and biodegradability. Aliphatic polyesters have attracted tremendous attention for diversified applications. Polybutylene succinate (PBS) is among the widely studied aliphatic polyester. Phua et al. [84] investigated the impact of nanoclays on mechanical performance of polybutylene succinate (PBS) nanocomposites. In their study, they investigated mechanical properties to determine the biodegradation behaviour of nanocomposites. Before soil burial, they observed that the mechanical properties improved when organoclays were incorporated. The mechanical properties of nanocomposites deteriorated after soil burial and further reduced with soil burial time. In another study, the incorporation of nanoclays improved the mechanical performance of PLA. It was also reported that the increase in nanoclays loading increased linearly the tensile modulus while inversely effect was observed for elongation at break [43]. In contrast, the inclusion of organoclays in PHBV did not reinforce as anticipated due to the aggregation of clay in a polymer matrix [30]. Thereafter, numerous researchers fabricated nanocomposites from blended aliphatic polyesters with other biodegradable polymers and nanoclays. One of the limitations of biodegradable polymers is low mechanical properties which are not suitable for other applications such as packaging. The poor mechanical properties can be enhanced by blending biopolymers with other polymers or reinforced with stiffer fillers. Ayana et al. [11] and Lendvai et al. [59] blended thermoplastic starch with PLA and PBAT, respectively and subsequently reinforced with nanoclays. Ayana et al. [11] reported that the introduction of nanoclays enhanced tensile properties of the blends with an increase in loading. On the other hand, in the case of TPS/PBAT blend the inclusion of nanoclays did not show any effect on the tensile strength and modulus [59].

Agro-polymers such as starch, cellulose, protein, chitin and chitosan-based nanocomposites have recently attracted more interest due to their renewability, biocompatibility, biodegradability and non-toxicity with outstanding adsorption properties. The major drawbacks of agro-polymers are moisture absorption, difficulty processability, and poor mechanical properties. The inclusion of nanoclays in agro-polymers could result in the reduction of moisture absorption as well as enhance mechanical performance of nanocomposites. Numerous researchers [5, 34] are investigating efforts to overcome the drawbacks of agro-polymers.

The inclusion of nanoclays reduced water absorption and a further increase in nanoclays loading showed a decrease in water absorption [5]. They also reported that tensile strength and elongation at break decreased with increasing loading of nanoclays. Farahnaky et al. [34] prepared gelatin nanocomposites reinforced with nanoclays by a solvent casting method. They showed that tensile modulus increased linearly with increasing nanoclays loading while elongation at break decreased with increasing loading. A similar trend was observed in the case of chitosan nanocomposites reinforced with nanoclays [39, 40].

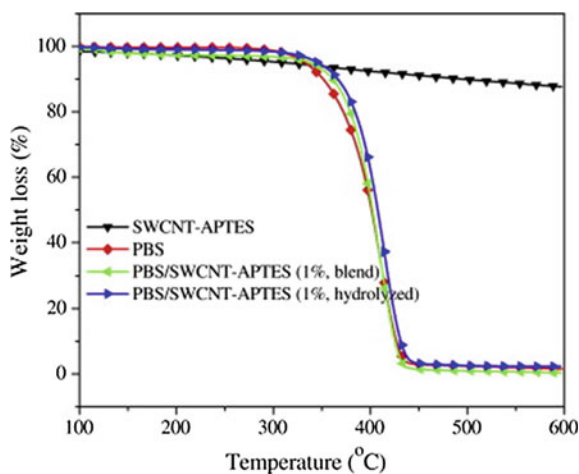
3 Thermal Properties

3.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is widely used to investigate the thermal degradation of polymer nanocomposites. A typical thermogram of polymer nanocomposite shows a material subjected to heat will suffer mass loss, followed by a sharp drop in mass over a narrow range and subsequently back to the flat slope as reactant is exhausted [12]. TGA and derivative thermogravimetric (DTG) are used to determine the mass loss and degradation of the material at a certain temperature as well as the remaining char content. Typical TGA curves are shown in Fig. 4.

