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ORIGINAL PAPER

Injection-Molded Bioblends from Lignin and Biodegradable Polymers: Processing and Performance Evaluation

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Abstract This paper investigates the effects of the incorporation of lignin and small quantities of epoxidized natural rubber (ENR) as an impact modifying agent on blends of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(ε-caprolactone) (PCL). The addition of lignin resulted in a slight improvement of flexural strength and modulus of the ternary blending system. Incorporation of ENR into the blend resulted in an increase in notched Izod impact strength from 40 to 135% depending on the concentration of ENR. The addition of lignin into the blend resulted in an improvement of thermal stability of the ternary blend system. Morphological analysis showed a good dispersion of PHBV phases and lignin within the PCL matrix. Rheological characterization revealed that the presence of lignin resulted in increased storage modulus of the bioblend.

Keywords Bioplastic · Lignin · Epoxidized natural rubber · Toughened · Bioeconomy

Introduction

Bioplastics have been known to the scientific community for many years [1]; however, they have only recently begun to enter into the marketplace as commercial products [2]. Polyhydroxyalkanoates (PHAs) are a class of biodegradable polyesters that are synthesized via bacterial cultures [3, 4]. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) is a member of the PHA family with potential for future commercial applications [5]. This is because the chemical structures of these polymers are comparable with isotactic polypropylene and, therefore, can be expected to possess many properties that are similar to this widely used commodity plastic. Because of the structure of this material, PHBV has a tendency to form a stiff material.

One method of solving the problem of brittle formulations is to blend a stiff polymer, such as polylactide (PLA) (high modulus and low elongation), with a tougher polymer, such as poly(butylene adipate-co-terephthalate) (PBAT) (high elongation and low modulus), to achieve an optimal combination of stiffness and toughness properties [6–8]. There are many tough polymers on the market. However, many of these polymers cannot claim biodegradable status. Poly (ε-caprolactone) (PCL) is a biodegradable polymer that is synthesized from ring-opening polymerization of caprolactone molecules in the presence of a catalyst [9]. PCL manifests as a semi-crystalline tough polymer. Because of these properties, PCL is often blended with other polymers to provide improved resistance against crack propagation or toughness of their respective matrices under loading. One of the factors that can account for the lag in adaptation of the biopolymers by industries stems from the high cost of these materials compared to commodity plastics with similar properties [10]. Therefore, these materials can be made

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more attractive is the selection of low-cost filler materials to substitute a percentage the matrix.

Lignin is the second most prevalent naturally occurring biopolymer on the planet. Therefore, this status represents a potentially valuable co-product of both the pulp and paper industry, as well as the second-generation cellulosic ethanol industry [11, 12]. Lignin is an attractive macromolecule for use in bioplastic composites because its low cost can help offset the cost of a number of currently available bioplastics. Additionally, lignin possesses an abundance of hydroxyl functionalities, which allows for potential interactions between lignin and the polymer matrix [11–15]. Currently, researchers are investigating value-added applications for lignin in composites and blends, as well as many areas in other disciplines [11].

In an experiment conducted by Nitz et al. [16], PCL was blended only with lignin. This study demonstrated a steep reduction in impact properties with the addition of lignin, with a slight increase or maintenance of tensile/flexural properties in the presence of lignin [16]. Although many other attempts have been made to utilize lignin as a filler material in polymer systems [17–22], each of these studies has encountered similar difficulties. The presence of lignin in the polymer matrix causes brittleness in the final product, likely due to a lack of interactions between the matrix and lignin particles. In traditional filler systems, these difficulties are addressed using an additive such as a compatibilizing agent or impact modifiers [5, 23, 24].

