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Full Length Article

Chain extension of poly(butylene terephthalate)/organically modified clay nanocomposites

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ABSTRACT

Thermal degradation of poly(butylene terephthalate) (PBT)/organically modified clay (organoclay) nanocomposites at elevated extrusion temperatures is inevitable and restricts the extensive use for these nanocomposites. This study aimed to prepare PBT/organoclay nanocomposite with enhanced properties by chain extender assisted reactive extrusion approach. A commercial organoclay, Cloisite 30B (C30B), was employed to prepare nanocomposite and a chain extender having multi epoxy functional groups, Joncryl ADR 4300 (Joncryl), was used to compensate thermal degradation of PBT accelerated by the organoclay for the first time. The morphological observations revealed high delamination of C30B within the matrix and the incorporation of Joncryl led to a well-exfoliated structure. The non-chain extended nanocomposite showed the matrix degradation in the rheological tests, where the notable benefit of the chain extender to offset degradation was observed by improvements in the viscoelastic properties. Compared to neat PBT, the tensile modulus of non-chain extended nanocomposite increased by 33 %, whereas a 56 % enhancement was measured for nanocomposite with chain extender. Thermogravimetric analyses indicated higher thermal decomposition temperature with addition of Joncryl into the nanocomposites. It was concluded that Joncryl recoupled degraded chains of PBT and effectively improved the features of nanocomposites.

1. Introduction

Poly(butylene terephthalate) (PBT) has been considered as significant engineering thermoplastic from polyesters group and synthesized by condensation polymerization of alcohols with acids. PBT has been widely used today because of its eminent mechanical and thermal properties, electrical insulation and resistance to solvents. It is used as the base material in the production of electrical switches, sockets, fiber optic cable covers, fuse panels, interior accessories of cars, toys, kitchen and sports goods [1–3]. In an attempt to enhance the properties of PBT and make its usage in wider applications, preparation of PBT nanocomposites with various nanoparticles is an appropriate approach [4,5]. Nanoclays are commonly preferred to develop PBT nanocomposites as tremendous surface area of nanoclays enables high interaction with the polymer matrix and builds up many features like tensile, rheology and barrier [6,7].

The most crucial issue for development of polymer nanocomposites with layered silicates is delamination and distribution of nanoclays through polymer matrix with an exfoliated morphology [8,9]. The exfoliated state of layered silicates is dependent several factors like modification of the clay and nanocomposite preparation method [10]. The hydrophilic characteristic of the clay restricts its use with organic polymers and makes the modification of clay by organic cations essential [11,12]. Compared to solvent casting and in-situ polymerization, the melt compounding becomes prominent technique to develop polymer–clay nanocomposites which is applicable to industry allowing high-volume production and being environmentally friendly without requirement of solvents [13–15]. The major obstacle in the melt compounding of polymer-organically modified clay (organoclay) nanocomposites is lower thermal stability of quaternary ammonium salts applied to organically modify the clays. Most of polymers require high processing temperatures than 180 °C, where ammonium modifiers undergo thermal degradation reactions inevitably [16]. Although imidazolium and phosphonium treated montmorillonites show enhanced thermal stability, they have poor intercalation within the polymer matrix [17,18]. Thermal degradation of ammonium surfactants occurred either the nucleophilic replacement or Hofmann elimination reactions. An alkyl halide resulted from the nucleophile attacking on the surfactants via halide ions. For Hofmann elimination, hydroxyl functionalities in the organoclay extracts hydrogen as proton (H^+) from the ammonium

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surfactant's carbon atoms and results in generation of Bronsted acids which have catalytic effect on scission of polymer chains [19].

The decomposition occurred in the ammonium modifiers of the clays induces the PBT matrix degradation further during melt-processing and leads to carboxyl and hydroxyl chain end groups [7,20]. The chain scission of PBT diminishes the molecular weight and performance of the nanocomposites. Solid state polymerization is commonly applied to enhance molecular weight of polyesters however, this batch process has been performed under elevated vacuum and temperature for extended times of 8–24 h [21,22]. The employment of chain extenders in the extrusion of polycondensates is a favorable method which has been applied to control thermal degradation and enhance molecular weight of poly(ethylene terephthalate) (PET) [16,19,23], poly(lactic acid) (PLA) [24–26], polyamide (PA) [27] and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) [28] based organoclay nanocomposites in the literature. These studies confirmed that chain extender approach compensated thermal degradation of polymer matrix with improved properties of the nanocomposites and increased exfoliation level of organoclays without requirement of further processing. Chain extender type directly influences yield of reaction with end groups of thermally degraded polymer, therefore determination of the appropriate chain extender is a critical issue [29,30].

Joncryl 4300 (Joncryl), a chain extender having multi epoxy functional groups, was reported as a good candidate for offsetting thermal degradation of polyesters such as PET and PLA prepared by commercial organoclays in the melt-compounding. Najafi et al. [24] reported that Joncryl had a more profound effect to compensate thermal degradation and increase molecular weight of PLA/organoclay nanocomposites during extrusion. Compared to phosphite and diimide chain extenders, the multiple reactive groups of Joncryl reacted with more PLA chains and significantly increased the rheological properties by formation cross-linking or branching in the polymer chains. Meng et al. [25] used diisocynate, dianhydride and Joncryl to improve thermal stability of PLA based organoclay nanocomposites during melt processing. It was concluded that reactivity of Joncryl was much larger and this extender remarkably offset thermal degradation of nanocomposites to an extent of organoclay loading (6 wt%). Another work by Najafi et al. [26] reported that PLA based organoclay nanocomposites containing Joncryl presented higher extent of clay dispersion and lower permeability than those having no extender. The higher molecular weight of chain extended nanocomposites reflected a profound enhancement in toughness, drawability and modulus of the nanocomposites. In a study conducted with PET [16], Joncryl was utilized to eliminate thermal degradation during the extrusion of PET/organoclay nanocomposites. The effect of Joncryl on the improvement of thermal stability of the nanocomposites was confirmed by the increases in the complex viscosity and elastic modulus of the samples. The epoxy functionalities of the chain extender reacted with the chain reactive endings of PET thus connected the polymer chains and improved the rheological properties. Transmission electron microscopy (TEM) images showed enhancement of clay distribution through the polymer matrix in the presence of chain extender. This finding was explained that the Joncryl augmented the viscosity of the polymer creating higher shear stresses during extrusion and leading the clay aggregates to disperse within the polymer matrix. The incorporation of Joncryl also caused enhancement in tensile modulus of the nanocomposites due to higher molecular weight of the polymer matrix and clay exfoliation. Compared to neat PET, the modulus of the nanocomposites containing Joncryl increased by 66 %, while nearly 30 % enhancement was observed for the nanocomposites without Joncryl.

The efficiency of Joncryl for organoclay nanocomposites based on the blends of PLA with various polymers were also reported in the literature. In the study by Khojasteh-Khosro et al. [31], scanning electron microscopy (SEM) analysis showed that the incorporation of Joncryl to PLA/Polycarbonate (PC) organoclay nanocomposites enhanced dispersion of clay particles due to stronger shear forces applied during mixing by higher molecular weight of the blend. Moreover, Joncryl led to decrease in PC domain size for nanocomposites. On the other hand, flexural and tensile strength, elastic and flexural modulus and elongation at break were increased with addition of Joncryl to nanocomposites. The chain extender lowered interfacial tension therefore improved compatibility of the blends and provided higher stiffness and toughness to the nanocomposites due to a large extent of clay dispersion. The benefit of Joncryl was also reported for PLA/ Poly(butylene adipate-co-terephthalate) (PBAT)/organoclay nanocomposite films as the incorporation of Joncryl at 1 wt% increased tensile strength, elongation at break and elastic modulus of the nanocomposites by higher interactions between PLA and PBAT and enhanced molecular weight of the samples [32]. A study conducted by Kahraman et al. [33] focused effects of Joncryl on the PLA/thermoplastic urethane (TPU)/organoclay nanocomposites. TEM and SEM images presented the compatibilization effect and viscosity enhancement of the nanocomposites with chain extender which reflected smaller TPU domain size and better clay dispersion. The impact strength, tensile strength and modulus of blend nanocomposites increased with Joncryl indicating improvements in droplet morphology, compatibilization of polymer phases and clay dispersion. Since these studies dictated the benefit of Joncryl to improve thermal stability and properties of various polymer-organoclay nanocomposites during melt-processing, there is a research gap in the use of Joncryl chain extender for PBT/organoclay nanocomposites during melt-compounding and highlights novelty of the present study.