In the published literature, it has been reported that the improvement in thermal stabilities of the nanocomposites is mainly attributed to the reinforcement effect of nanomaterials on polymers [57, 97, 119]. For instance, [3] investigated the effect of CNCs on thermal properties of polyfurfuryl alcohol (PFA) nanocomposites. They reported that the incorporation of CNCs improved the thermal stability of the PFA. Both the neat PFA and the nanocomposites showed two degradation steps at above

Fig. 4 TGA curves of SWNTs functionalized with acyl aminopropyltriethoxysilane (APTES), neat PBS, PBS/SWNTs-APTES (1%, hydrolyzed) [108], copyright with the permission from Elsevier



200 °C and in the temperature range of 320–400 °C which involves the scission of the weaker chemical bonds. According to Sanchez-garcia et al. [97], high thermal stabilities of PCL was achieved when 1 and 3 wt% of CNTs were incorporated, though increasing CNTs loading above 5 wt% result in filler agglomeration which reduced thermal stabilities of resultant nanocomposites. Similar behaviour was observed in the case of PHBV nanocomposites. Lai et al. [57] reported that the thermal stabilities of PLA nanocomposites increased with increasing in nanoclays loading. Interestingly, char content also increased with increasing in nanoclays loading. Other studies on thermal properties of nanocomposites are listed in Table 2.

Other researchers reported that the functionalization of either filler or polymer matrix enhances thermal stabilities of the resultant materials. For instance, [119] investigated the effect of unmodified and modified CNCs with phthalic anhydride on thermal stabilities of PBSA. They reported that degradation temperature of neat PBSA was above 300 °C due to chain scission and inter and intramolecular transesterification reactions. PBSA reinforced with CNCs modified with phthalic anhydride exhibited higher degradation temperature in comparison to those of PBSA reinforced with unmodified CNCs and neat PBSA. This enhancement was due to the addition of phthalic anhydride. Similar observations were reported in the case epoxy reinforced with GO modified with silane [111]. Majeed et al. [64] studied the incorporation of CNTs in neat LDPE and maleic anhydride grafted polyethylene (MAPE). They reported that MAPE reinforced with CNTs was thermally more stable in comparison to LDPE reinforced with CNTs and neat LDPE. The improved thermal stability with the inclusion of MAPE could result in improved compatibility and better dispersion of CNTs. In another study, they investigated thermal properties of rHDPE/rPET blend mixed with 3 wt% MAPE and 5 wt% ethylene-glycidyl methacrylate and subsequently reinforced with 3 wt% nanoclays and 70 wt% rice husk. Nanocomposites of polymer blends reinforced with nanoclays only exhibited a single step degradation pattern with improved thermal stability. However, the addition of rice husk resulted in three degradation steps which represent moisture evaporation at temperatures ranging from 135 to 145 °C, depolymerisation of hemicellulose and decomposition of cellulose at temperatures ranging from 230 to 370 °C and decomposition of nanocomposites and slightly decomposition of lignin at temperatures ranging from 476 to 482 °C. Incorporation of rice husk and nanoclays in compatibilizing matrix resulted in improvement of thermal stability in comparison to uncompatibilizing matrix.

Nanomaterials have been reported in numerous studies to enhance the thermal stabilities of polymer matrices. In contrast, [112] reported that the inclusion of CNTs did not affect the single stage decomposition pattern of PLA and remain unaltered. However, the incorporation of 1 wt% CNTs in PLA exhibited no alterations in thermal stability in comparison to neat PLA. However, the incorporation of 10 wt% CNTs in PLA resulted in a decrease in thermal stability but, the char content was higher in comparison to that of neat PLA and PLA reinforced with 1 wt% CNTs. The decrease in thermal stabilities after incorporation 10 wt% CNTs was due to the agglomeration of CNTs in PLA. Therefore, they reported that excessive CNTs prevent stress transfer and other superior properties to PLA.