In addition to blending with neat polymer systems, lignin has found application in many systems where two polymers are blended together. Abdelwahab et al. [6] experimented on biomaterial systems that consist of blends of PLA, PBAT and lignin. This work revealed that the addition of a chain extender provided an improvement of mechanical properties through facilitation of interactions. Chen et al. [7] also experimented with polymer blends of PLA and PBAT. Their study involved the use of lignin solvents to isolate fractions that are similar to lignin. A promising improvement of properties was observed, which was attributed to the improvement of lignin heterogeneity via fractionation of the lignin molecule using methanol.

Epoxidized natural rubber (ENR) has a history of utilization as an impact modifier for neat polymers, polymer blends, and composite systems. Zhang et al. [25] studied this behavior when they blended ENR with PLA and found that the tensile and flexural strengths, as well as their respective moduli, of the samples were shown to decrease with the addition of any type of ENR [25]. Effectiveness of the presence of the epoxy group in rubber-based impact modifiers was measured by Tanrattanakul et al. [26] in a study of melt that blended ENR with Nylon 6. It was also observed that increase of the ENR loading continued to improve the impact strength of the material. Unfortunately, such promising gains are not seen in every system. Another study, conducted by Parulekar et al. [27], blended ENR with poly(hydroxybutyrate) (PHB) and maleated polybutadiene to determine whether the impact of modification offered by ENR could be improved by the presence of a compatibilizing agent. It was shown that ENR, which did not normally offer improved impact behaviors with PHB alone, could be used as an impact modifying agent in the presence of maleated polybutadiene and PHB [27]. From this case, it can be understood that as long as there was a component in the blend that could react with ENR, it could be used as an impact modifier in that system [27].

The objective of this paper is to provide value-added applications for lignin through the development of PHBV–PCL/lignin bioblends. The main challenge associated with the use of lignin in bioblends is the manifestation of brittle behavior, which is caused by the presence of lignin in the polymer matrix. In this study, small quantities (1–5%) of ENR were compounded with bioblends to operate as an impact modifying agent. The effects of epoxidized natural rubber on morphology, tensile and flexural properties, impact strength, and thermal properties of the blends were examined.

Experimental

Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) grade Biopol D411GN was a product of Monsanto, Canada. Kraft Lignin was obtained from FP Innovations, Point-Claire, Quebec, Canada and possesses > 90% lignin, < 10% water, < 5% hexamethylene tetramine and < 4% sugar (xylose). The particle size of lignin is less than 210 micrometers. Injection grade poly(ε-caprolactone) (PCL), under the trade name Capa 6500, was purchased from Perstorp LTD, Perstorp, Sweden. Epoxidized natural rubber with a 25% epoxy functional group loading (ENR-25) was purchased from Muang Mai Guthrie Public Company Limited, Thailand.

Sample Preparation and Processing

PHBV, ENR, and lignin were dried at 80 °C for 24 h to remove moisture prior to processing. The samples were kept isolated and mixed together at the point of loading into the compounder. Epoxidized natural rubber was sliced into small strips for loading into the compounder. Aside from drying and cutting, all materials were utilized in their as-received form.

Materials were processed using a DSM Xplore combination 15 cc micro-compounder and a 12 cc DSM injection molding machine. The samples were compounded at a temperature of 180 °C. The piston-cylinder assembly, which was used to transfer the extruded materials between the compounder and injection molder, was kept at a temperature of 180 °C. The mold temperature was maintained at 30 °C. The injection pressure was set to 5, 4 and 10 bars for 6, 10, 14 s, respectively. Bioblends were prepared through the addition of pellets, lignin, and ENR material to the compounder in a batch process at a ratio of 20 wt% lignin, 1–5 wt% ENR, and 80–75 wt% (30/70 PHBV/PCL), as shown in Table 1. Each sample was prepared with 13 g of materials fed into the extruder to produce one test bar. For purposes of nomenclature, when referred to in formulations other than simply 30wt%PHBV/70wt%PCL, this combination of components will be written as PHBV–PCL.