The aim of this study was to prepare PBT/Cloisite 30B (C30B) organoclay nanocomposites with enhanced properties by reactive extrusion approach using Joncryl chain extender with multi epoxy functionalities for the first time. The effect of organoclay and chain extender on the morphological, rheological, thermal and mechanical properties of PBT were investigated.

2. Experimental

2.1. Materials

An extrusion grade PBT (Ultradur B2550) was purchased from BASF in granular form. The density of the polymer is 1300 kg/m^3 and it has a melting temperature of 223 °C [34]. The organoclay, Cloisite 30B from Southern Clay Products Inc, is a montmorillonite treated by bis-2-hydroxyethyl quaternary ammonium chloride having a cation exchange capacity of 90 meq/100 g clay and the interaction of hydroxyl radicals of the clay modifier with carboxyl endings of polyesters makes this organoclay preferred in the present study [26]. Joncryl ADR 4300, a styrene-acrylic copolymer chain extender having multi epoxy reactive groups, was kindly supplied from BASF. It possesses a molecular weight (M_w) of 6800 g/mol, a density of 1080 kg/m^3, a glass transition temperature (T_g) of 54 °C and it can react with chain end groups of polycondensates [16,25]. In the study Joncryl ADR 4300 and Cloisite 30B were abbreviated to JC and C30B, respectively.

2.2. Sample preparation

A co-rotating twin-screw laboratory scale compounder (Haake Minilab II Micro-compounder, Thermo Scientific) was used to prepare the samples. Prior to processing, PBT granules, chain extender and organoclay powder were dried at 85 °C for overnight to remove moisture and avoid thermo-oxidative degradation during melt compounding. The barrel temperature was set at 245 °C and screw rotation speed was fixed at 50 rpm. All materials were directly and simultaneously fed into compounder and mixed for 3 min. The nanoclay and chain extender loadings were kept at 4 wt% and 1 wt%, respectively. At the end of mixing time, the extrudate was cooled down, pelletized and placed in a vacuum oven at 85 °C for overnight. The dried extrudate granules were then molded at 245 °C under 250 MPa for 3 min using a hot press to

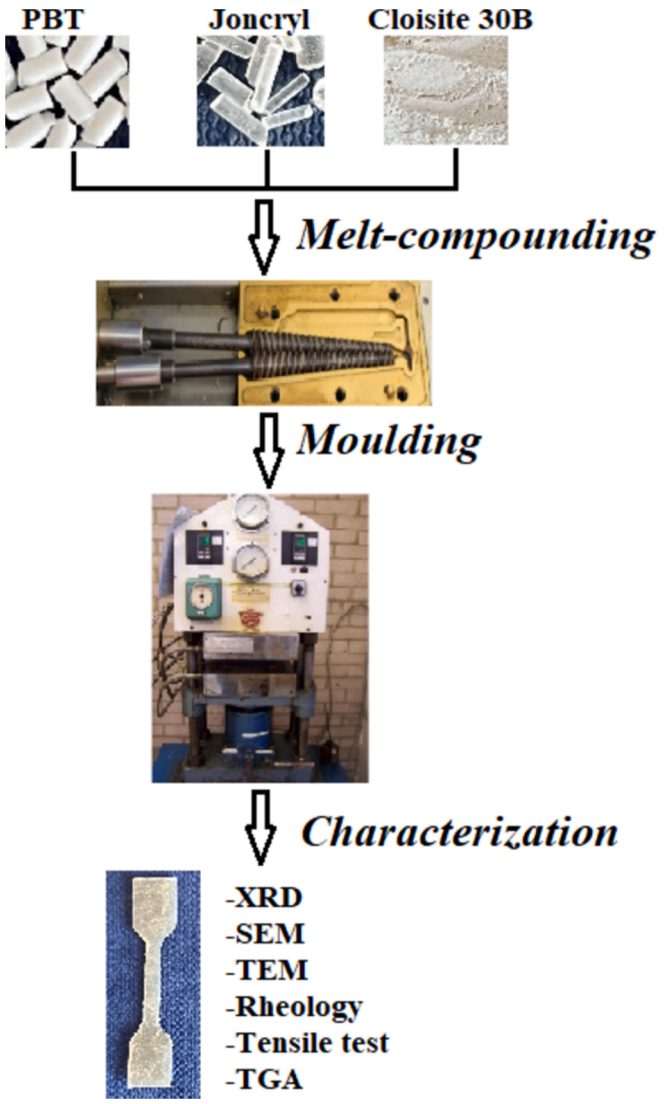

Fig. 1. The overview of experimental work.

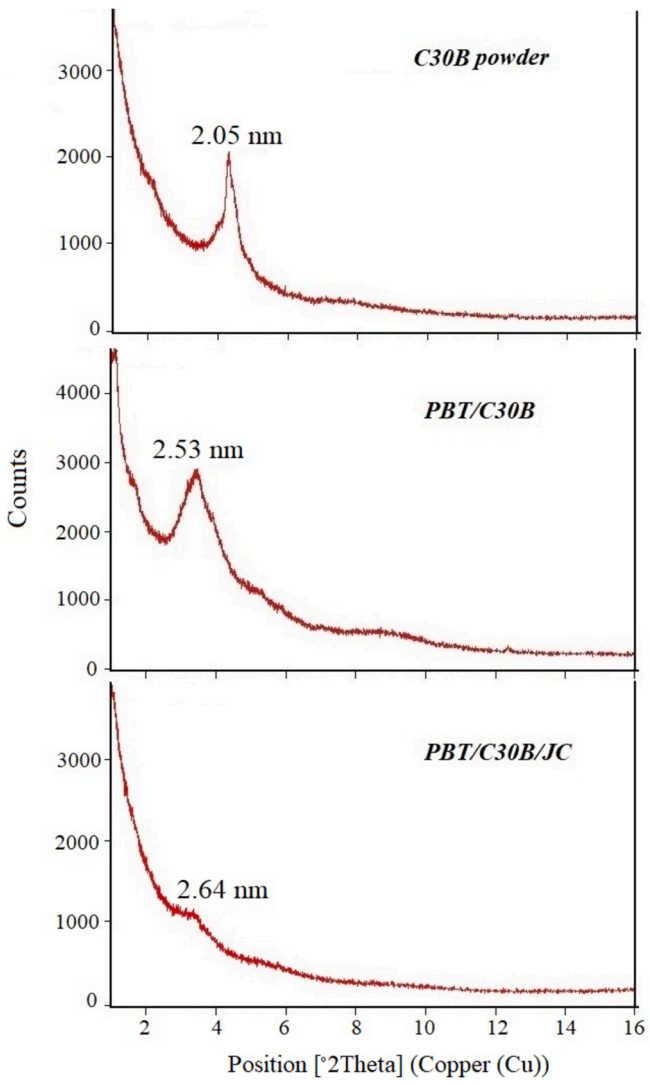

Fig. 2. XRD patterns of C30B powder, PBT/C30B nanocomposite without chain extender and PBT/C30B nanocomposite with chain extender.

prepare testing specimens. The experimental work is summarized in Fig. 1.