Table 2 TGA degradation temperatures of polymers and nanocomposites

Sample	Degradation temperature (°C)	References
PCL	413	Sanchez-garcia et al. [97]
PCL + 10 wt% carbon nanofibres (CNF)	412	
PHBV	286	Sanchez-garcia et al. [97]
PCL + 10 wt% CNF	293	
Poly (acrylic acid) grafted onto amylose (PAA-g-amylose)	311	Abdollahi et al. [2]
PAA-g-amylose + 5 wt% graphene oxide (GO)	385	
Epoxy	341	Wan et al. [111]
Epoxy + 0.5 wt% pristine GO	354	
LDPE	479	Majeed et al. [64]
LDPE + 3 wt% CNTs	390	
Epoxidized natural rubber	430	Krainoi et al. [55]
Epoxidized natural rubber + 7 wt% CNTs	448	
PLA	385	Wang et al. [112]
PLA + 10 wt% CNTs	370	
rHDPE/rPET (75/25)	472	Chen and Ahmad [23]
rHDPE/rPET + 3 wt% clay	478	
rHDPE/rPET + 3 wt% clay + 70 wt% rice husk	481	
PLA	308	Fukushima et al. [37]
PLA + 7 wt% nanoclays	324	
PP/LDPE (80/20)	350	Mofokeng et al. [72]
PP/LDPE + 4 wt% nanoclays	380	
Whey protein isolate	301	Azevedo et al. [10]
Whey protein isolate + 3 wt% nanoclays	307	
Poly(methylmethacrylate) (PMMA)	367	Dong et al. [31]
PMMA + 41 wt% CNCs	384	
Thermoplastic polyurethane (TPU)	307	Floros et al. [36]
TPU + 2.5 wt% CNCs	334	
PMMA	183	Liu et al. [62]
PMMA + 8 wt% CNCs	192	
Epoxy	384	Xu et al. [113]
Epoxy + 15 wt% CNCs	388	
PLA	351	Shi et al. [102]
PLA + 10 wt% CNCs	356	

3.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a thermal analysis technique that assesses quantitative information on thermal transitions of materials through changes in heat capacity (C_p) by temperature. A sample of known weight (5–10 mg) is subjected to

Table 3 DSC analysis of polymer nanocomposites reinforced with various nanoparticles

Sample	$T_m/^\circ\text{C}$	$\Delta H_m/\text{J g}^{-1}$	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$\chi_c/\%$	References
PE	138.6	186.06	113.3	–	63.5	Nikkhah et al. [80]
In situ PECN-3%	139.8	174.80	118.8	–	59.6	
In situ PECN-5%	140.2	155.38	122.6	–	53.03	
PP	168.8	95.0	109.7	–	46.8	Baniasadi et al. [15]
In situ PPCN-3%	168.4	90.4	119.7	–	44.5	
In situ PPCN-5%	167.5	89.15	122.5	–	43.9	
PLA	148	27.2	110 ^a	16.14 ^b	12	Valapa et al. [110]
PLA-GR-0.3wt%	152.8	27.8	113 ^a	9.8 ^b	19.2	
PLA-GR-0.5wt%	152.6	23.3	110 ^a	6.84 ^b	17.5	
PP	165.1	–	–	102	48.8	Pedrazzoli et al. [82]
PP-xGnP-3wt%	165.3	–	–	102.1	50.4	
PP-xGnP-5wt%	165.9	–	–	100.4	50.6	
PBS	114.5	79.7	80.1	–	–	Han et al. [44]
PBSSi-3	112.0	77.2	64.3	–	–	
PBSSi-5	110.7	63.5	55.8	–	–	

T_m melting temperature, T_c crystallization temperature, ΔH_m and ΔH_c melting and crystallization enthalpy, χ_c percentage of crystallinity

