Iranian Polymer Journal (2023) 32:103–114
https://doi.org/10.1007/s13726-022-01106-z

ORIGINAL RESEARCH

Effects of different catalysts on the mechanical, thermal, and rheological properties of poly(lactic acid)/polycarbonate blend

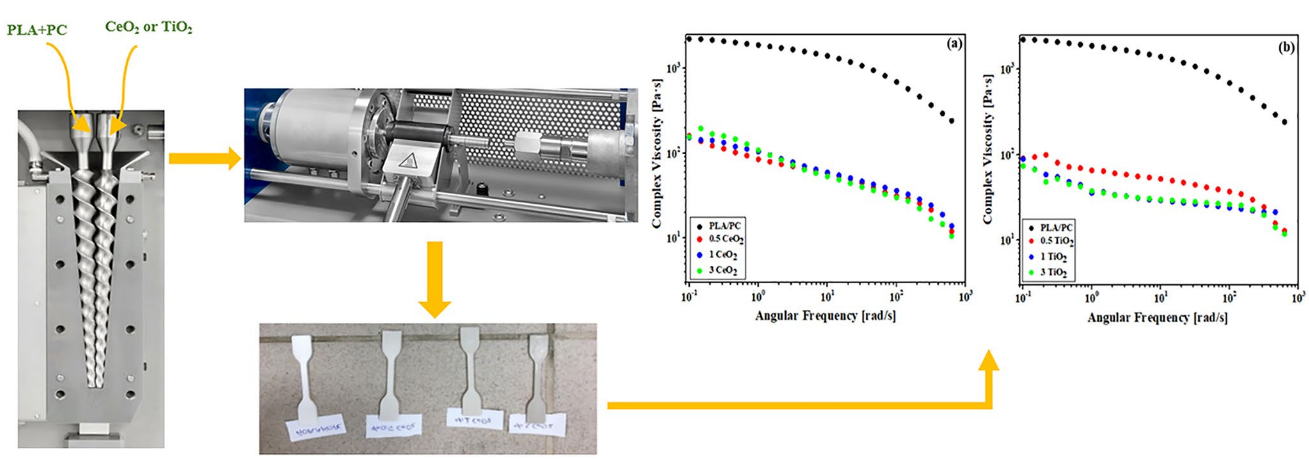
Esra Zengin[1] · Bedriye Ucpinar Durmaz[1] · Meltem Yıldız[1] · Ayse Aytac[1,2]

Received: 11 May 2022 / Accepted: 10 September 2022 / Published online: 8 December 2022

Abstract

Poly(lactic acid)/polycarbonate (PLA/PC) blends are often explored for use in durable applications such as mobile phones, laptops, and automotive parts. With the use of this blend, while reducing the dependence on the petroleum-based polymers, environmental pollution can be prevented. However, PLA/PC blend is immiscible and needs to be compatibilized. To encourage compatibilization and improve of the performance of the PLA/PC blend, TiO_2 and CeO_2 were incorporated into the blend. The effects of catalysts type and amount on the structural (Fourier transform infrared analysis-FTIR), morphological (scanning electron microscopy-SEM), rheological, mechanical, and thermal properties (thermogravimetric analysis-TGA, differential scanning calorimeter-DSC) of the PLA/PC blends were evaluated in this study. FTIR results revealed that the catalysts promoted the reaction between PLA and PC. The modulus of the blend increased with the addition of catalyst. The CeO_2 containing blends exhibited brittle behavior which was also supported by SEM micrographs. The added catalysts acted as a lubricant, lowered the complex viscosity of the blend, and made processing easier. With the addition of fillers at all amounts, thermal decomposition temperature decreased while the residual weight at 800 °C increased with the inclusion of 3 wt% CeO_2. Mechanical results revealed that the highest tensile strength and elongation values were obtained for 0.5 wt% CeO_2 and 0.5 wt% TiO_2, respectively. It was observed that the loading level and type of catalyst significantly affected the PLA/PC blends mechanical and thermal properties.

Graphical abstract



Keywords Poly(lactic acid) · Polycarbonate · Blends · Catalyst · Mechanical properties

✉ Ayse Aytac
aaytac@gmail.com

Extended author information available on the last page of the article

Introduction

Nowadays, the bioplastic sector is developing with the aim of improvement of bioplastics with high biological content and resistant. New studies on the use of renewable resources instead of fossil fuels are increasing [1]. Poly(lactic acid) (PLA) is a biodegradable polyester obtained through the synthesis of lactic acid. PLA is a polymer that replaces oil-based plastics due to its high elastic modulus and tensile strength, low cost, and biodegradability [2, 3].

Durable bioplastics are demanded in electronics, automotive industry, and other industrial sectors, thus, PLA-based composites have been developed for this purpose in recent years [1, 4]. However, due to degradation at low temperatures (~ 330 °C) [5], low impact strength, high brittleness, relatively low crystallization rate, and low glass transition temperature (T_g), their uses are limited [6–8]. To overcome these poor properties, different strategies can be considered such as blending with other thermoplastics, e.g., polyethylene [9], polypropylene [10], polyolefin elastomers [11], and polycarbonate (PC) [12, 13]. Besides, PLA/PC blends have been reinforced via various fillers, e.g., clays [10, 14], and fibers [14, 15]. Among the cited PLA blend research works, blending with PC provided acceptable tensile strength, elongation, and thermal stability for durable applications in mobile phones, laptops, and automobiles.

PC is widely used in electronic, and packaging fields with high tensile and impact strength, flexibility, and heat resistance [6, 8, 16]. The good characteristics of PLA such as biodegradability can be combined with the good mechanical and thermal properties of PC in the PLA/PC blends to create ideal materials for industry [5, 16]. Several studies in the literature have examined the blending of PLA and PC to increase their thermal resistance and toughness [17–19].

On the other hand, PLA and PC are incompatible polymers due to aliphatic structure of PLA, aromatic structure of PC, higher viscosity of PC than PLA, and high surface tensions. Therefore, the interfacial adhesion and mechanical properties of the PLA/PC blend are poor, and it is important to find a way to improve it. Generally, a third component is added as a compatibilizer or catalyst to improve the compatibility between two immiscible components for PLA/PC and polyester/PC blends [17, 20, 21]. Some catalysts or metallic fillers can improve the performance of the PLA/PC blend by promoting the transesterification reactions between PLA and PC.

Chelghoum et al. [17] studied the compatibilization of the PLA/PC blends by adding samarium acetylacetonate (Sm-Acac) to catalyze the reaction. Hedayati et al. [8] and Phuong et al. [20] used dicumyl peroxide (DCP) and cobalt (II) acetylacetonate (Co), tetrabutylammonium tetraphenylborate (TBATPB) and triacetin catalysts in PLA/PC blends. Liu et al. [19] investigated the effect of zinc borate, titanium pigment, and tetrabutyl titanate catalysts on the transesterification reactions between PLA and PC under flow field. It was reported that tetrabutyl titanate was the most effective catalyst.

Among the various catalysts, it has been reported that titanium-based catalysts are effective in accelerating the transesterification reactions of polyester blends such as PLA/PC [19], PLA/polypropylene carbonate [22], PC/poly(ethylene terephthalate) [23], poly(butylene succinate-*co*-adipate) and poly(ε-caprolactone) [24]. Titanium dioxide (TiO_2) is a key catalyst with its nontoxicity, environmentally friendly structure, chemical inertness, low cost, and abundance [25, 26]. TiO_2 is found in nature in three crystalline forms, i.e., rutile, anatase, and brookite. Anatase and rutile are the most commonly used forms of TiO_2 due to their high photocatalytic activity [27]. Besides catalytic effects, TiO_2 is frequently used as UV blocking, flame retardant, antioxidant and mechanical, and thermal property enhancement [28–30]. Due to these features and being an environmentally friendly photocatalyst TiO_2 was preferred as a catalyst in this study for PLA/PC blend.