2.3. Characterization

X-Ray Diffraction (XRD) analysis was applied for determination of the basal spacing (d_{001}) for organoclay powder and PBT/organoclay systems. The analyses were carried out by a Philips X'Pert Pro X-Ray diffractometer, using CuKα radiation ($\lambda = 1.54056$ Å) at 45 kV and 40 mA. The distance between silicate layers was calculated from Eq. (1) using Bragg's law:

$$n\,\lambda = 2d\sin\,\theta \tag{1}$$

where n, λ, d and θ address to order (integer) of the wavelength ($n = 1$), wavelength of X-Rays, space of diffracting planes and angle of diffraction, respectively.

Scanning electron microscopy (SEM) was employed to evaluate the internal structure of the nanocomposites and the influence of the Joncryl on the micron scale distribution of the nanoclays within PBT matrix. SEM observation was performed using a Carl Zeiss 300VP SEM operating at 5 kV. Prior to analysis, surfaces of specimens were coated with a conductive gold layer by Quorum Q150 RES.

The influence of the Joncryl on the nano scale distribution of the organoclay within PBT matrix was investigated using the FEI TECNAI F30 transmission electron microscope (TEM) at 200 kV. Ultrathin sections of the specimens were cut at cryogenic temperature of −100 °C by LEICA EM UC6 Ultramicrotome.

The rheological analyses of the samples were conducted by Anton Paar Physica MCR 501 rotational rheometer. The frequency and time sweep tests were performed by using a parallel plate flow geometry with 25 mm plate diameter and 1 mm gap size at 240 °C. Time sweep tests were conducted at 1 Hz frequency over 900 s to evaluate thermal stability of the samples. Frequency sweep analyses were carried out between 0.1 and 100 Hz angular frequency range. In the tests, the strain amplitude was adjusted at 0.5 %, which was in the linear viscoelastic region.

The determination of tensile properties of the specimens were achieved by an Instron Universal Testing Machine (Model 5564) at room temperature according to ISO 37/4 test standard. Five dumbbell-shaped test specimens from each group were measured at a cross-head speed of 5 mm/min and the average results with standard deviations were reported.

Thermogravimetric analysis (TGA) was conducted by Hitachi Exstar SII TG/DTA 7300 analyzer under nitrogen atmosphere. The analyses were implemented on specimens of 8 mg from room temperature to 750 °C at a heating rate of 10 °C/min.

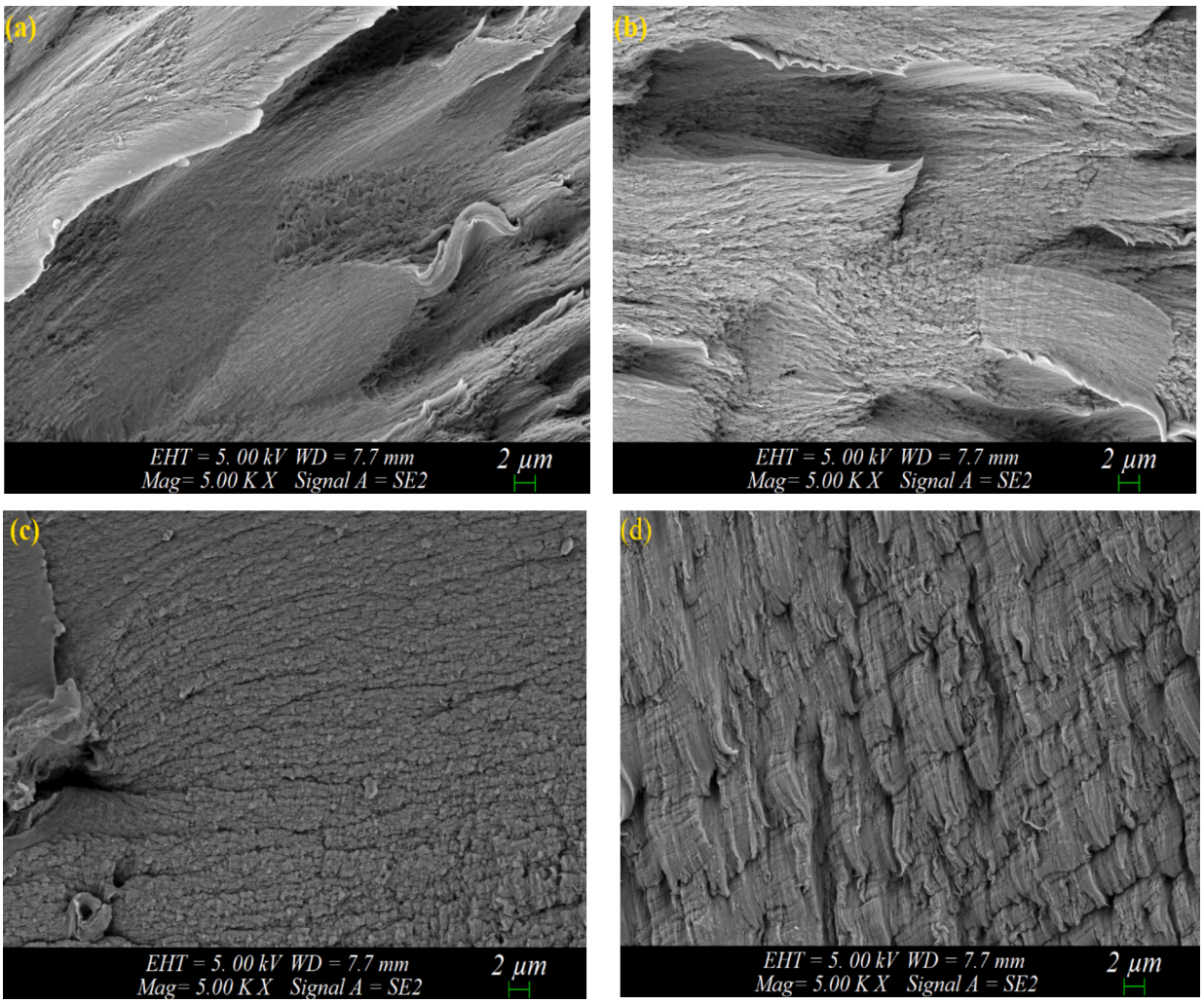

Fig. 3. SEM images of (a) and (c) PBT/organoclay nanocomposite without chain extender, (b) and (d) PBT/organoclay nanocomposite with chain extender.

3. Results and discussion

3.1. Morphological properties

Fig. 2 shows the XRD diffractograms of organoclay and PBT/organoclay nanocomposite systems in the presence and absence of chain extender. The existence, intensity and position of the peaks obtained from XRD analyzes allow a primary evaluation of the internal structure of the nanocomposites. The peak intensity and the d_{001} diffraction of PBT/C30B nanocomposite corresponding to 2θ had lower angle (3.48°) than C30B powder (4.31°) which can be attributed to diffusion of PBT chains into the basal spaces of organoclay during extrusion [16]. As a matter of fact, the gallery spacing of nanolayers in C30B powder increased after melt-compounding with PBT from 2.05 nm to 2.53 nm. The introduction of Joncryl in the nanocomposite decreased the intensity of the peak and shifted it to lower angle as 3.34°. Since the basal spacing for PBT/C30B/JC was found to be 2.64 nm, the enhancement of gallery spacing in chain extended nanocomposite can be explained that extended and branched PBT chains exerted larger shear forces on clay particles and brokedown them into multiple smaller stacks [24,27].