^acold crystallization temperature (T_{cc})

^benthalpy of cold crystallization (ΔH_{cc})

heating and cooling through programmed temperature conditions and changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of thermal transitions such as melting temperature (T_m), melt crystallization/cooling temperature (T_c), melting enthalpy (ΔH_m), melt crystallization/cooling enthalpy (ΔH_c), a glass transition (T_g), curing and phase changes. Various studies on polymer matrices reinforced with different nanomaterials/nanoparticles/nanofillers (nanoclays, carbonaceous (carbon nanotubes and graphene), nanocellulose and inorganic oxide) have used DSC analysis to investigate the influence of nanoparticles on their thermal transitions [8, 21, 24, 29, 41, 42, 53, 56, 79, 80, 83, 98, 103–106, 110, 115, 118]. The melting and crystallization behaviours of polymer matrices which affect morphology, mechanical and thermal properties of the resulting nanocomposites are well documented in the literature and some of the undertaken studies investigated the influence of nanoparticles in polymer matrices are summarised in Table 3. Furthermore, the performance of polymer nanocomposites does not only depend on their molecular weight and chemical structure but significantly influenced by their crystallization properties such as crystallization rate, crystallization temperature and crystallinity [118]. In addition, it also reported in the literature that polymer crystallization is usually preceded by heterogeneous or homogeneous nucleation, or self-nucleation and then by crystal growth with respect to crystallization time [106]. These properties can be determined by using various mathematical models reported in literature to determine the crystallization kinetics [41], and the degree of

crystallinity (χ_c) which is the most used parameter [8, 16, 21, 24, 98, 107, 118], and is calculated according to Eq. 1.

$$\chi_c = \left(\frac{\Delta H_m / w_p}{\Delta H_m^o} \right) \times 100\% \quad (1)$$

where ΔH_m is the experiment of melting enthalpy of the nanocomposite, w_p is the weight fraction of the polymer in the nanocomposite and ΔH_m^o is the melting enthalpy of 100% crystalline polymer.

Studies on reinforcing polymers such as linear low-density polyethylene (LLDPE), polypropylene (PP), ethylene vinyl acetate (EVA) and poly(lactic acid) with exfoliated or expanded graphite and functionalized graphite nanoplatelets were investigated on their influence on thermal behaviour in polymer nanocomposites [8, 56, 71, 83, 98, 105, 110]. From these studies, incorporation of graphite nanoplatelets in polymer matrices enhanced the melting and crystallization temperature, melting endotherm and the crystallinity of the nanocomposites. For instance, improvement in the crystallinity for graphene (GR)/PLA composite samples were observed up to 0.3 wt% loading in comparison to neat PLA [110], while in binary PP nanocomposites the addition of exfoliated graphite nanoplatelets (xGnP) resulted in a significant increase in the crystallization temperature up to 5 wt% xGnP content [83]. A similar observation was recorded on poly(butylene succinate)/carbon nanotubes nanocomposites (PBS/CNT) [7] and poly(ϵ -caprolactone) (PCL) blended with a polycarbonate/multi-wall carbon nanotubes masterbatch (PC/MWCNT) [41]. This has demonstrated that the graphene/exfoliated graphite nanoplatelets, MWCNT and CNT dispersed in the composites can facilitate the polymer's crystallization process or act as nucleating agent [8, 98, 105]. On the other hand, slight decreases in the enthalpy and crystallinity were also observed when graphite or carbon nanotubes loadings were increased and this was attributed to agglomeration and poor dispersion of the nanoparticles which restricted polymer chain mobility and reduced the extent of crystallization [41, 70, 83].