The other metal oxide catalyst, cerium dioxide (CeO_2), which is the most interesting as a rare earth oxide, is used as an active ingredient in nanoparticle or bulk heterogeneous catalysis due to its chemical stability. CeO_2 shows high catalytic activity due to its high oxygen storage capacity and higher redoxability between Ce^{3+} and Ce^{4+} ions [31]. Beside this catalytic activity, CeO_2 has good thermal stability, fire retardancy, and noncorrosive nature [32, 33]. Due to all these properties and catalytic activity, CeO_2 was preferred as the second catalyst for the PLA/PC blend.

It is important to produce environmentally friendly materials with improved thermal and mechanical properties that can be used in many areas of the industry. Because of that, this work focused on the property enhancement of PLA/PC blends by using CeO_2 and TiO_2 catalysts. Thus, it was aimed to combine the good properties of PLA such as biodegradability with the good mechanical and thermal properties of PC by compatibilizing both polymers with the help of catalysts. To the best of our knowledge, there was no research work in which PLA and PC were prepared with these catalysts. In this study, the effects of these two catalysts on the thermal, mechanical, structural, and morphological properties of the PLA/PC blends were compared.

Experimental

Materials

Poly(lactic acid) (PLA, 2003 D) was supplied from Nature Works, USA (T_g: 50–55 °C, MFI: 10–30 g/10 min (190 °C, 2.16 kg). PC W110 was purchased from Kempro, Turkey (T_g: 145 °C, MFI: 10 g/10 min (300 °C, 1.2 kg). Cerium dioxide (CeO_2) and titanium dioxide (TiO_2) powders were used as catalysts. Commercial TiO_2 (CAS No: 13463-67-7) crystal powder in anatase form was purchased from Acros Organic, (Thermo Fisher Scientific, USA) with Mw of 79.866 g/mol and density of 3.78 g/cm^3. Cerium (III) nitrate hexahydrate (Ce $(NO_3)_3$. $6H_2O$, ≥ % 98.5, 1.02274, Merck, Germany) was used to prepare CeO_2.

Processing

Firstly, the CeO_2 catalyst was prepared by calcining cerium (III) nitrate hexahydrate at 650 °C for 4 h. After calcination, it was sieved to less than 45 mesh size. Previously, the authors used this catalyst for another reaction and in that work, they prepared and used CeO_2 with the same method and determined that the CeO_2 has particulate crystalline structure [34]. Before the preparation of blends, PLA was dried in a vacuum oven at 80 °C for 24 h.

All samples were prepared in a laboratory twin-screw extruder (MC15, Xplore Instruments, The Netherlands). PC, PLA, and catalysts were simultaneously added to the extruder. The barrel temperature and screw speed of the extruder were kept constant at 260 °C and 100 rpm, respectively. The residence time was 3 min. At the end of the compounding process, the molten compound was subsequently injection molded by using an appropriate machine (Xplore 10 mL, The Netherlands) to obtain ISO 527-5A tensile bars. The melt and mold temperatures were 260 °C and 45 °C, respectively. The injection pressure was 10 bar.

The compositions and designations are tabulated in Table 1. The PLA/PC blends matrix ratio was 50/50 wt/wt which was based on the Hazer et al. [5] work that prepared various ratios of the PLA/PC blends and they found that the 50/50 wt/wt blend exhibited the highest strain-at-break and high tensile strength values.

Table 1 Compositions and designations of the samples

Sample code	PLA (wt%)	PC (wt%)	CeO_2 (wt%)	TiO_2 (wt%)
PLA/PC	50	50	–	–
0.5 CeO_2	50	50	0.5	–
1 CeO_2	50	50	1.0	–
3 CeO_2	50	50	3.0	–
0.5 TiO_2	50	50	–	0.5
1 TiO_2	50	50	–	1.0
3 TiO_2	50	50	–	3.0

Characterization

Fourier transform infrared analysis (FTIR) was performed by a Spectrum 100 PerkinElmer (USA) equipment. The spectra were obtained in the 650–4000 cm^{-1} wavelength range.

The tensile properties of the samples were determined by using an Instron Universal Testing Machine (Model 3345, USA) according to ISO 527-5A. The crosshead speed was 5 mm/min. For each sample type, at least five specimens were tested, and an average value of each group was reported with SDs.

The thermal stability of the samples was investigated by using Mettler Toledo (USA) thermal gravimetric analyzer (TGA) under nitrogen atmosphere. The analyses were carried out at a heating rate of 10 °C/min from 25 to 800 °C.

The thermal and crystallization behaviors of the blends were investigated by differential scanning calorimeter (DSC, Mettler Toledo, USA) under N_2 atmosphere. The DSC test was accomplished at the heating rate of 10 °C/min from 25 to 200 °C. To erase the thermal history, the molten sample was kept isothermally at 200 °C for 3 min. It was then cooled to 25 °C with 10 °C/min cooling rate and immediately reheated to 200 °C at 10 °C/min. The percentage crystallinity of the samples was calculated using the following equation: $X_c = (\Delta H_m/\Delta H_{m100}) \times 100$, where, ΔH_{m100} is the theoretical melting heat of PLA containing 100% crystalline phase (93 J/g) [8].

The rheological properties of the samples were examined using an Anton Paar (MCR 102, Austria) modular compact rheometer, with plate-plate geometry of 25 mm diameter. Frequency sweep measurements were carried out at the range of 0.1–628 rad/s angular frequency at 260 °C and a shear strain of 1%.

The morphologies of the fracture surfaces of the blends were observed via a scanning electron microscopy (SEM), (Quanta 400F Field Emission, FEI, USA). Before the measurement, samples surfaces were coated with gold to prevent arching.

Results and discussion

FTIR analysis

FTIR was used to characterize the chemical structure of pure polymers, uncatalyzed, and catalyzed PLA/PC blends. The obtained spectra from FTIR are given in Figs. 1 and 2. It can be said that in Fig. 1, uncatalyzed PLA/PC blends

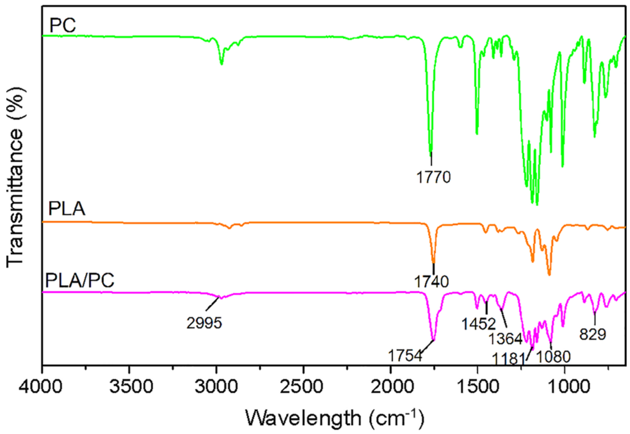


Fig. 1 FTIR spectra of the pure PLA, PC and PLA/PC blend

exhibited characteristic peaks of PLA and PC. The PLA and PC are typically characterized by C=O ester-carbonyl stretching vibrations at 1740 cm^{-1} and 1770 cm^{-1}, respectively [3, 12]. The PLA/PC blend spectrum also showed a significant peak at 1754 cm^{-1}. The peaks around 2995 cm^{-1} and 2947 cm^{-1} are corresponded to the symmetric stretching of -CH- groups. The peaks at 1364, 1381, and 1452 cm^{-1} can be assigned to C–H vibration in CH_3 groups [3, 35]. The C–O–C ether group and O–CH–CH_3 peaks are observed at 1047, 1181, 1219, and 829 cm^{-1} [35].