Since XRD analyzes cannot directly provide visual information about the extent of exfoliation and clay particle size, microscopy studies using SEM and TEM were carried out in an effort to better elucidate the XRD data. Fig. 3 presents SEM images of the nanocomposites. A few small clay agglomerates can be observed in the non-chain extended nanocomposite from Fig. 3a, whilst C30B particles were homogeneously distributed in the PBT matrix at the submicron particle size and without formation of large agglomerates for the chain extended nanocomposite in Fig. 3b. The breakdown of the large clay agglomerates to submicron particles could be attributed to strong shear forces by the help of chain extender during melt-compounding. With regard to fracture morphology of the nanocomposites, non-chain extended nanocomposite showed mainly brittle features which could be characterized by microcracks within the PBT matrix from Fig. 3c. In addition to that, there were some voids, where initiated to crazing in the matrix. On the other hand, the nanocomposite with chain extender exhibited rather ductile features as shown in Fig. 3d. The incorporation of Joncryl led to fibrillation in the polymer matrix that was indication of plastic deformation. Since the exfoliated layers and smaller tactoids could not be detected by SEM, further visual observations using TEM were performed to examine influence of chain extender on the extent of organoclay dispersion.

Fig. 4 shows TEM images of the chain extended and non-chain extended nanocomposites, where dark/black lines show clay layers and light/gray areas represent PBT matrix. Fig. 4a presents that no large agglomerates were appeared for PBT/C30B nanocomposite and the nanoclay particles were homogeneously dispersed in the PBT matrix. High shear and elongational stresses during melt compounding broke down clay particles into tactoids consisting of a few thin layers and exfoliated platelets therefore PBT chains diffused into the gallery spaces of the organoclays and increased the distance between the silicate layers [35]. Moreover, the strong polar interactions between hydroxyl groups of the methyl tallow bis(2-hydroxyethyl) ammonium cation in the

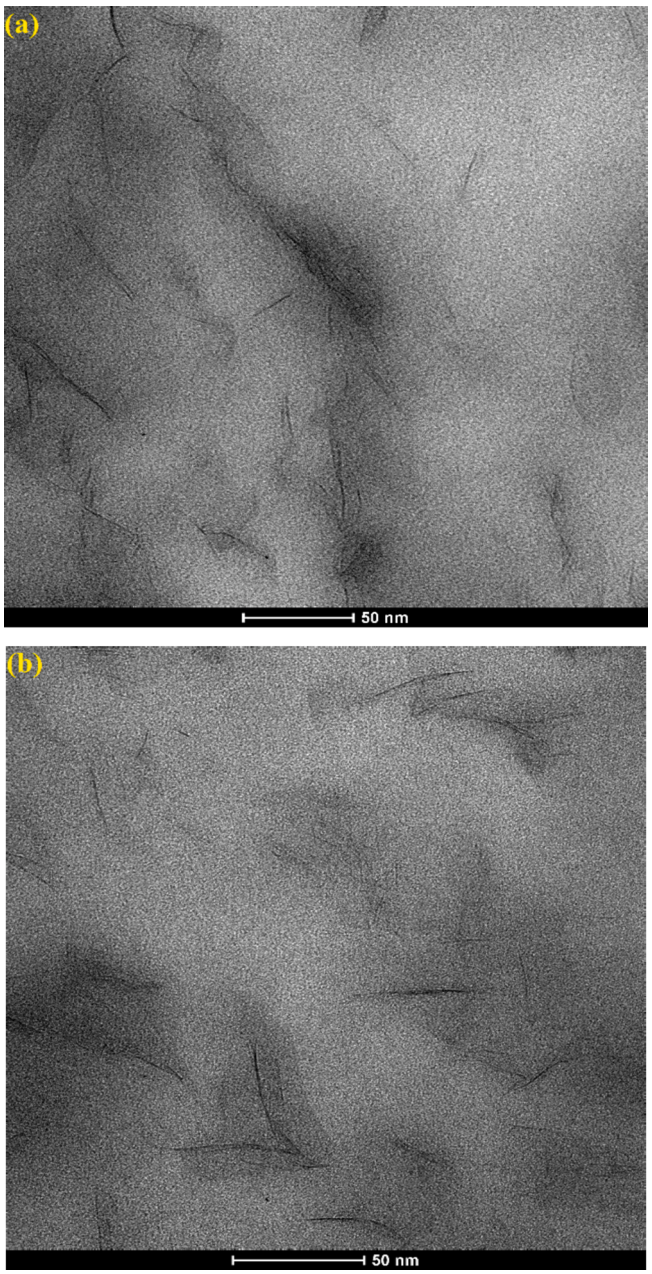

Fig. 4. TEM images of (a) PBT/organoclay nanocomposite without chain extender and (b) PBT/organoclay nanocomposite with chain extender.

Cloisite 30B and the carboxyl groups of PBT likely facilitated the extent of intercalation and further exfoliation of Cloisite 30B within PBT matrix [36]. On the other hand, Joncryl increased the dispersion of organoclays in the PBT matrix leading to mainly exfoliated structure for PBT/C30B/JC in Fig. 4b. The chain extended and/or branched structure of PBT by Joncryl exerted strong shear and elongational forces on clay particles during extrusion thus the tactoids lost their stacked state and disorderly distributed within PBT [19,27].

3.2. Rheological properties

Rheology enables to get a deeper insight on molecular structure of polymeric materials such as particle-filled systems. While rheological analyses are generally used to investigate interactions between filler and polymer, the measurements also reflect the structural changes occurred by heat and mechanical deformation during melt-processing. The complex viscosity (η^*) and elastic modulus (G') of the specimens over time is presented in Fig. 5. The viscosity and modulus of PBT/C30B decreased monotonically over time and stated that the organomodifier in the clay accelerated thermal degradation of PBT under shear and high temperature during rheological measurements. Even though the nanocomposite exposed to serious thermal degradation, the magnitude of complex viscosity and modulus for PBT/C30B had higher than PBT, which could be arisen from polymer-organoclay interactions [37]. Expectedly, the introduction of Joncryl significantly changed the viscosity and modulus for PBT/C30B. The chain extender not only stabilized complex viscosity and elastic modulus of the nanocomposite over time, but it also enhanced the magnitudes of viscosity and modulus for the respective system. These results dictated benefit of Joncryl on recoupling of the degraded chains of PBT and upgrading thermal stability of the PBT/organoclay nanocomposites. Joncryl reacts with either hydroxyl or carboxyl chain ends of degraded PBT and chain branching may occur due to multiple reactive groups of the chain extender [38]. Compared to PBT/C30B, the stable viscosity and elastic modulus of the PBT/C30B/JC along time asserted that epoxy functional groups of Joncryl continued to react with chain endings of degraded PBT, preferably carboxyl groups, during the rheological tests [39]. On the other hand, the complex viscosity and elastic modulus of PBT and PBT/JC remained stable over time as matrix degradation is less in the absence of organoclays. Compared to nanocomposite sample, the incorporation of Joncryl into neat PBT reflected relatively small enhancement in the viscosity and modulus that may be arisen from formation of lower amount of degraded chain ends in the neat polymer.