Testing and Characterization

Injection-molded test samples were conditioned for 48 h at room temperature and 50% relative humidity. The reported tensile and flexural properties are an average of five samples tested using an Instron Universal Testing Instrument Model 3382. Flexural tests were conducted according to ASTM D790 at 1.4 mm/min. Tensile tests were conducted in accordance with ASTM D638 at 5 mm/min. Notched Izod impact strength of bioblends was measured using six samples based on the recommendations of ASTM D256 using a TMI 43-02 Impact Testing device with a 5 ft-lb pendulum. Notching occurred immediately after processing; testing occurred 48 h after notching.

Thermogravimetric analysis was conducted using a TGA Q500 from TA Instruments, USA. A 7–15 mg sample was heated at a rate of 20 °C/min to 600 °C under nitrogen atmosphere. Fourier transform infrared spectroscopy (FTIR) analysis was conducted using a Thermo Scientific Nicolet 6700 spectrometer with a resolution of 4 cm^{-1} and 64 scans per sample. A thin strip of polymer material was excised from the whole sample using a cutting implement. The results were analyzed using OMNIC Spectra software from the same company.

Table 1 Composition of blends of PHBV, PCL, lignin, and ENR

Code	Content (wt%)			
	PHBV	PCL	Lignin	ENR
Neat PHBV	100	–	–	–
80% PHBV/20% Lignin	80	–	20	–
Neat PCL	100	–	–	–
80% PCL/20% Lignin	–	80	20	–
30/70 PHBV/PCL	30	70	–	–
80% (PHBV–PCL)/20% Lignin	24	56	20	–
79%(PHBV–PCL)/20%Lignin/1% ENR	23.7	55.3	20	1
77%(PHBV–PCL)/20% Lignin/3% ENR	23.1	53.9	20	3
75%(PHBV–PCL)/20% Lignin/5% ENR	22.5	52.5	20	5

Scanning electron microscope (SEM) analysis was conducted using a Phenom Pro X desktop scanning electron microscope (Phenom World BV, Netherlands). In this analysis, the tested impact samples which are fractured during testing were utilized for scanning at an acceleration voltage of 10 kV. Then, these samples were analyzed at a range of magnification levels.

Rheological characterization was conducted using an Anton Paar MCR302 rheometer (Anton Paar GmbH, Graz, Austria) using a parallel plate configuration. The plate diameter used was 22 mm, with a measurement gap distance set at 1 mm. Dynamic sweep analyses were conducted for all samples to determine linear viscoelastic ranges. These tests were conducted at a strain of 1% for oscillation measurements. Frequency sweep analysis was conducted from 0.1 to 100 rads at 190 °C.

Results and Discussion

Mechanical Behavior

In this study, PHBV, PCL, lignin, and ENR were blended in several systems. The systems, which included lignin, contained 20% lignin by weight, while the ENR content was blended under loadings of 1, 3 and 5% by weight, as shown in Table 1. The bioplastic content of the blends existed as a ratio of 30% PHBV/70% PCL by weight. This ratio of PHBV to PCL was selected to maximize the notched Izod impact strength of the blend system. As shown in Table 2, the blending of PHBV and PCL at a ratio of 30/70 results in a 460% improvement of impact strength in comparison with neat PHBV. It is also shown that in the case of both the PHBV/lignin and the PCL/lignin binary blend, there is an observed decrease in notched Izod impact strength, which correlates with the addition of lignin. This can be attributed to the physical brittle nature of lignin, and incompatibilities between the phases in the respective blends [17, 18]. However, it is observed that in the case of blends of PHBV, PCL and lignin, there is an overall decrease in notched Izod impact strength in comparison with the PHBV/PCL bioblend. This decrease occurs due to the brittle nature of lignin in comparison with the polymer matrix [6]. However, the addition of 20% lignin results in a large drop in the notched Izod impact strength of the 30/70 PHBV/PCL matrix. Similar results have been observed in the works of Saito et al. [20]. Using the 80%(PHBV–PCL)/20% lignin system as a base, the addition of ENR at a loading of 1% can be seen to improve the notched izod impact strength of the composite