As shown in Fig. 2 (magnified figure), with the addition of TiO_2 and CeO_2 to the PLA/PC blend, two new peaks are observed in the spectra at around 1449 cm^{-1} and 1712 cm^{-1}. It has been suggested in various studies that PLA and PC can give an ester-ester interchange reaction [13, 17, 19]. As a result of this transesterification reaction, PLA-*co*-PC can be obtained. The peak at 1449 cm^{-1} can be attributed to the vibrations of new C–H groups in the structure of this copolymer. Another peak in 1712 cm^{-1} is related to the C=O stretching vibration. The intensity of the peak at 1712 cm^{-1} was the lowest at 0.5 wt% CeO_2, when the amount of CeO_2 was increased to 1 wt%, there was an increase in the peak intensity. Apart from that, the amounts of fillers did not make any significant differences in the intensity of these new peaks.

Rheological properties

Figures 3a–c show the complex viscosity (η^*), storage modulus (G'), and loss modulus (G'')-angular frequency curves of uncatalyzed and catalyzed PLA/PC blends at 260 °C, respectively. According to Fig. 2a, all samples exhibited non-Newtonian behavior which represents the shear thinning of polymers. From the curves, it is clearly seen that the η^* values of the PLA/PC blends outstandingly decreased with the addition of TiO_2 and CeO_2 catalysts. It can be said that the amount of the added CeO_2 catalyst did not have any significant effect on the η^* values.

On the other hand, the use of 0.5 wt% TiO_2 decreased the η^* value of the PLA/PC blend less than the other loading ratios. The reduction of complex viscosity can be assigned to the changes in the free volume and decrease of chain entanglements [36, 37]. Some authors reported an increment in the complex viscosity of the polymer matrix by adding TiO_2 [29, 38]. According to Cai et al. [29] TiO_2 acts as a physical entanglement point and increase the η^* value of the polymer matrix. Alternatively, similar to our result, several authors have mentioned a reduction in the complex viscosity of the

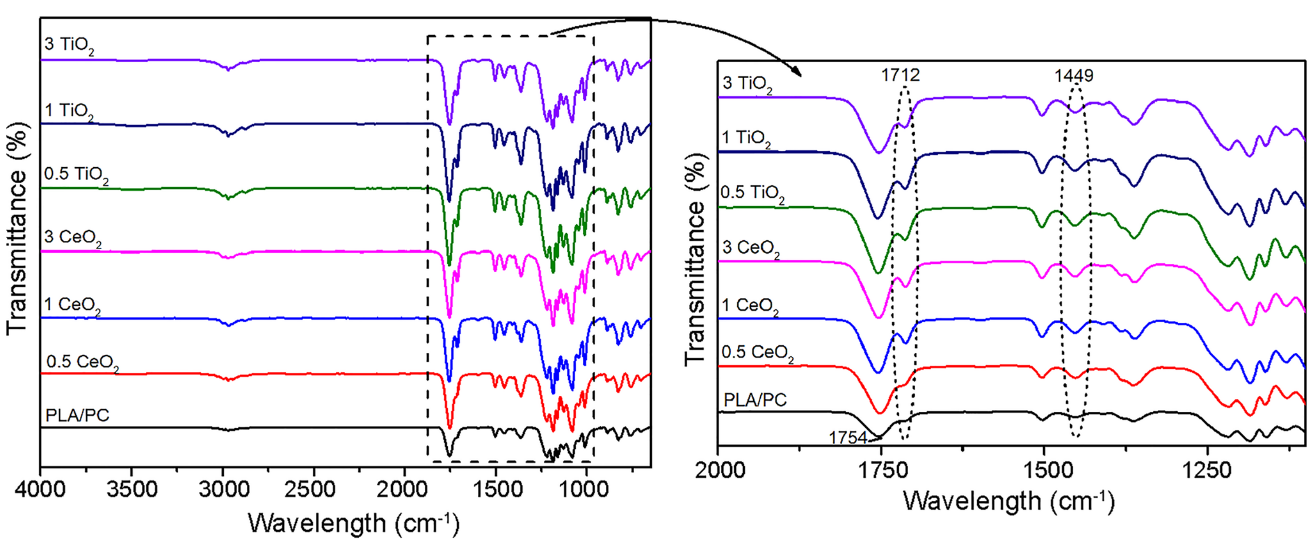


Fig. 2 FTIR spectra of the uncatalyzed and catalyzed PLA/PC blends with CeO_2 and TiO_2 particles

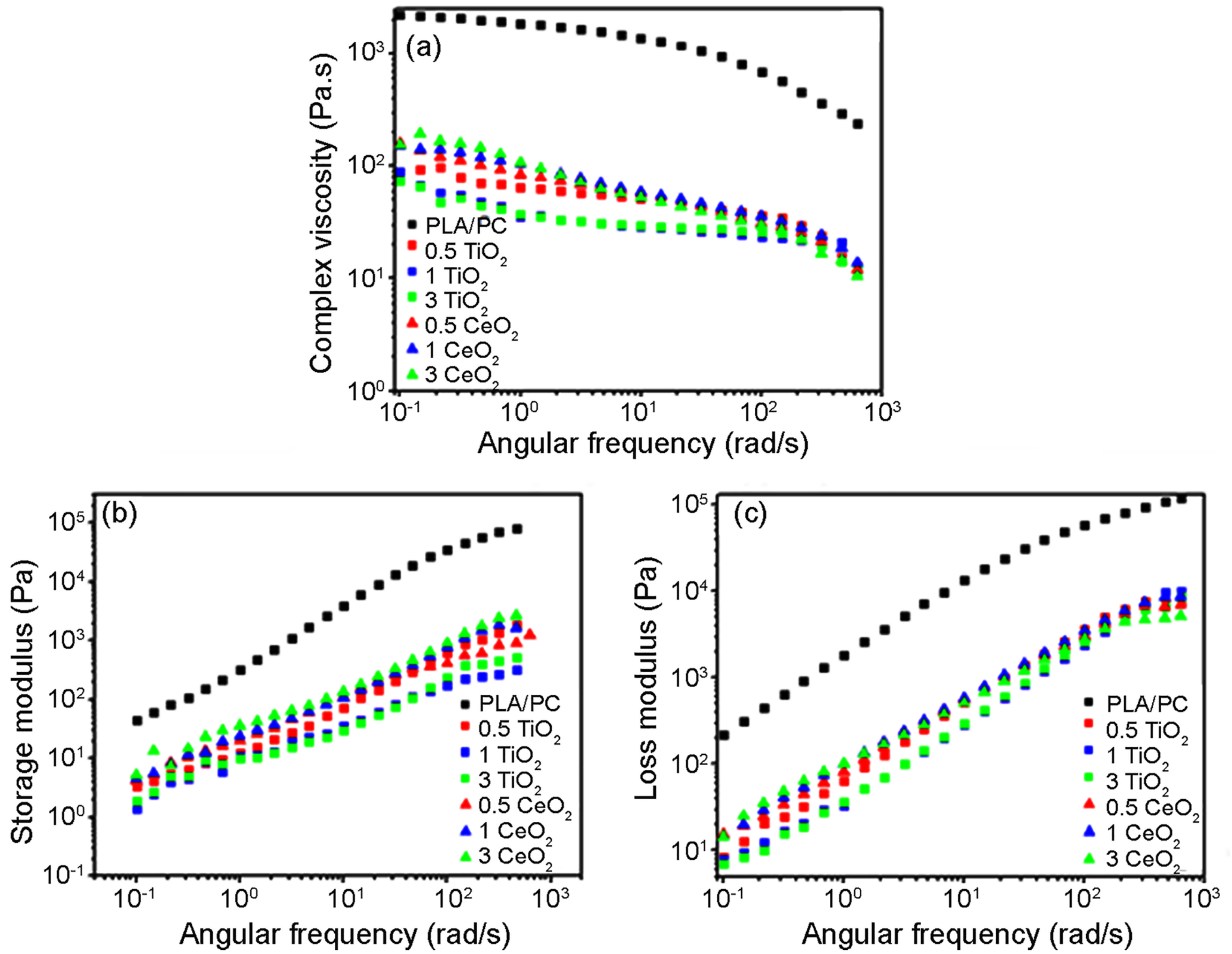


Fig. 3 Variations of **a** complex viscosities, **b** storage modulus and **c** loss modulus of the uncatalyzed and catalyzed PLA/PC blends with CeO_2 and TiO_2 particles

blends by adding TiO_2 or other globular-shaped particles [36, 37, 39].