Fig. 6 illustrates the complex viscosity and elastic modulus of the samples along frequency. The viscosity and elastic modulus of the nanocomposites had larger than that of neat PBT irrespective from the presence of chain extender over the frequency range. Such changes in viscoelastic behaviour of the nanocomposites may be arisen from particle-particle and polymer-particle interactions with a higher extent of clay exfoliation verified by TEM images [40]. Joncryl showed a striking influence on the rheological features of the PBT and corresponding nanocomposite proving chain extension. For example, PBT/C30B/1JC nanocomposite presented 12840 Pa.s complex viscosity at a frequency of 0.1 Hz whilst this was 6588 Pa.s for PBT/C30B. The chain extension of the Joncryl with PBT was also concluded from the results, PBT/JC had higher viscosity (3461 Pa.s) than neat PBT (2369 Pa.s) at the same frequency. The structural changes in the nanocomposites can be also seen from Fig. 6b, PBT and PBT/JC indicated pseudo-Newtonian behaviour that was more profound at lower frequencies, whereas the nanocomposites exhibited shear-thinning characteristics due to polymer-organoclay interactions [41,42].

The low loading of chain extender (1 wt%) makes difficult to detect changes in the polymers by fourier-transform infrared spectroscopy [27,43]. In order to get more information about the structural change of the polymer with chain extender, the loss angle ($\delta = \arctan(G''/G')$) vs. frequency was plotted in Fig. 7. In the figure, the samples depicted two distinct behaviors according to presence of chain extender. Neat PBT showed typical linear system characteristics as having loss angles values closed to 90° at low frequencies. On the other hand, PBT with Joncryl had lower loss angles at all frequencies and the decline in loss angle was more notable with increased frequency. Such change in the PBT was an indication of chain branching due to multiple epoxy functional groups of Joncryl. Since the chain extended PBT had more elasticity and chain entanglements, the relaxation of polymer chains became slower and loss angle showed a stepped reduction along frequency. These observations for polymer-chain extender systems are in good agreement with the outcomes of Najafi et al. (2012) [24], Ghanbari et al. (2013) [19] and Tuna (2023) [29].

3.3. Mechanical properties

Mechanical properties are directly related to the molecular structure

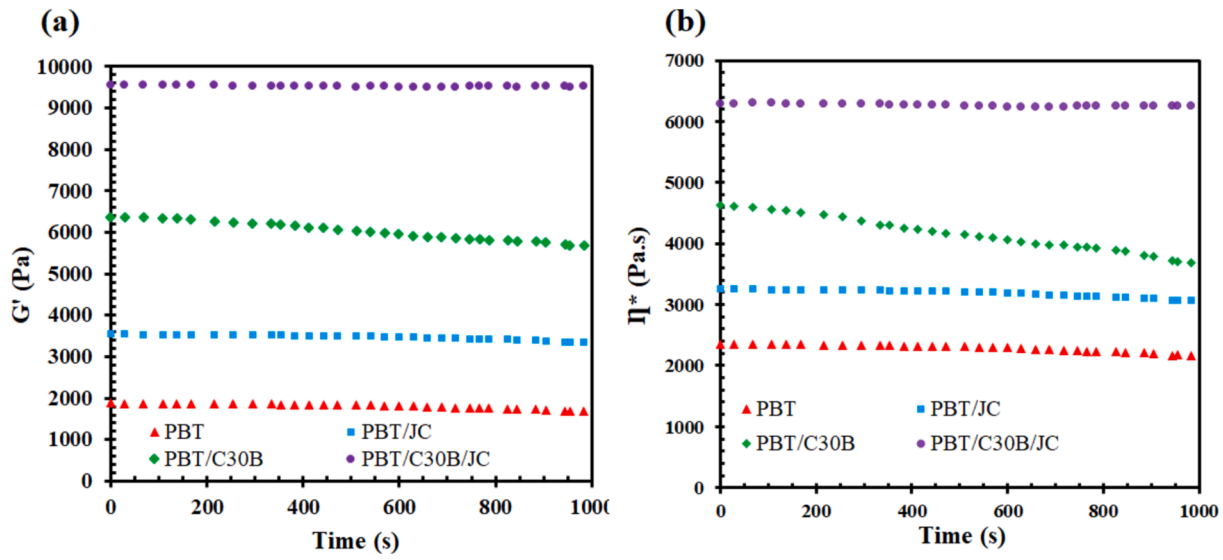

Fig. 5. (a) Elastic modulus and (b) complex viscosity of the samples over time.

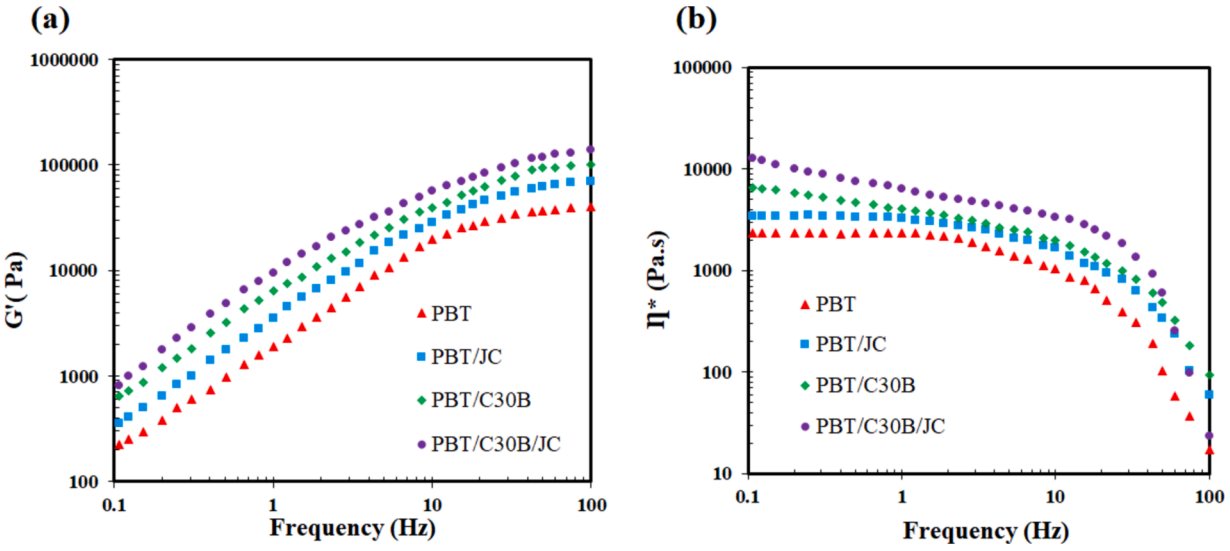

Fig. 6. (a) Elastic modulus and (b) complex viscosity of the samples over frequency.

of the materials and tensile tests enable to detect any structural change of polymers used in solid state form. Table 1 summarizes tensile modulus, tensile strength and elongation at break data of the samples undertaken. As can be seen, Joncryl slightly increased tensile modulus of neat PBT by 3 % that can be attributed to the enhancement in the molecular weight of the polymer [28]. In the case of nanocomposite, nanoclay showed its reinforcing feature in the neat polymer where tensile modulus increased by 33 % for PBT/C30B compared to PBT. Such increase in the modulus of nanocomposite may be arisen from the high strength applied by the nanoclay itself and/or high delamination and distribution of nanoclays in the matrix [44–46]. The notable benefit of chain extender incorporation to the nanocomposites was observed by enhanced tensile modulus of the nanocomposite systems. Compared to PBT, a 56 % enhancement in tensile modulus was reported for PBT/C30B/JC nanocomposite. Joncryl increased molecular weight of the thermally degraded nanocomposites, moreover, improved exfoliation of clay layers in the matrix and these reflected on higher modulus of chain extended nanocomposites.

Similar to tensile modulus results, nanocomposite indicated higher tensile strength than PBT since a substantial ratio of the applied load during the test was carried by nanoclay. Joncryl enhanced the tensile strength of the nanocomposite due to higher exfoliation of nanoclays within PBT matrix which was observed by TEM images. Accordingly, the stress routing from the matrix to the inorganic part proportionally enhances with contact area of nanoclay, causing the chain extended samples to show higher strength values [26].