In clay reinforced polymer nanocomposites, it has been reported that the presence of small amount of well-dispersed clay nanolayers can act as effective nucleating agents to accelerate crystallization in the polymer, thereby slightly increasing the melting and crystallization temperatures of the polymer composite [15]. On the other hand, the inclusion of clay nanolayers in polymer matrices has been observed to decrease the degree of crystallinity and does not significantly change the thermal transitions of the resulting nanocomposites. This is mainly attributed to the following observations (i) the additions of organoclays into crystalline polymer matrices do not ensure the enhancement of the polymer matrix crystallization rate [29, 103], (ii) that presence of clay nanolayers can form strong polymer-clay network which can limit the mobility of polymer chains and as a result decrease the degree of crystallinity especially at high clay concentration [15, 80, 104]. On the other hand, [73] recently investigated the effects of clay localization and its distribution in an immiscible blend of PP/LDPE on the non-isothermal crystallization and degradation kinetics. The authors observed that

the non-isothermal crystallisation analysis for the localization of clay particles in the blend composites had two opposing effects, (i) the poorly dispersed clay particles at the PP/LDPE interface in the non-compatible blend composite had no significant effect on the crystallisation temperature of PP but allowed the free movement of PP chains, which resulted in a higher crystallinity of PP than that of PP in the neat blend; (ii) the well-dispersed clay particles in the compatibilized blend composites disrupted the free movement of PP chains, resulting in a lower crystallisation temperature and crystallinity than that of PP in the neat blend.

In the case of inorganic oxides reinforced polymer composites, a heterogeneous nucleation effect was observed to play a significant role in polymer crystallization which can be exploited for the shortening of cycle time during processing [99]. The nanoparticles turn to increasing the crystallization temperature and the rate of the polymer composite, while in other cases the heterogeneous nucleation becomes dominating with increasing filler concentration [106], but was seen to decrease the crystallization activation energy and crystallinity of the polymer with the addition of hydroxyapatite nanorods (HAP) by Zhan et al. [118]. The authors investigated the crystallization and melting properties of PBS composites with titanium dioxide nanotubes (TNTs) or (HAP). This was caused by strong hydrogen bonding interaction that exists between HAP and PBS, which reduced the transport of the PBS macromolecules and as a result lowered the crystallization rate of PBS/HAP composite than that of pure PBS.

On the other hand, PBS/nano-CaCO₃ composites showed independence of the crystallization behaviour with increasing nano-CaCO₃ content. Furthermore, the nanoparticles had little influence on the crystallization and melting behaviour of PBS. This implied that the nano-CaCO₃ might not have played an active role in the heterogeneous nucleation of PBS matrix. For natural fiber reinforced polymer composites, natural fibers were observed to act as nucleating agents promoting crystallization of polymer matrices [16, 32, 107]. For instance, [32] prepared poly (3-hydroxy butyrate) (PHB)/poly lactic acid (PLLA)/Tributyl citrate (TBC) blend reinforced with CNCs to increase the elongation at break of PLLA for food packaging. The well dispersed CNCs and PHB in PLLA matrix acted as bio-nuclei in PLLA matrix to help the crystallization rate and reduce the size of spherulites and thereby improving the elongation at break from 6% for pure PLLA to 40–190% for the composites with CNCs. It is also worth noting that reinforcing with natural fibers could lead to different nucleation activity due to the different surface structure of the fibers [16].

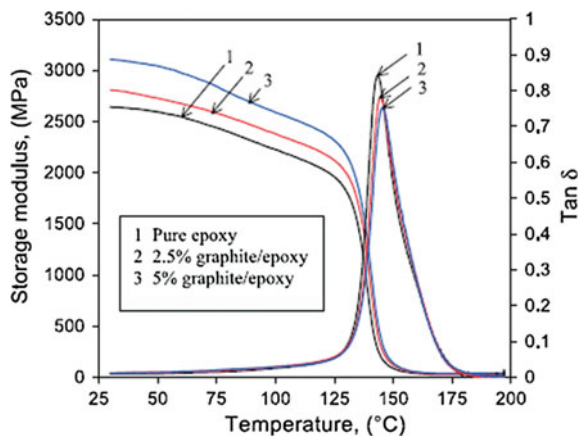
4 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analysis is a technique that determines the viscous modulus (loss modulus, G''), elastic modulus (storage modulus, G') and damping coefficient ($\tan\delta$) as a function of temperature, time or frequency. The DMA is used to identify transition regions in polymer materials, such as the glass transition