Table 2 Mechanical properties of blends of PHBV, PCL, lignin, and ENR

Code	Notched izod impact (J/m)	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
Neat PHBV	28.3 ± 1.76	29.9 ± 1.07	1.14 ± 0.05	21.2 ± 0.79	0.95 ± 0.05	4.92 ± 0.14
80% PHBV/20% Lignin	17.2 ± 0.79	17.93 ± 0.1	1.61 ± 0.03	13.9 ± 0.54	1.58 ± 0.07	1.42 ± 0.01
Neat PCL	NB	18.29 ± 0.4	0.42 ± 0.02	16.7 ± 0.40	0.45 ± 0.02	314 ± 11
80% PCL/20% Lignin	43.2 ± 2.43	22.52 ± 1.87	0.65 ± 0.05	18.8 ± 1.36	0.61 ± 0.04	69.3 ± 4.3
30/70 PHBV/PCL	131 ± 9.7	25.58 ± 0.87	0.65 ± 0.05	19.6 ± 1.84	0.92 ± 0.1	260 ± 35
80% (PHBV–PCL)/20% Lignin	37.1 ± 1.6	27.51 ± 2.99	0.86 ± 0.05	17.1 ± 0.57	1.14 ± 0.04	3.2 ± 0.17
79%(PHBV–PCL)/20% Lignin/1% ENR	51.8 ± 2.96	24.78 ± 2.27	0.86 ± 0.07	14.7 ± 0.47	0.11 ± 0.02	2.53 ± 0.51
77%(PHBV–PCL)/20% Lignin/3% ENR	73.5 ± 8.98	23.45 ± 1.14	0.81 ± 0.66	13.6 ± 1.13	0.75 ± 0.13	5.35 ± 0.51
75%(PHBV–PCL)/20% Lignin/5% ENR	87.5 ± 9.63	20.51 ± 0.69	0.69 ± 0.03	13.0 ± 0.36	0.60 ± 0.03	5.14 ± 0.26

NB non-break samples

base material by 40%. This trend continues for the 3% ENR blend, which shows an improvement of 98% over the notched Izod impact strength of the 80%(PHBV–PCL)/20% system. Zhang et al. [25] found that in a system of PLA alone, 10% ENR was required to provide this degree of impact modification. However, that study involved a binary system of PLA and ENR, whereas this study involves a quaternary system, which involves lignin. The discrepancy between the two studies can be attributed to the fact that the presence of lignin has already reduced the impact strength of the material in comparison with the PHBV/PCL binary blend. The largest degree of impact modification can be seen in the 5% ENR blend, which shows a large improvement of impact properties of 135% above the ternary blend baseline. From this, it can be observed that the increase of the ENR content from 3 to 5% can be seen to show a smaller improvement in notched izod impact strength than the increase in ENR content from 1 to 3%. This increase in ENR content can be attributed to the dispersed rubbery phase within the polymer matrix, which is capable of interacting with the polymer phases by opening the epoxy ring, targeting the terminal –OH, or side chain –OH groups that are found in the polymer chains of PHBV and PCL. These observations have been made in other PHB by Lee et al. [28].