Based on these works, various factors can affect on the viscosity of the blends. Joshi et al. [36] reported that, there were weak interactions between the polyethylene and polyhedral oligomeric silsesquioxane (POSS) nanoparticles which caused more free volume and lower chain entanglement. Xie et al. [39] and Luo et al. [37] have mentioned the "ball bearings" effect of the globular particles on the viscosity of the blends. The fillers act as a lubricant to hinder the entanglement of polymer chains and decrease the interlayer interactions which results in a lower viscosity.

Another factor causing viscosity reduction may be chain scissions during melt blending. The transesterification reaction, which is expected to take place in the presence of a catalyst, first occurs as the macromolecular backbone splits into shorter chains (degradation), and then randomly reconnections these chains (compatibilization) [24, 33, 40]. In a study by Zhou et al. [22], PLA/poly(propylene carbonate) (PPC) was blended in the presence of tetrabutyl titanate (TTB) catalyst. It was observed that as the amount of catalyst increased, the chain scission reaction became dominant, and the molecular weight gradually decreased. In a similar study, Wang et al. [40] prepared PLA-*co*-PPC in the presence of TTB and showed that low molecular weight short chains formed as a result of the reaction that caused viscosity reduction.

In their study, Cai et al. [33] prepared poly(methyl methacrylate) (PMMA) and polystyrene nanocomposites by in situ polymerization in the presence of CeO_2. They mentioned that CeO_2 accelerated the chain scissions of PMMA and paved the way for the formation of low molecular weight structures. In our study, it was suggested that the viscosity decreased as the chain scission step was dominant during this mechanism. The increase in the degradation rate observed in the TGA results also supported this suggestion.

There was not any significant difference between the viscosity-reducing effects of TiO_2 and CeO_2 catalysts. Both of them showed similar effects since they were globular in nature and accelerated the degradation mechanism.

The storage modulus (G') and loss modulus (G'') of the blends were presented in Fig. 3b, c, respectively as a function of angular frequency. As a typical polymer behavior, the G' and G'' values of all samples increased with frequency. Both moduli showed a reduction with the addition of catalysts similar to the complex viscosity of the blends. Luo et al. [37] reported that the storage and loss modulus of PLA decreased by adding TiO_2. In this study, as in Luo's et al., there was no change in the slope of the curves or frequency dependency level of the catalyzed PLA/PC blends. Thus, it can be said that the addition of the CeO_2 catalyst did not affect the chain dynamics at used loading levels. In the use of TiO_2 catalyst, the same loss and storage modulus values were obtained approximately at 1 and 3 wt% loading levels, while higher values were observed at 0.5 wt% loading level. Therefore, it can be said that the TiO_2 loading level was effective on the viscoelastic properties of the PLA/PC blends.

Morphological analysis

SEM analysis was used to determine the morphological properties of the uncatalyzed and catalyzed PLA/PC blends. The SEM micrographs of the tensile fractured specimen surfaces are given in Fig. 4. There are no clear interface boundaries or cavities between phases in the uncatalyzed PLA/PC blend (Fig. 4a). Equally blended PLA and PC exhibit good compatibility and interfacial adhesion.

In various studies, it has been reported that when PLA and PC were blended at 50/50 ratio, a droplet morphology was changed to a co-continuous morphology [6, 17]. Furthermore, fibrous structures indicating plastic deformation of the blend can be seen in the SEM micrograph of Fig. 4a. Considering the 1 and 3 wt% CeO_2 containing PLA/PC blends, unlike the uncatalyzed blend, a droplet structure was observed in Fig. 4b, c, respectively. It can be said that the addition of CeO_2 does not positively affect the compatibility between the polymers, on the contrary, the CeO_2 particles were aggregated and caused a brittle structure. The observed morphology also explained the low strain-at-break values of PLA/PC/CeO_2 composites obtained as a result of tensile test.

When PLA/PC blends containing TiO_2 were examined, the fibrous and ductile structure of the PLA/PC matrix could also be seen at Fig. 4d, e. Agglomeration of TiO_2 particles was also observed in the polymer matrix, which caused plastic deformation. In tensile test, the PLA/PC/TiO_2 composites exhibited higher elongation values than the CeO_2 containing blends. The ductile diagram of PLA/PC/TiO_2 composites exhibited a yield point followed by a decrease in the strength and a plastic deformation region occurred. In the FTIR analysis, it was mentioned that the copolymer structure may have formed as a result of the possible transesterification reaction. However, it can be said that these reaction products were not sufficient to overcome the melt viscosity differences and did not support the interpenetration of PLA and PC molecular chains at the interface, and thus morphological compatibility [6]. In addition, the chain scissions mentioned in the rheology analysis also negatively affected the morphology.

DSC analysis

The thermal behaviors of the materials were examined by DSC analysis. The obtained parameters for glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_m), and degree of crystallinity of PLA phase (X_c%) are gathered in Table 2. The T_g values of the neat PLA and PC were about 60 °C and 150 °C, respectively. The blending did not have any significant effect on the T_g of PLA which was 59.2 °C, in the blend. On the other hand, the T_g of the PC phase could not be observed as it was in the temperature range at which PLA melting began. A shift in T_g would be expected if the two polymers were compatible. However, the absence of a significant shift in the T_g of PLA indicated the incompatible of PLA and PC.

According to these results, although PLA and PC exhibited a morphologically compatible structure according to SEM micrographs, they are immiscible. No significant change was observed in the T_g value in the catalyzed blends compared to pure PLA, either. A similar result was reported for PLA/TiO_2 composite [37].

The pure PLA thermogram exhibited an exothermic peak at 120 °C, indicating cold crystallization of PLA. As a result of the increased molecular mobility with increasing temperature, the amorphous domains were rearranged to form crystalline domains. On the other hand, the T_{cc} peak was not observed in the blends with and without catalysts. This could be ascribed to the changes in the crystallization behavior of PLA and decrease of its amount in the blend.