temperature (T_g) and to recognize transitions corresponding to other molecular motions which are beyond the resolution of DSC. The viscoelastic properties of the polymer matrices reinforced with various nanofillers have been investigated from the measurements of storage modulus and the loss factor using dynamic mechanical analysis to evaluate the effect polymer/nanofiller interface with changing polymer mobility. These measurements provide indications about the increase in the storage or decrease in modulus of the resulting nanocomposites, shift in the glass transition temperature due to the polymer chain restriction or mobility [44, 65, 82].

Song et al. [105] fabricated exfoliated graphene-based polypropylene nanocomposites with enhanced mechanical and thermal properties prepared by melt blending technique. The exfoliated graphene nanosheets were varied from 0.1 to 5 wt% to evaluate the influence of graphene loading on polypropylene. The storage modulus of the PP/graphene nanocomposites increased with increasing graphene loading up to 1 wt%, while further increases in graphene loading led to a slight decrease in the storage modulus in the entire temperature range (-50 – 150 °C). The results were in agreement with their tensile modulus and the reduction in the storage modulus was attributed to the plasticization effect of low modulus of PP matrix. The glass transition temperature of PP improved by ~ 2.5 °C at 0.1 wt% (0.041 vol.%) graphene content, which indicated a restriction in chain mobility of PP. Similar observation was recorded in the study on mechanical and thermal properties of graphite platelet/epoxy composites [115]. At 2.5 and 5 wt%, graphite platelet/epoxy composites showed increased storage modulus (about 8 and 18%) higher than the pure epoxy matrix. As the temperature was increased, both pure epoxy and its composites showed a gradual drop in storage modulus followed by a sudden drop at the glass transition temperature. The drop in modulus is associated with the material transition from a glassy state to a rubbery state as seen in Fig. 5. Furthermore, with increasing graphite contents of 0, 2.5 and 5 wt% the T_g gradually increased to 143, 145 and 146.8 °C, respectively. This was attributed to the good adhesion between the polymer and graphite platelets, which restrict the segmental motion of cross-links under loading.

Fig. 5 Dynamic mechanical properties of pure epoxy and its composites [115], copyright with the permission from Elsevier



In a comparison of the effect of expanded graphite (EG) and modified graphite flakes (i-MG) on the physical and thermo-mechanical properties of styrene butadiene rubber/polybutadiene rubber (SBR/BR) blends [65]. A drastic increase in the storage modulus of EG and i-MG loaded SBR/BR composites in the presence of carbon black (CB) was observed in a wide range of temperature compared to the BR based nanocomposites. This was attributed to good dispersion of nanofillers in the rubber blend which increased its stiffness, and as a result, increased the storage modulus of SBR/BR based nanocomposites. In addition, as a result of isocyanate surface modification on graphite sheets (i-MG), higher basal spacing and exfoliated structure of i-MG sheets than EG flakes was achieved. Exfoliated graphite i-MG sheets were uniformly dispersed in different rubber matrices in the presence of CB, and resulted in superior mechanical, dynamic mechanical and thermal properties compared to the EG filled rubber composites. Surface modification of graphite sheets prior to nanocomposite preparation is one of the significant aspects that facilitate the compatibility between the polymer matrix and the nanofiller to form a homogeneous dispersion of nanoparticles and enhance adhesion in the polymer composites. Modification of graphene/graphite sheets by a range of techniques employing various organo modifying agents to improve mechanical properties of polymer nanocomposites are reported in the literature [20, 56, 69]. Among these reported techniques, the nucleophilic addition of organic molecules to the surface of graphene/graphite is an effective way to the bulk production of surface-modified graphene.