The flexural behavior of binary systems of PHBV/lignin and PCL/lignin can be seen in Table 2. Here, it is observed that the addition of 20% lignin to the PHBV matrix causes a loss in flexural strength, which is coupled with an increase in flexural modulus, whereas the addition of the same concentration of lignin to the PCL matrix results in a small increase in flexural strength and a larger increase in modulus. This behavior of PHBV/lignin blends has also been observed by Camargo et al. [18], who reported a loss in flexural strength with the addition of lignin coupled with a small gain in flexural modulus. Similar behavior in PCL has been reported by Nitz et al. [16]. In their experiment, PCL maintained flexural strength with the addition of lignin, and they observed an increase in flexural modulus. In comparison with the impact strength, the flexural strength begins to show some losses as ENR is added to the system. The addition of lignin results in an increase in flexural strength and modulus in both the neat PCL and the ternary blend, as shown in Table 2. This is an expected behavior in a PCL dominated system because PCL is known to have low stiffness properties, and filling solids, such as lignin in this system, are noted to stiffen materials when blended with these materials [16]. This is in contrast to PHBV, where the mechanical strength of the brittle polymer is dependent on the crystallinity and continuous matrix of the material, which the presence of lignin disrupts [18]. With the addition of ENR, it can be seen that there is a drop in both flexural modulus and flexural strength. These changes in flexural strength reveal that the presence of ENR in the system modifies the mechanisms through which the polymer systems transfer stress. Particularly, based on the morphological changes that are present in these bioblends, the dispersion of the rubbery phases of the material causes randomly distributed phases of low stiffness distributed across the phases, which has the effect of compromising the stiffness and, therefore, the flexural strength of these properties. Similar losses in flexural strength have been observed to correlate with the addition of ENR to PHB by Parulekar et al. [27].

Tensile properties of PHBV, PCL and Lignin bioblend systems, when toughened by ENR, demonstrate similar trends and behaviors to flexural behavior, as discussed above. In Table 2, it can be seen that PHBV and PCL demonstrate different tensile behaviors when blended with lignin. PHBV, an already brittle polymer, experiences a reduction in tensile strength and elongation at break with the addition of lignin, coupled with an increase in modulus. This behavior has been observed in blends of lignin and PHBV by Camargo et al. [18] and can be attributed to lignin disrupting the crystallinity of the polymer and restricting adhesion through incompatibilities with the matrix [18]. Tensile behavior of this material is interesting in terms of elongation. Here, it can be seen that when lignin is added to the 30/70 PHBV/PCL matrix, there is a significant drop in elongation of the material, which is similar to the behavior observed in neat PCL and lignin both in this study and in the work of Teramoto et al. [17]. This behavior suggests that lignin within the matrix disrupts the movement of polymer chains in the material during elongation [6]. This affects the ability of the material to undergo the type of elongation behavior that can be seen in the matrix of the PHBV/PCL blend. Using the 80%(PHBV–PCL)/20%Lignin blend as a baseline, the addition of ENR above 3% causes a noticeable increase in the elongation behavior of the material. This correlates with the impact test behavior, and is evidence that ENR has toughened the material. This increase in elongation has been observed in many other studies with a variety of polymers, such as PHB [27], PLA [29], and nylon [30], where morphological changes in the polymer matrix have caused an improvement in the stress transfer between the phases of the material. This improvement occurs because the rubbery phase of the material stretches and adheres to the polymer matrix, which causes additional expansion to occur after plastic deformation has begun in the otherwise brittle material [27, 29, 30]. Unfortunately, there is also a decrease in tensile strength, which can be observed with the addition of ENR. This decrease can be attributed to the low modulus of rubber, as well as to the effect on stress transfer by the rubbery phases, which are dispersed in the matrix [26].