The T_m value of the blends did not show a noticeable changes with TiO_2, i.e., an increase of 1 °C was achieved when only 3 wt% TiO_2 was added. In contrast to TiO_2, the addition of CeO_2 caused a decrease in T_m value. Also, it can be said that addition of 0.5–1 wt% filler did not change the ΔH_m. When the amount of filler was increased to 3 wt%; a decrease was observed in the ΔH_m value of the blend containing TiO_2, but an increase in that of the blend with CeO_2. An increase in the ΔH_m value while T_m decreased with the addition of CeO_2 in the PLA/PC blend suggested that the high amount of CeO_2 facilitated the movements of the polymeric chains. As a result, the crystallinity of the PLA/PC blend with 3 wt% CeO_2 was significantly higher than that of the uncatalyzed blend. A high amount of TiO_2, on the other

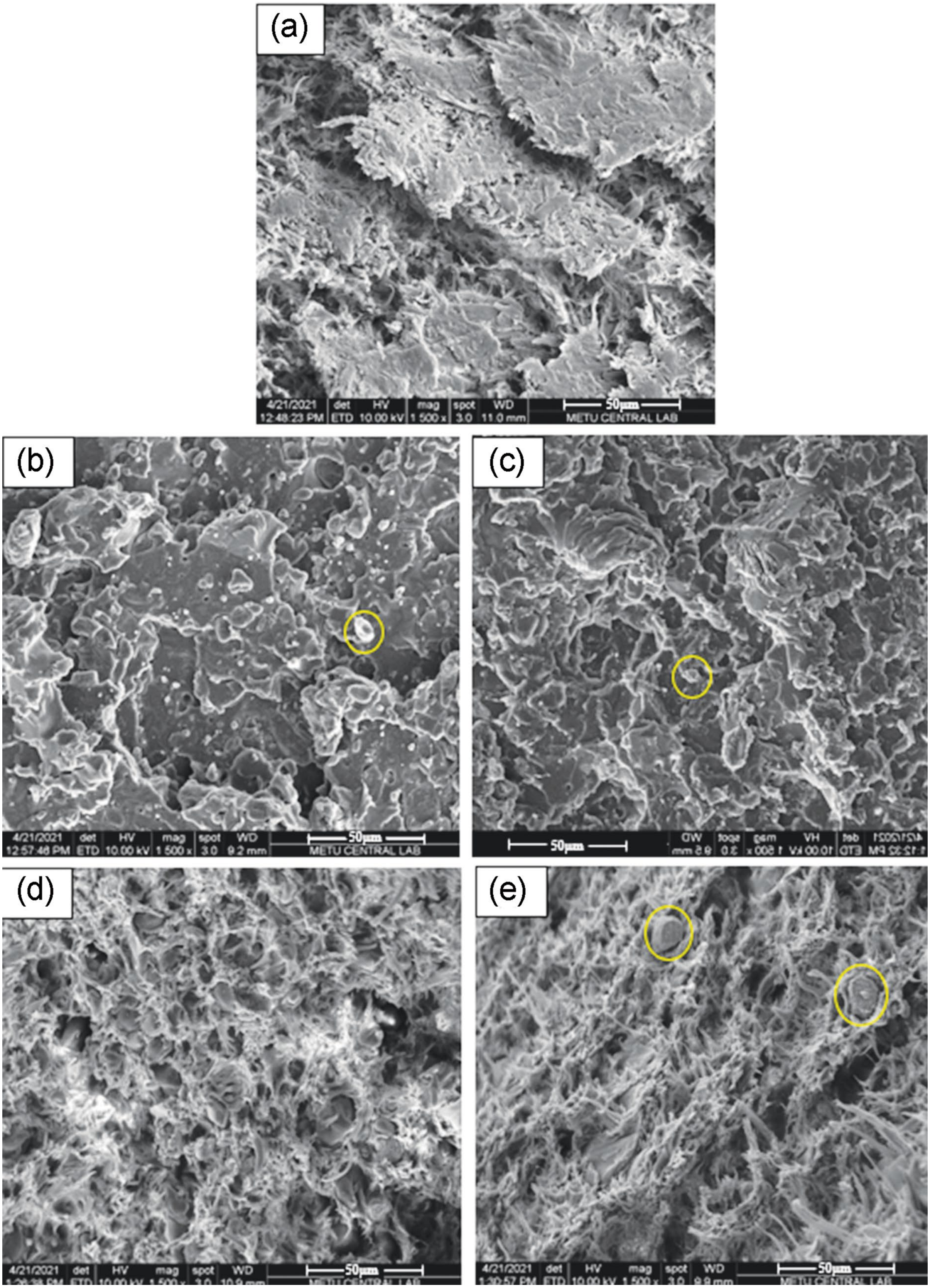


Fig. 4 SEM micrographs of tensile fractured specimen surfaces of: **a** PLA/PC **b** 1 CeO_2 **c** 3 CeO_2 **d** 1 TiO_2 **e** 3 TiO_2 samples (×1500, 50 µm)

Table 2 DSC results of uncatalyzed and catalyzed PLA/PC blends with CeO_2 and TiO_2 particles

Sample code	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_{cc} (J/g)	X_c (PLA) (%)
PLA	60.7	120.0	151.7	21.2	19.5	1.9
PC	150.7	–	–	–	–	–
PLA/PC	59.2	–	150.8	6.1	–	12.9
0.5 CeO_2	60.3	–	150.8	5.7	–	12.3
1 CeO_2	58.8	–	149.9	5.1	–	10.9
3 CeO_2	57.9	–	147.2	8.2	–	17.9
0.5 TiO_2	60.2	–	150.7	6.8	–	14.5
1 TiO_2	61.2	–	151.6	6.9	–	14.8
3 TiO_2	61.0	–	151.7	4.2	–	9.3

hand, prevented chain packing by restricting chain movements, thus reducing crystallinity [41].

Mechanical characteristics

The tensile test was carried out to examine the effects of catalyst on the mechanical properties of the PLA/PC blend. The tensile strength, strain-at-break, and modulus values are shown in Figs. 5a-c, respectively. Stress transfer from matrix to filler can be increased if there was good interfacial interaction among the PLA/PC matrix and fillers particles and catalyst fulfilled its compatibilization function. Thus, higher tensile strength can be obtained.

Examining Fig. 5a, the tensile strength of the uncatalyzed PLA/PC blend, about 65 MPa, had not shown any significant changes by the addition of TiO_2. Blends containing 0.5, 1 and 3 wt% TiO_2 had tensile strengths of 62, 61, and 59 MPa, respectively. The highest reduction was observed by the addition of 3 wt% TiO_2. This can be attributed to the aggregation of fillers in the matrix, which was also observed in SEM micrograph of Fig. 4e. Luo et al. [37] reported that 2 wt% and more g-TiO_2 significantly reduced the tensile strength of PLA.