Analysis of thermomechanical properties for polymer matrices reinforced with nanomaterials is important in ascertaining the performance of the nanocomposite under stress and temperature. In polypropylene/clay nanocomposites (PPCNs) prepared by in situ polymerization [15], the presence of clay nanolayers dispersed in PP matrix resulted in a significant increase in stiffness (storage modulus) for all nanocomposites with increasing clay content and temperature. The reinforcing effect was at a maximum in the region above the glass transition temperature of the matrix, primarily due to the larger difference in mechanical properties between the filler and the matrix as it changes from the glassy to the rubbery state. Moreover, a marginal increase in T_g with increasing clay concentration (between 1 and 5 wt%) was observed. This was attributed to the interactions between polymer and filler which delay the segmental motion of the chains. Better dispersion of clay particles in a polymer provides greater reinforcement and higher chain immobility, thereby resulting in high storage modulus values [72]. Similar observations were recorded in the extraction of CNCs from flax fibers and their reinforcing effect on poly (furfuryl) alcohol (PFA) [78]. Incorporation of CNCs into PFA matrix resulted in increased storage modulus over the whole temperature range, the loss modulus peak shifted to higher temperatures and the magnitude of the peak decreased due to the presence of CNCs, the glass transition temperature values increased after the inclusion of CNCs into PFA. The overall results implied that the presence of CNCs in PFA improved the stiffness of the composite, restricted polymer chain mobility as a result of good interaction between the polymer and the filler.

5 Melt Rheology Properties

The study on melt rheological properties for polymer materials is very important from the processing point of view. In addition, information on the microstructure of the polymer materials in the melted state can be provided from the melt rheology [7]. Rheological properties are known as mechanical properties of the material that undergoes deformation and flow in the presence of stress. The melt rheology is usually measured from the melt phase of the polymer from its melting temperature at the desired strain that is well within the linear viscoelastic range. Viscoelastic properties of thermoplastic and nanofiller reinforced composites can be measured over a range of frequencies to gauge the rate of the viscosity changes with shear rate. Various studies on the effect of the nanofiller addition, such as carbonaceous [7, 17], natural fibers/cellulose [53], inorganic oxides [24, 82, 106] and nanoclays [72] on the isothermal frequency dependence of the dynamic shear storage modulus (G') and complex viscosity (η^*) were investigated. For instance, [7] prepared PBS/CNTs nanocomposites fabricated by melt mixing and investigated the rheological properties. The viscoelastic properties of PBS/CNTs composites at high frequencies behaved the same while low frequencies the nanocomposites were frequency independent (Fig. 6a, b). The nanocomposites showed gradual changes in the