Morphological Behavior

To study the effect of Kraft lignin and ENR on the behavior of bioblends of PHBV and PCL, morphological analysis was conducted. The behavior of the polymer systems outlined in this study was analyzed using SEM. Figure 1 shows SEM images of neat PHBV and PHBV with 20% lignin (Fig. 1A, B, respectively). It can be seen that the lignin particles vary in size, but become distributed within the PHBV matrix. The lignin particles dispersed in matrix can be observed inside red circles in the SEM images (Fig. 1B). In contrast, when comparing the PCL and PCL/20% Lignin images (Fig. 1C, D, respectively), it is observed that there are incompatibilities between the PCL matrix and the overall lignin particle. This is apparent based on the prevalence of voids and the evidence of pull-out. These features suggest that there is poor adhesion between the PCL matrix and the lignin particles. Similar features have been observed in studies by Teramoto et al. of lignin esters blended with a PCL matrix [17]. From this collection of SEM images (Fig. 1A–D), it can be understood that the presence of lignin within the matrix provides disruptions in the continuous matrices of these polymer systems. It is also apparent that incompatibilities resulted in gaps between the polymer and lignin phases. Together, the disruption of continuous matrix that is caused by the presence of lignin and the resulting discontinuities between the lignin and matrix phases can account for the dramatic loss in impact strength, which comes with the addition of lignin to both the neat PHBV matrix and the neat PCL matrix. In the 30/70 PHBV/PCL matrix (Fig. 2A), it can be seen that the polymer blend separates into two distinct polymer phases, where PHBV is surrounded by PCL. One distinct feature that can be seen is that the PHBV phases have a tendency towards evenly distributed spherical shapes (blue circles mark PHBV phases in PCL Matrix as shown in Fig. 2A). This phenomenon is commonly observed in morphological studies of immiscible phases [31]. Kubo and Kadla [31] state that this phase geometry forms in an immiscible system to minimize surface area at phase boundaries. Additionally, rheological differences between the PHBV and PCL phase of the matrix also likely contribute to the peculiarities of lignin distribution in this polymer system. In filled polymer systems, the distribution of filler within the matrix depends on the rheological conditions that the polymer is subjected to during injection molding [32]. With the addition of lignin to the blend (Fig. 2B), it can be seen that the behavior of this system is similar to that of neat polymers. The lignin particles become dispersed within the dominant PCL matrix. Similar to neat polymer blends, it can be seen that the presence of lignin causes an increase in the number of dimples and interfacial gaps between the lignin particles and the polymer matrix due to the compatibility of these materials. With the addition of ENR, it can be seen that there is a reduction in the presence of this type of morphological behavior [33]. In Fig. 2C, it can be seen that the addition of ENR causes a change in this morphology, with different phases still clearly visible, but increased overlap between the phases.

The addition of ENR appears to have other effects on the morphology of the composite system. Figure 3 presents the blend of 77(30 PHBV/70 PCL)/20 Lignin/3 ENR at four levels of magnification. In Fig. 3, it can be seen that the addition of ENR has also caused a reduction in the amount of pull-out and dimples that are observed in the blend. Distinct PHBV phases are still observable in the matrix, which indicates that the compatibility of PHBV and PCL phases has not been improved by the addition of ENR. Therefore, this result means that the presence of rubber must be affecting this on a mechanical basis. The mechanical properties, such