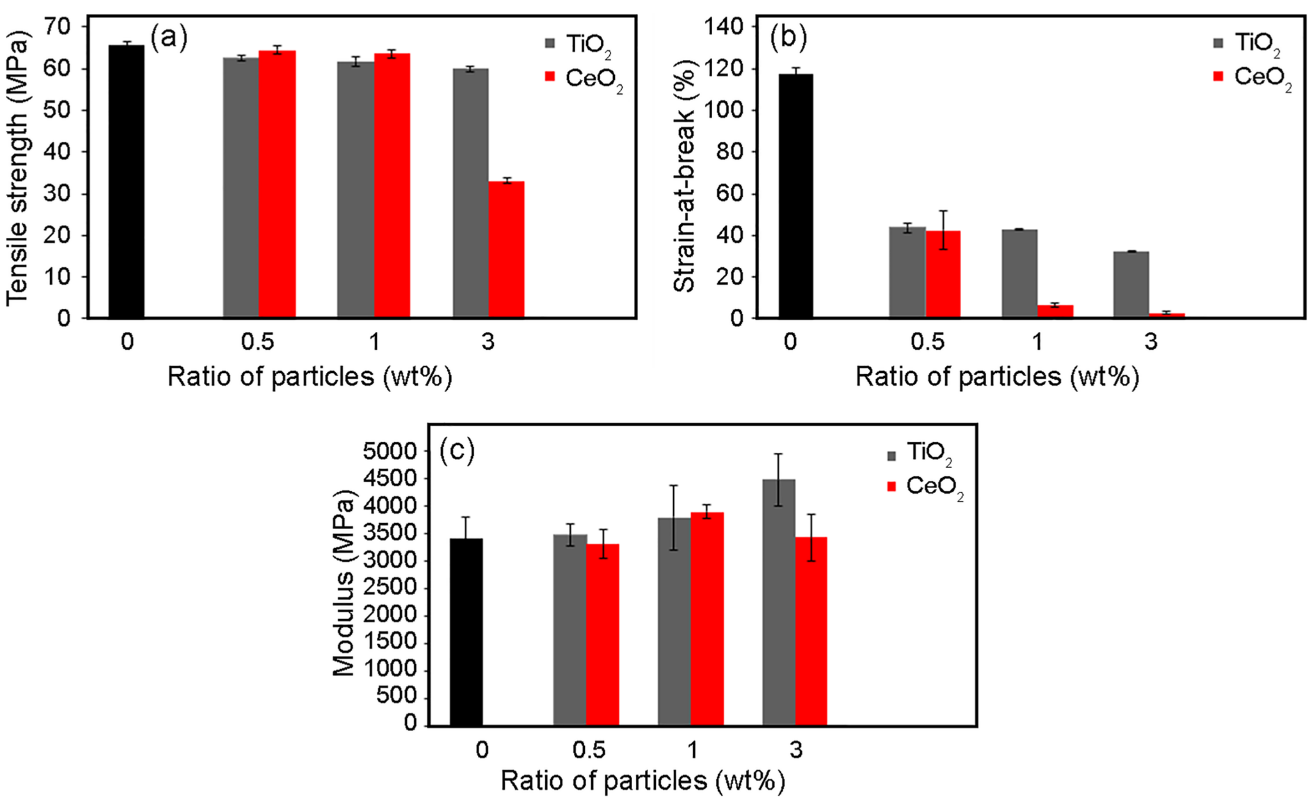


Fig. 5 Mechanical properties of the uncatalyzed and catalyzed PLA/PC blends with CeO_2 and TiO_2 particles: **a** tensile strength, **b** strain-at-break and (c) modulus

Herein, it is seen that the addition of 0.5 and 1 wt% CeO_2 did not cause any significant changes in the tensile strength of the PLA/PC blends. However, when the amount of CeO_2 increased to 3 wt%, the tensile strength showed a decrease of 49% and was measured as 33 MPa. In general, it has been reported that mechanical property losses in polymer composites are due to the agglomeration of the filler [41]. It can be said that the decrease in strength caused by a high amount of CeO_2 was also due to agglomeration which is also observed in SEM micrographs (Fig.4c). In addition, the acceleration of degradation by the catalyst that was observed in the rheology and TGA results might also be a factor in the decrease of tensile strength [22].

The modulus of the uncatalyzed PLA/PC blend was 3400 MPa and this value was increased with the incorporation of TiO_2 in the blend. With increasing TiO_2 amount, the modulus showed an increase of 2–32%. This can be attributed to the increase of interfacial area between the filler and matrix. This ensured that the load transferred from matrix to filler was high at low strain [28]. Although there is not any significant interaction between matrix and filler, weak Van der Walls forces in the low-stress region where the modulus is measured were sufficient to bond fillers to the polymer matrix. These weak bonds can transfer the load between fillers and the polymer matrix, thus it showed a higher modulus at low-stress or –strain region.

The modulus value increasing with increasing TiO_2 content was also observed for polypropylene/TiO_2 composites [28]. Considering the modulus of PLA/PC/CeO_2 samples, it is seen that 0.5 wt% addition has not any significant effect. When the amount of CeO_2 increased to 1 wt%, there was a 15% increase in the modulus compared to the uncatalyzed blend. At 3 wt% CeO_2 content, the modulus decreased to the level of the uncatalyzed blend. The modulus of the blend was first increased as a result of the inclusion of a filler and increasing of interfacial interaction area and then decreased again as a result of the agglomeration of filler particles.

In Fig. 5b, it is seen that the uncatalyzed PLA/PC blend exhibits a ductile behavior with a strain-at-break value of 117%. But it drastically decreased with the incorporation of fillers. The highest elongation-at-break value was observed for the sample including 0.5 wt% TiO_2 among the catalyzed blends. Rheological results had supported this observation. While PLA/PC/TiO_2 composites had an elongation-at-break value of 42–32%, the elongation-at-break value of PLA/PC/CeO_2 composites decreased to 2%. As evidenced by the SEM results, by the addition of CeO_2, the blend became completely brittle because of the agglomeration of filler particles. Also, it was stated that the complex viscosity decrease observed in the rheology results might be due to the decrease in molecular weight. Here, too, it can be said that the elongation-at-break value has decreased paralleled with the decrease in molecular weight [29]. Mechanical test results showed that TiO_2 particles had a better interaction with the PLA/PC matrix in general, while CeO_2 particles tended to agglomerate.

Thermal stability

TGA was performed to determine the effects of CeO_2 and TiO_2 catalysts on the thermal stability of the PLA/PC blends. The TGA curves, DTG curves, and corresponding data of the samples are represented in Fig. 6a, b and Table 3. The table shows the temperatures at 5 wt% (T_{d5}) and 50 wt% (T_{d50}) degradations and DTG curves peak temperatures (T_{max}).

As showed in Table 3, pure PLA and PC exhibited the single-step degradations starting at 301 and 449 °C,

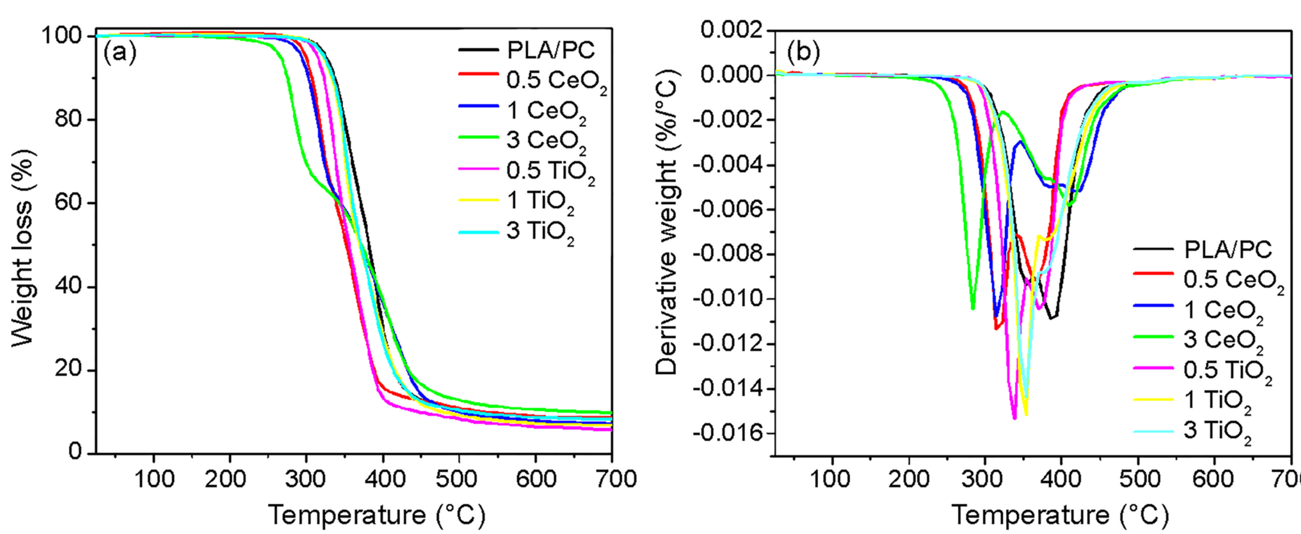


Fig. 6 **a** TGA and **b** DTG curves of the uncatalyzed and catalyzed PLA/PC blends with CeO_2 and TiO_2 particles

Table 3 TGA results of uncatalyzed and catalyzed PLA/PC blends with CeO_2 and TiO_2 particles