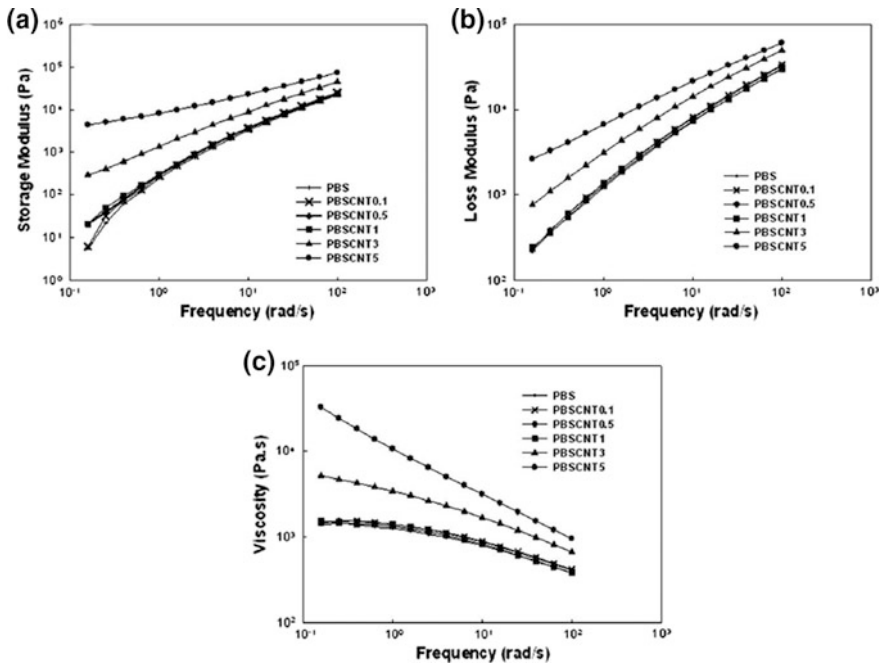


Fig. 6 Viscoelastic properties of PBS and PBS/CNTs composites in the melted state **a** Storage modulus of **b** loss modulus and **c** complex viscosity [7], copyright with the permission from Elsevier

composites from liquid-like to solid-like behaviour, especially for PBS/CNT3 and PBS/CNT5 samples. This was attributed to interactions between nanotubes which formed interconnected structures of CNTs in the PBS/CNTs composites, thereby enhancing the relaxation behaviour and increased the storage modulus. In addition, improvement in the complex viscosity was also observed due to the flow restriction of the polymer by filler in the melted state (Fig. 6c). On contrary, the G' and G'' of pure PBS and PBS/nano-CaCO₃ composites with various nano-CaCO₃ loadings as a function of frequency exhibited a liquid-like a behaviour for both PBS and CaCO₃ filled composites [24]. The results implied that the nano-CaCO₃ particles had little influence on the microstructure of PBS; the relaxation mechanism and the microstructure of the PBS/nano-CaCO₃ composites mainly depended on the PBS matrix than on nano-CaCO₃ content. Furthermore, a similar decrease in G' and η^* was observed for linear-low-density polyethylene reinforced boehmite alumina (LLDPE-BA) [82]. The observation was attributed to the highly branched LLDPE whose chains would tend to get entangled; apparently even poorly bonded plain BA particles fill in the spaces between chain branches and enable an easier flow. Khumalo et al. [54] in a similar study suggested that there was no strong interaction between the BA and LDPE in the nanocomposites.

6 Conclusions

In this chapter, the mechanical, thermal, dynamic mechanical and rheological properties of polymer nanocomposites reinforced with nanomaterials were presented. It can be concluded that nanomaterials have the power to alter the properties of polymer nanocomposites which can be exploited in a variety of applications. By combining nanomaterials with the polymer matrix, novel materials with multi-properties can be achieved. The development of polymer nanocomposite with multi-properties depends on various factors such as filler particle size, surface area, aspect ratio, compositions, purity, crystallinity, shape, properties (mechanical, antibacterial, thermal, electrical etc.), dispersion, filler loading and interaction between filler and polymer matrix. Nanomaterials which were reviewed in this study are nanocellulose, carbonaceous fillers, and nanoclays and they have received significant attention globally particularly due to their extraordinary properties. The major drawback of polymer nanocomposites is a homogeneous dispersion of nanomaterials in the polymer matrix. To address such drawback, functionalization of either filler or polymer is the effective approach to alter the functional groups of the material, thus improving the interfacial adhesion between filler and polymer matrix which enhances the properties of the resultant material. In this chapter, it was noticed that loading nanomaterials in polymer matrix improved their properties and further increase filler loading to threshold amount enhanced the properties polymer. Many researchers indicated that adding filler after threshold amount deteriorates the properties of the material due to agglomeration which led to poor interaction between filler and polymer matrix and therefore, this result in poor properties of the

resultant material [55, 112]. The novel polymer nanocomposites with multi-properties can be used in medical, agricultural, food packaging, automotive etc. Much research is required to further develop the commercially available polymer nanocomposites and develop other novel materials.

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