The inclusion of nanoclays turned the PBT into a more brittle structure causing the nanocomposites to exhibit very low elongation at break values [47]. This behavior in polymer-organoclay nanocomposites is explained by formation of silicate aggregates by Vander Waals interactions between silicate layers of C30B. The agglomerates induce occurrence of microvoids and therefore trigger propagation of cracks in the polymer [6]. Moreover, the coalescence of such microvoids creates larger cracks leading the nanocomposites to behave brittle [48]. On the other hand, the chain entanglement density of the samples increased due higher molecular weight and chain branching in the presence of Joncryl, which made the samples more resilient to mechanical deformation and increased the elongation at break values [49].

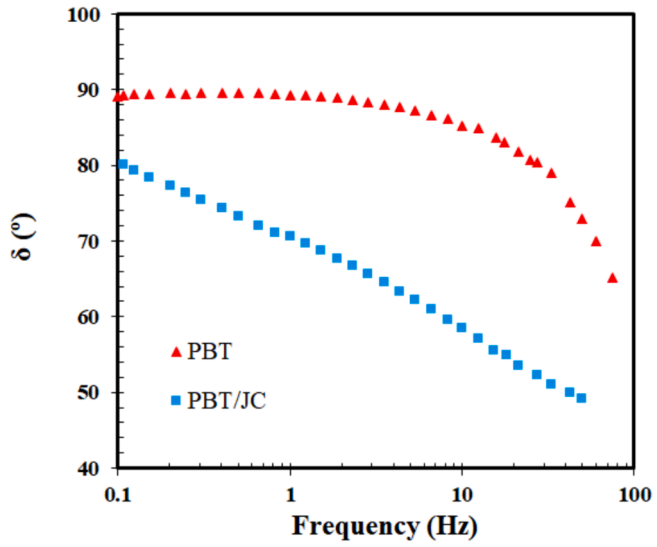

Fig. 7. The loss angle of PBT and PBT/JC over frequency.

Table 1
Tensile properties of the samples.

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PBT	2291.6 ± 79.5	77.3 ± 3.8	33 ± 2.1
PBT/JC	2367.8 ± 94.2	76.8 ± 4.7	36.3 ± 3.8
PBT/C30B	3036.6 ± 0.62.7	85.9 ± 2.1	8.5 ± 2.2
PBT/C30B/JC	3567.9 ± 86.4	91.2 ± 3.5	12 ± 3.6

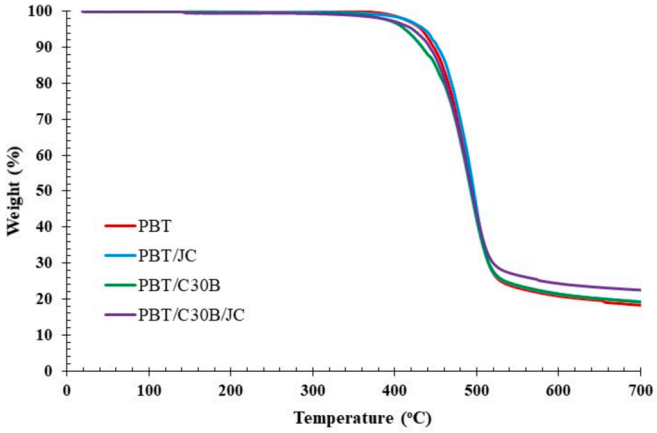

Fig. 8. TGA curves for the samples.

Table 2
TGA data of the samples.

Sample	T_{d10} (°C)	T_{d20} (°C)	T_{d50} (°C)	Residue at 700 °C (wt%)
PBT	447.5	465.4	495.4	18.3
PBT/JC	452.2	469.1	496.3	19.3
PBT/C30B	433.6	459.9	492.6	20.2
PBT/C30B/JC	442.7	462	493.9	22.4

3.4. Thermal properties

TGA tests were applied to examine the influence of nanoclay and chain extender on the thermal degradation behavior of PBT under inert atmosphere. TGA curves are depicted in Fig. 8 and the degradation temperatures at 10 %, 20 % and 50 % weight losses (T_{d10}, T_{d20} and T_{d50}) with residue weight of the samples at 700 °C are given in Table 2. The findings indicated that the incorporation of organoclay into the PBT decreased thermal stability considerably. During extrusion of PBT, the ammonium surfactant in the organoclay thermally degraded and resulted to reactive radicals such as Bronsted acids by Hofmann elimination which increased thermal degradation of PBT matrix further [50]. With the addition of the Joncryl into the nanocomposite, degraded reactive chain end groups of the PBT were recoupled to each other and increased thermal resilience of the nanocomposites with shifting degradation temperatures to higher values. PBT organoclay nanocomposite with chain extender presented 442.7 °C for T_{d10} which was explicitly higher than the T_{d10} of nanocomposite without chain extender, 433.6 °C. Furthermore, chain extender increased T_{d10} of neat PBT from 447.5 °C to 452.2 °C. Such improvement in the thermal stability can be also observed from T_{d20} of the samples, incorporation of chain extender enhanced T_{d20} from 465.4 °C to 469.1 °C for neat PBT and from 459.9 °C to 462 °C for PBT organoclay nanocomposite. The efficiency of Joncryl on the thermal stability of neat PBT and nanocomposite were relatively less at higher degradation temperatures (T_{d50}). This could be attributed to degradation of chain extender at very high temperatures due to its polymeric nature that caused to insufficient reaction activity. Herein, one should be noted that improvement of the thermal stability of PBT organoclay nanocomposites during extrusion is the main objective of this study. It is known that temperature profile for extrusion of PBT is typically between 200 °C and 300 °C, not very high temperatures. Therefore, T_{d10} values could more reflect the thermal degradation of the samples during extrusion. When the residue amount of the samples at 700 °C are examined in Table 2, the nanocomposites showed slightly higher amounts of char due to presence of organoclay in the structure.

4. Conclusion

In the present study, reactive extrusion approach using a chain extender with multiple epoxy functional groups was pursued to compensate thermal degradation of PBT/organoclay nanocomposites in the melt processing. Following conclusions have been inferred from the research:

- The morphological analyses revealed that C30B particles were highly delaminated in the PBT matrix and a well-exfoliated structure was obtained in the nanocomposite containing Joncryl in consequence of robust shear and elongational forces by the larger molecular weight matrix in the compounding.
- The rheological time sweep tests enabled to observe simultaneous viscosity and modulus change of the samples under high temperatures and shear likewise to extrusion conditions. The gradual decrease in the viscosity and modulus of the non-chain extended nanocomposite over time backed our argument that the organoclay accelerated thermal degradation of PBT during extrusion. On the other hand, the addition of chain extender controlled thermal degradation and stabilized viscosity and modulus of the nanocomposite during test proving the chain extension of Joncryl with PBT.
- The samples having chain extender showed higher elastic modulus and complex viscosity than those without chain extender in time sweep and frequency sweep tests due to recoupling of degraded PBT chains by epoxy groups of chain extender. Moreover, a structural change in the sample with chain extender was observed from the plot of the loss angle vs. frequency. These results supported chain extension of PBT with Joncryl.
- The chain extension of PBT by using Joncryl was also detected from mechanical properties. The samples having Joncryl showed higher tensile modulus and strength than those without chain extender due to recoupling of degraded chains and enhanced molecular weight.

The higher molecular weight caused more entanglements in the polymer chains which made the PBT more resistant to deformation.
– The notable benefit of chain extender on the thermal stability of the samples was determined from TGA tests. With addition of Joncryl, T_{d10} of PBT/C30B increased from 433.6 °C to 442.7 °C due to chain extension of PBT.