Sample code	T_{d5} (°C)	T_{d50} (°C)	$T_{max\text{-}1}$ (°C)	$T_{max\text{-}2}$ (°C)	$T_{max\text{-}3}$ (°C)	Residue at 800 °C (wt%)
PLA	301.3	342	347.1	–	–	0
PC	449.2	493	–	495.8	–	20.6
PLA/PC	326.9	381.1	355.1	389.0	–	8.3
0.5 CeO_2	299.2	352.3	318.4	365.3	–	8.2
1 CeO_2	293.5	372.1	316.7	380.6	419.0	6.8
3 CeO_2	266.4	372.1	283.9	376.0	410.5	9.4
0.5 TiO_2	314.9	355.7	336.5	372.1	–	5.7
1 TiO_2	323.5	369.8	350.6	379.4	–	6.8
3 TiO_2	324.0	371.5	352.3	378.3	–	8.2

respectively. It is also seen that while PLA completely degraded at 800 °C, PC exhibited 20% residue. The thermal resistance of PC is quite high compared to PLA. The PLA/PC blend exhibited two degradation steps. The $T_{max\text{-}1}$ and $T_{max\text{-}2}$ were 355 °C and 389 °C corresponding to maximum degradation temperatures of PLA and PC phases, respectively. The similar result was reported by Chelghoum et al. [17] for the 50/50 wt/wt PLA/PC blend. At the end of the test, 8.3 wt% ash was remained from the PLA/PC blend.

Considering the catalyzed blends, it is seen that both catalysts reduce the thermal degradation temperatures of the PLA/PC blends. The additions of CeO_2 and TiO_2 catalysts have facilitated the thermal degradation of PLA and PC. Furthermore, this effect was more pronounced in the PLA/PC blends containing CeO_2. Similar catalytic effects have been reported by Wang et al. [35] for PLA/ZnO and PLA/TiO_2 and also reported by Chelghoum et al. [17] for PLA/PC/samarium (III) acetylacetonate hydrate blends. They stated that these results were due to the catalytic effect of the added metal oxide catalysts.

As mentioned in the rheology section, during the transesterification reaction in the presence of a catalyst, chain scission (decomposition) dominates esterification, thus there is the presence of small chains. It was also possible that the molecular weight had decreased. This adversely affected the thermal stability of the PLA/PC blends [4, 8, 33]. Other factors affecting the polymer blends thermal stability were compatibility and crystallinity. It can be said that the decrease in crystallinity observed in some samples, also negatively affected the thermal stability of the polymer blends in DSC analysis [8]. If the two polymers were compatible, improved thermal stability could be achieved as per an improved and uniform morphological structure would be formed [41]. When TiO_2 and CeO_2 catalysts were added to the PLA/PC blend, the expected improvement in thermal resistance could not be achieved because full compatibility did not occur, and a morphologically uniform structure was not formed.

The DTG curves in Fig. 6b show that the peak temperatures have shifted to lower temperatures. The peak temperatures of the DTG curves showed a marked shift to lower temperatures when Ce_2O catalyst was used. Moreover, it is seen that the height of the first peak, which was attributed to PLA degradation and observed at 355 °C in the uncatalyzed blend, increased with the addition of both catalysts. The increase in peak height is related to the increase in the decomposition rate. It indicates that the degradation of the PLA phase was accelerated by the catalyst effect. In addition to the two peaks belonging to PLA and PC phases, a third peak was formed for 1 CeO_2 and 3 CeO_2 blends at 419 and 410 °C, respectively. The appearance of this peak can be attributed to the presence of a copolymer phase [17].

Conclusion

This study has evaluated the effects of TiO_2 and CeO_2 catalysts on the properties of the PLA/PC blend to improve the properties and expand the usage areas of this blend. Uncatalyzed PLA/PC blend and those containing 0.5, 1 and 3 wt% catalysts were prepared by melt extrusion and injection molding methods. FTIR, rheology, DSC, mechanical test, SEM, and TGA were used to characterize the blends. FTIR spectra showed that PLA and PC could suffer transesterification reactions via the effect of catalysts. However, the chain scission mechanism suppressed the transesterification. The complex viscosity decreased due to the short chains formed as a result of chain scissions and reduced molecular weight. It was also seen in the TGA results that the chain scission step was dominant. The fillers accelerated the thermal degradation of the blend. On the other hand, char residue increased with the inclusion of 3 wt% CeO_2. The morphological characterization of the uncatalyzed PLA/PC (50/50 wt/wt) blend revealed compatibility of the studied composition. Besides, DSC results showed that PLA and PC were immiscible. It was observed that uncatalyzed and

TiO_2-catalyzed PLA/PC blends exhibited plastic deformation, on the contrary, brittle behavior was observed with the addition of CeO_2. It was observed from the tensile test, that there was no significant change in the tensile strength values with the addition of TiO_2, while it decreased with the inclusion of CeO_2 due to particles agglomeration. The elongation-at-break value of PLA/PC blend drastically decreased with the incorporation of fillers. On the other hand, the modulus showed an increase of 2–32% with increasing the amount of TiO_2. The highest elongation was observed for the 0.5 TiO_2 sample among the catalyzed blends. It was found that the loading levels and types of the selected fillers significantly affected the mechanical properties of the PLA/PC blends.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