CRediT authorship contribution statement

Basak Tuna: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] N.B. Quispe, E.G. Fernandes, F. Zanata, J.R. Bartoli, D.H.S. Souza, E.N. Ito, Organoclay nanocomposites of post-industrial waste poly(butylene terephthalate) from automotive parts, Waste Manag. Res. 33 (10) (2015) 908–918, https://doi.org/10.1177/0734242X15600049.
[2] F. Knappich, F. Hartl, M. Schlummer, A. Maurer, Complete recycling of composite material comprising polybutylene terephthalate and copper, Recycling 2 (2) (2017) 9, https://doi.org/10.3390/recycling2020009.
[3] C. Meng, J. Qu, Mechanical and thermal properties of polybutylene terephthalate/ethylene-vinyl acetate blends using vane extruder, e-Polymers 18 (1) (2018) 67–73, https://doi.org/10.1515/epoly-2017-0073.
[4] N. Heidarzadeh, M. Rafizadeh, F.A. Taromi, H. Bouhendi, Preparation of poly (butylene terephthalate)/modified organoclay nanocomposite via in-situ polymerization: characterization, thermal properties and flame retardancy, High Perform. Polym. 24 (7) (2012) 589–602, https://doi.org/10.1177/0954008312446646.
[5] Y. Bas, A.S. Dike, Comprehensive characterizations of organoclay types based on their integration to poly (butylene terephthalate) nanocomposites, J. Nanopart. Res. 26 (2024) 60, https://doi.org/10.1007/s11051-024-05972-x.
[6] M.A.S. Colombo, F.R.V. Díaz, D. Kodali, V. Rangari, O. Güven, E.A.B. Moura, Influence of reinforcing efficiency of clay on the mechanical properties of poly (butylene terephthalate) nanocomposite, Ceramics 6 (1) (2023) 58–73, https://doi.org/10.3390/ceramics6010005.
[7] A. McLauchlin, X. Bao, F. Zhao, Organoclay polybutylene terephthalate nanocomposites using dual surfactant modified montmorillonite prepared by the masterbatch method, Appl. Clay Sci. 53 (4) (2011) 749–753, https://doi.org/10.1016/j.clay.2011.07.006.
[8] S. Mohanty, S.K. Nayak, Effect of clay exfoliation and organic modification on morphological, dynamic mechanical, and thermal behavior of melt-compounded polyamide-6 nanocomposites, Polym. Compos. 28 (2) (2007) 153–162, https://doi.org/10.1002/pc.20284.
[9] S. Suin, N.K. Shrivastava, S. Maiti, B.B. Khatua, Optically transparent polycarbonate/clay nanocomposites with improved performance using phosphonium modified organoclay: preparation and characterizations, Polym. Compos. 37 (1) (2016) 199–212, https://doi.org/10.1002/pc.23171.
[10] R. Rafiee, R. Shahzadi, Mechanical properties of nanoclay and nanoclay reinforced polymers: a review, Polym. Compos. 40 (2) (2019) 431–445, https://doi.org/10.1002/pc.24725.
[11] Kusmono, Z.A.M. Ishak, W.S. Chow, T. Takeichi Rochmadi, Water absorption behavior of different types of organophilic montmorillonite-filled polyamide 6/polypropylene nanocomposites, Polym. Compos. 31 (2) (2010) 195–202, https://doi.org/10.1002/pc.20784.
[12] X. Huang, H. Su, X. Wang, B. Zhang, J. Li, Effect of oligomeric-modified montmorillonite on morphology and properties of polycarbonate/montmorillonite nanocomposites, Polym. Compos. 34 (5) (2013) 722–731, https://doi.org/10.1002/pc.22475.
[13] Y. Wang, J.-Y. Guo, Melt compounding of PMMA/clay nanocomposites with styrene-maleic anhydride copolymers: effect of copolymer type on thermal, mechanical and dielectric properties, Polym. Compos. 31 (4) (2010) 596–603, https://doi.org/10.1002/pc.20832.
[14] F. Guo, S. Aryana, Y. Han, Y. Jiao, A review of the synthesis and applications of polymer–nanoclay composites, Appl. Sci. 8 (9) (2018) 1696, https://doi.org/10.3390/app8091696.
[15] D.E. Abulyazied, A. Ene, An Investigative study on the progress of nanoclay-reinforced polymers: preparation, properties, and applications: a review, Polymers 13 (24) (2021) 4401, https://doi.org/10.3390/polym13244401.
[16] A. Ghanbari, M.C. Heuzey, P.J. Carreau, M.T. Ton-That, A novel approach to control thermal degradation of PET/organoclay nanocomposites and improve clay exfoliation, Polymer 54 (4) (2013) 1361–1369, https://doi.org/10.1016/j.polymer.2012.12.066.
[17] H. Ghasemi, P.J. Carreau, M.R. Kamal, J. Uribe-Calderon, Preparation and characterization of PET/clay nanocomposites by melt compounding, Polym. Eng. Sci. 51 (6) (2011) 1178–1187, https://doi.org/10.1002/pen.21874.
[18] K. Stoeffler, P.G. Lafleur, J. Denault, Thermal decomposition of various alkyl onium organoclays: effect on polyethylene terephthalate nanocomposites' properties, Polym. Degrad. Stab. 93 (7) (2008) 1332–1350, https://doi.org/10.1016/j.polymdegradstab.2008.03.029.
[19] A. Ghanbari, M.-C. Heuzey, P.J. Carreau, Polyethylene terephthalate/organoclay nanocomposites: improvement of morphology and viscoelastic properties by using a chain-extender, Appl. Clay Sci. 225 (2022) 106551, https://doi.org/10.1016/j.clay.2022.106551.
[20] B. Guo, C.-M. Chan, Chain extension of poly(butylene terephthalate) by reactive extrusion, J. Appl. Polym. Sci. 71 (11) (1999) 1827–1834, https://doi.org/10.1002/(SICI)1097-4628(19990314)71:11<1827::AID-APP13>3.0.CO;2-7.
[21] F.R. Beltrán, E. Climent-Pascual, M.U. de la Orden, J.M. Urreaga, Effect of solid-state polymerization on the structure and properties of mechanically recycled poly (lactic acid), Polym. Degrad. Stab. 171 (2020) 109045, https://doi.org/10.1016/j.polymdegradstab.2019.109045.
[22] Y. Ma, U.S. Agarwal, D.J. Sikkema, P.J. Lemstra, Solid-state polymerization of PET: influence of nitrogen sweep and high vacuum, Polymer 44 (15) (2003) 4085–4096, https://doi.org/10.1016/S0032-3861(03)00408-7.
[23] X. Xu, Y. Ding, Z. Qian, F. Wang, B. Wen, H. Zhou, S. Zhang, M. Yang, Degradation of poly(ethylene terephthalate)/clay nanocomposites during melt extrusion: Effect of clay catalysis and chain extension, Polym. Degrad. Stab. 94 (1) (2009) 113–123, https://doi.org/10.1016/j.polymdegradstab.2008.09.009.
[24] N. Najafi, M.C. Heuzey, P.J. Carreau, P.M. Adams, Control of thermal degradation of polylactide (PLA)-clay nanocomposites using chain extenders, Polym. Degrad. Stab. 97 (4) (2012) 554–565, https://doi.org/10.1016/j.polymdegradstab.2012.01.016.
[25] Q. Meng, M.C. Heuzey, P.J. Carreau, Control of thermal degradation of polylactide/clay nanocomposites during melt processing by chain extension reaction, Polym. Degrad. Stab. 97 (10) (2012) 2010–2020, https://doi.org/10.1016/j.polymdegradstab.2012.01.030.
[26] N. Najafi, M.C. Heuzey, P.J. Carreau, Polylactide (PLA)-clay nanocomposites prepared by melt compounding in the presence of a chain extender, Compos. Sci. Technol. 72 (5) (2012) 608–615, https://doi.org/10.1016/j.compscitech.2012.01.005.
[27] B. Tuna, H. Benkreira, Chain extension of polyamide 6/organoclay nanocomposites, Polym. Eng. Sci. 59 (6) (2019) 1233–1241, https://doi.org/10.1002/pen.25106.
[28] J. González-Ausejo, E. Sánchez-Safont, J. Gámez-Pérez, L. Cabedo, On the use of tris(nonylphenyl) phosphite as a chain extender in melt-blended poly (hydroxybutyrate-co-hydroxyvalerate)/clay nanocomposites: morphology, thermal stability, and mechanical properties, J. Appl. Polym. Sci. 133 (2) (2016) 42390, https://doi.org/10.1002/app.42390.
[29] B. Tuna, Reactive extrusion of recycled polycarbonate using chain extenders, Russ. J. Phys. Chem. B 17 (2023) 196–205, https://doi.org/10.1134/S1990793123010281.
[30] B. Tuna, H. Benkreira, Chain extension of recycled PA6, Polym. Eng. Sci. 58 (7) (2018) 1037–1042, https://doi.org/10.1002/pen.24663.
[31] S. Khojasteh-Khosro, A. Shalbafan, H. Thoemen, Improving the compatibility of polylactic acid/polycarbonate blends with nanoclay and Joncryl as chain extenders, J. Appl. Polym. Sci. 141 (41) (2024) e56081, https://doi.org/10.1002/app.56081.
[32] C. Alpaslan Güler, S. Deniz, The effect of different clay types on the barrier properties of PLA/PBAT/clay bio-nanocomposite packaging films, J. Disper. Sci. Technol. 44 (13) (2023) 2367–2378, https://doi.org/10.1080/01932691.2023.2225609.
[33] Y. Kahraman, B. Özdemir, B.E. Gümüş, M. Nofar, Morphological, rheological, and mechanical properties of PLA/TPU/nanoclay blends compatibilized with epoxy-based Joncryl chain extender, Colloid Polym. Sci. 301 (2023) 51–62, https://doi.org/10.1007/s00396-022-05043-4.
[34] BASF, Product Datasheet Ultradur® B 2550, 2024. https://download.basf.com/p1/8a8081c57fd4b609017fd657f7ab6c0c/en/ULTRADUR%253Csup%253E%25C2%25AE%253Csup%253E_B2550.
[35] Y.-W. Chang, S. Kim, Y. Kyung, Poly(butylene terephthalate)–clay nanocomposites prepared by melt intercalation: morphology and thermomechanical properties, Polym. Int. 54 (2) (2005) 348–353, https://doi.org/10.1002/pi.1686.
[36] X. Li, T. Kang, W.-J. Cho, J.-K. Lee, C.-S. Ha, Preparation and characterization of poly(butyleneterephthalate)/organoclay nanocomposites, Macromol. Rapid Commun. 22 (16) (2001) 1306–1312, https://doi.org/10.1002/1521-3927(20011101)22:16<1306::AID-MARC1306>3.0.CO;2-I.
[37] J.S. Narkhede, V.V. Shertukde, Mechanical properties and rheological behavior of poly(butylene terephthalate)/clay nanocomposites with different organoclays, J. Appl. Polym. Sci. 119 (2) (2011) 1067–1074, https://doi.org/10.1002/app.32616.
[38] M. Guclu, Y. Alkan Goksu, B. Ozdemir, A. Ghanbari, M. Nofar, Thermal stabilization of recycled PET through chain extension and blending with PBT,

J. Polym. Environ. 30 (2022) 719–727, https://doi.org/10.1007/s10924-021-02238-8.
[39] A. Himmelsbach, T. Standau, J. Kuhnigk, T. Bubmann, Y. Akdevelioglu, M. Nofar, H. Ruckdäschel, Investigation of the reaction kinetics of poly(butylene terephthalate) and epoxide C-chain extender, Macromol. Mater. Eng. 308 (7) (2023) 2200683, https://doi.org/10.1002/mame.202200683.
[40] A.K. Barick, D.K. Tripathy, Effect of organoclay on the morphology, mechanical, thermal, and rheological properties of organophilic montmorillonite nanoclay based thermoplastic polyurethane nanocomposites prepared by melt blending, Polym. Eng. Sci. 50 (3) (2010) 484–498, https://doi.org/10.1002/pen.21556.
[41] P. Scarfato, L. Scatteia, G. Costa, D. Acierno, Effect of the organoclay structure on morphology and rheological response of PBT nanocomposites, Macromol. Symp. 228 (1) (2005) 125–139, https://doi.org/10.1002/masy.200551011.
[42] A. Hajibaba, M. Masoomi, H. Nazockdast, The role of hydrophilic organoclay in morphology development of poly(butylene terephthalate)/polypropylene blends, High Perform. Polym. 28 (1) (2016) 85–95, https://doi.org/10.1177/0954008315571683.
[43] B. Tuna, Polimerik bir zincir uzatıcının geri dönüştürülmüş poli(bütilen tereftalat)'ın özelliklerine etkilerinin incelenmesi, Bilecik Şeyh Edebali Univ, Fen Bilim. Derg. 8 (2) (2021) 882–892, https://doi.org/10.35193/bseufbd.974092.
[44] W.S. Chow, Z.A. Mohd Ishak, Mechanical, morphological and rheological properties of polyamide 6/organo-montmorillonite nanocomposites, Express Polym. Lett. 1 (2) (2007) 77–83, https://doi.org/10.3144/expresspolymlett.2007.14.
[45] S. Mallakpour, M. Dinari, The effects of reactive organoclay onthe thermal, mechanical, and microstructural properties of polymer/layered silicate nanocomposites based on chiral poly(amide-imide)s, J. Therm. Anal. Calorim. 114 (2013) 329–337, https://doi.org/10.1007/s10973-012-2876-3.
[46] B.W. Chieng, N.A. Ibrahim, W.M.Z. Wan Yunus, Effect of organo-modified montmorillonite on poly(butylene succinate)/poly(butylene adipate-co-terephthalate) nanocomposites, Express Polym. Lett. 4 (7) (2010) 404–414, https://doi.org/10.3144/expresspolymlett.2010.51.
[47] B.H. Soudmand, K. Shelesh-Nezhad, S. Hassanifard, Toughness evaluation of poly (butylene terephthalate) nanocomposites, Theor. Appl. Fract. Mech. 108 (2020) 102662, https://doi.org/10.1016/j.tafmec.2020.102662.
[48] W.S. Chow, Cyclic extrusion of poly(butylene terephthalate)/organo-montmorillonite nanocomposites: thermal and mechanical retention properties, J. Appl. Polym. Sci. 110 (3) (2008) 1642–1648, https://doi.org/10.1002/app.28804.
[49] N. Yahyaee, A. Javadi, H. Garmabi, A. Khaki, Effect of two-step chain extension using Joncryl and PMDA on the rheological Properties of poly (lactic acid), Macromol. Mater. Eng. 305 (2020) 1900423, https://doi.org/10.1002/mame.201900423.
[50] R.M. Kooshki, I. Ghasemi, M. Karrabi, H. Azizi, Nanocomposites based on polycarbonate/poly (butylene terephthalate) blends effects of distribution and type of nanoclay on morphological behavior, J. Vinyl Addit. Technol. 19 (3) (2013) 203–212, https://doi.org/10.1002/vnl.21313.