References

1. Nagarajan V, Mohanty AK, Misra M (2016) Perspective on polylactic acid (PLA) based sustainable materials for durable applications: focus on toughness and heat resistance. ACS Sustain Chem Eng 4:2899–2916
2. Ucpinar Durmaz B, Aytac A (2022) Investigation of the mechanical, thermal, morphological and rheological properties of biobased polyamide11/poly(lactic acid) blend reinforced with short carbon fiber. Mater Today Commun 30:103030
3. Yemisci F, Aytac A (2017) Compatibilization of poly(lactic acid)/polycarbonate blends by different coupling agents. Fibers Polym 18:1445–1451
4. Ebrahimi H, Sharif F, Ramazani SAA (2022) Effects of modified titanium dioxide nanoparticles on the thermal and mechanical properties of poly(l-lactide)-*b*-poly(ε-caprolactone). Iran Polym J 31:893–904. https://doi.org/10.1007/s13726-022-01039-7
5. Hazer S, Coban M, Aytac A (2018) A study on carbon fiber reinforced poly(lactic acid)/polycarbonate composites. J Appl Polym Sci 135:46881
6. Lin L, Deng C, Wang YZ (2015) Improving the impact property and heat-resistance of PLA/PC blends through coupling molecular chains at the interface. Polym Adv Technol 26:1247–1258
7. Penco M, Rahman MA, Verstichel S, DeWilde BL, Cinelli P, Lazzeri A (2011) Biodegradable PLA/PC copolymers for automotive applications. Bioplastics 6:20–21
8. Hedayati F, Moshiri-Gomchi N, Assaran-Ghomi M, Sabahi S, Bahri-Laleh N, Mehdipour-Ataei S, Mokhtari-Aliabad J, Mirmohammadi SA (2020) Preparation and properties of enhanced nanocomposites based on PLA/PC blends reinforced with silica nanoparticles. Polym Adv Technol 31:566–573
9. Wang B, Zheng Q, Li M, Wang S, Xiao S, Li X, Liu H (2022) Enhancing interfacial interactions of cocontinuous poly(lactic acid)/polyethylene blends using vinylsilane grafted carbon nanotubes as generic reactive compatibilizers. Express Polym Lett 16:524–539
10. Rajan KP, Gopanna A, Abdelghani EAM, Thomas SP (2021) Halloysite nanotubes (HNT) as reinforcement for compatibilized blends of polypropylene (PP) and polylactic acid (PLA). J Polym Res 28:374
11. Khosravi A, Fereidoon A, Khorasani MM, Saeb MR (2022) Experimental and theoretical mechanical behavior of compatibilized polylactic acid/polyolefin elastomer blends for potential packaging applications. Iran Polym J 31:651–663
12. Phuong VT, Gigante V, Aliotta L, Coltelli MB, Cinelli P, Lazzeri A (2017) Reactively extruded ecocomposites based on poly(lactic acid)/bisphenol A polycarbonate blends reinforced with regenerated cellulose microfibers. Compos Sci Technol 139:127–137
13. Chen Y, Peng Y, Liu WY, Zeng GS, Yang JH, Yan XH (2013) The effect of various catalyzers on transesterification in reactive blending PC/PLA blends. Adv Mater Res 741:24–27
14. Yiga VA, Lubwama M, Olupot PW (2022) Thermal and alkali modification of kaolin for potential utilization as filler material in fiber-reinforced polylactic acid composites. J Therm Anal Calorim 147:11077–11091. https://doi.org/10.1007/s10973-022-11379-4
15. Xia X, Liu W, Zhou L, Hua Z, Liu H, He S (2016) Modification of flax fiber surface and its compatibilization in polylactic acid/flax composites. Iran Polym J 25:25–35
16. Karsli NG, Aytac A (2014) Properties of alkali treated short flax fiber reinforced poly(lactic acid)/polycarbonate composites. Fibers Polym 15:2607–2612
17. Chelghoum N, Guessoum M, Fois M, Haddaoui N (2018) Contribution of catalytic transesterification reactions to the compatibilization of poly(lactic acid)/polycarbonate blends: thermal, morphological and viscoelastic characterization. J Polym Environ 26:342–354
18. Liang J, Ding C, Wei Z, Sang L, Song P, Chen G, Chang Y, Xu J, Zhang W (2015) Mechanical, morphology, and thermal properties of carbon fiber reinforced poly(butylene succinate) composites. Polym Compos 36:1335–1345
19. Liu C, Lin S, Zhou C, Yu W (2013) Influence of catalyst on transesterification between poly(lactic acid) and polycarbonate under flow field. Polymer (Guildf) 54:310–319
20. Phuong VT, Coltelli MB, Cinelli P, Cifelli M, Verstichel S, Lazzeri A (2014) Compatibilization and property enhancement of poly(lactic acid)/polycarbonate blends through triacetin-mediated interchange reactions in the melt. Polym (Guildf) 55:4498–4513
21. Ganguly A, Channe P, Jha R, Mitra S, Saha S (2021) Review on transesterification in polycarbonate–poly(butylene terephthalate) blend. Polym Eng Sci 61:650–661
22. Zhou L, Zhao G, Jiang W (2016) Effects of catalytic transesterification and Composition on the toughness of poly(lactic acid)/poly(propylene carbonate) blends. Ind Eng Chem Res 55:5565–5573
23. Pilati F, Marianucci E, Berti C (1985) Study of the reactions occurring during melt mixing of poly(ethylene terephthalate) and polycarbonate. J Appl Polym Sci 30:1267–1275
24. Nicolino MVB, de Alimeida LA, Branciforti MC (2020) Reactive extrusion of poly (butylene succinate-co-adipate) and poly (ε-caprolactone) biodegradable blends through titanium-based transesterification catalyst. Polym Degrad Stab 181:109320
25. Reddy KR, Hassan M, Gomes VG (2015) Hybrid nanostructures based on titanium dioxide for enhanced photocatalysis. Appl Catal A Gen 489:1–16
26. Daghrir R, Drogui P, Robert D (2013) Modified TiO_2 for environmental photocatalytic applications: a review. Ind Eng Chem Res 52:3581–3599
27. Mohamed H, Deutou JGN, Kaze CR, Beleuk à Moungam LM, Kamseu E, Chinje Melo U, Leonelli C (2020) Mechanical and microstructural properties of geopolymer mortars from metahalloysite: effect of titanium dioxide TiO_2 (anatase and rutile) content. SN Appl Sci 2:1573
28. Wacharawichanant S, Thongyai S, Siripattanasak T, Tipsri T (2009) Effect of mixing conditions and particle sizes of titanium dioxide on mechanical and morphological properties of polypropylene/titanium dioxide composites. Iran Polym J 18:607–616

29. Cai L, Qi Z, Xu J, Guo B, Huang Z (2019) Study on the photodegradation stability of poly(butylene succinate-co-butylene adipate)/TiO_2 nanocomposites. J Chem 1:5036019
30. Liu HY, Chen L, Li W, Wang KW (2019) Effect of halloysite nanotube loading on structure, mechanical and thermal properties of poly (l-lactic acid)/poly-(butylene succinate) blend. IOP Conf Ser Mater Sci Eng 634:012012
31. Deori K, Kalita C, Deka S (2015) (100) surface-exposed CeO_2 nanocubes as an efficient heterogeneous catalyst in the tandem oxidation of benzyl alcohol, para-chlorobenzyl alcohol and toluene to the corresponding aldehydes selectively. J Mater Chem A 3:6909–6920
32. Larosa C, Saldābola R, Zicāns J, Merijs Meri R, Eggenhöffner R, Converti A (2021) Prediction of thermal behavior of polycarbonate/cerium oxide composite films. Chem Eng Technol 44:1534–1540
33. Cai G, Lu H, Zhou Y, Hao J, Wilkie CA (2012) Fire retardancy of emulsion polymerized poly (methyl methacrylate)/cerium(IV) dioxide and polystyrene/cerium(IV) dioxide nanocomposites. Thermochim Acta 549:124–131
34. Parlar Karakoc O, Kibar ME, Akin AN, Yildiz M (2019) Nickel-based catalysts for hydrogen production by steam reforming of glycerol. Int J Environ Sci Technol 16:5117–5124
35. Wang X, Huang Z, Wei M, Lu T, Nong D, Zhao J, Gao X, Teng L (2019) Catalytic effect of nanosized ZnO and TiO_2 on thermal degradation of poly(lactic acid) and isoconversional kinetic analysis. Thermochim Acta 672:14–24
36. Joshi M, Butola BS, Simon G, Kukaleva N (2006) Rheological and viscoelastic behavior of HDPE/Octamethyl-POSS nanocomposites. Macromolecules 39:1839–1849
37. Luo YB, Da LW, Wang XL, Xu DY, Wang YZ (2009) Preparation and properties of nanocomposites based on poly(lactic acid) and functionalized TiO_2. Acta Mater 57:3182–3191
38. Sangroniz L, Ruiz JL, Sangroniz A, Fernández M, Etxeberria A, Müller AJ, Santamaria A (2019) Polyethylene terephthalate/low density polyethylene/titanium dioxide blend nanocomposites: morphology, crystallinity, rheology, and transport properties. J Appl Polym Sci 136:46986
39. Xie X-L, Liu Q-X, Li RK-Y, Zhou X-P, Zhang Q-X, Yu Z-Z, Mai Y-W (2004) Rheological and mechanical properties of PVC/$CaCO_3$ nanocomposites prepared by in situ polymerization. Polymer (Guildf) 45:6665–6673
40. Wang Z, Zhang M, Liu Z, Zhang S, Cao Z, Yang W, Yang M (2018) Compatibilization of the poly(lactic acid)/poly(propylene carbonate) blends through in situ formation of poly(lactic acid)-b-poly(propylene carbonate) copolymer. J Appl Polym Sci 135:46009
41. Nguyen VG, Thai H, Mai DH, Tran HT, Tran DL, Vu MT (2013) Effect of titanium dioxide on the properties of polyethylene/TiO_2 nanocomposites. Compos Part B Eng 45:1192–1198

Authors and Affiliations

Esra Zengin[1] · Bedriye Ucpinar Durmaz[1] · Meltem Yıldız[1] · Ayse Aytac[1,2]

[1] Present Address: Department of Chemical Engineering, Engineering Faculty, Kocaeli University, 41380 Izmit, Kocaeli, Turkey

[2] Polymer Science and Technology Programme, Kocaeli University, Izmit, Kocaeli, Turkey