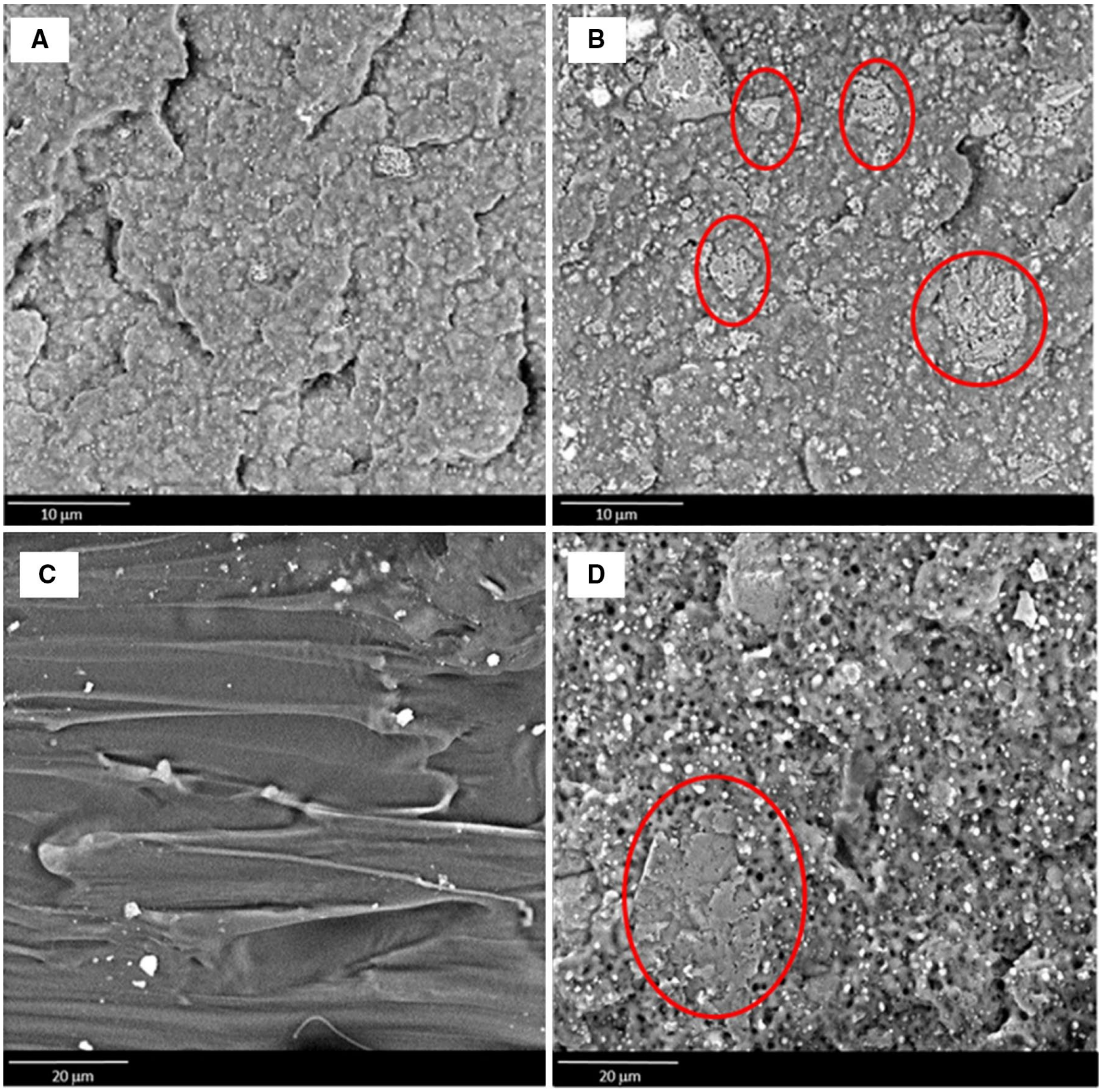


Fig. 1 Scanning electron microscope images of: **A** Neat PHBV, **B** PHBV/20% lignin, **C** neat PCL, **D** PCL/20% lignin at ×3000 magnification (red circle show mark lignin phases)

as impact strength, demonstrate that the presence of ENR affects the material behavior of the bioblends.

Thermal Behavior

Thermal degradation of bioblends and neat polymers has been studied to determine the effect of blending on thermal stability. Here, neat polymers, binary blends, ternary blend and toughened ternary blends have been subjected to TGA analysis from room temperature to 600 °C. TGA curves of the studied blends are presented in Fig. 4. In Fig. 4, it can be seen that neat PHBV has a thermal onset temperature of 226 °C, whereas neat PCL degradation begins at 334 °C. From this information, it can be understood that PCL is a more thermally stable polymer than PHBV. A study conducted by Aoyagi et al. [34] suggests that this difference in thermal stability can be explained via a different degradation mechanism. In their study, PHB was determined to degrade through cis-elimination mechanisms, whereas PCL underwent unzipping depolymerization [34]. In contrast to rapid degradations of PHBV and PCL, it can be seen in Fig. 4 that the thermal degradation of lignin occurs over a wider range of temperatures. This behavior is characteristic of lignin because the degradation of lignin is a multi-stage process [30, 35]. At temperatures above 200 °C, the weaker bonds in the lignin structure become more likely to form radicals and initiate the degradation process [35]. Additionally, due to its structural

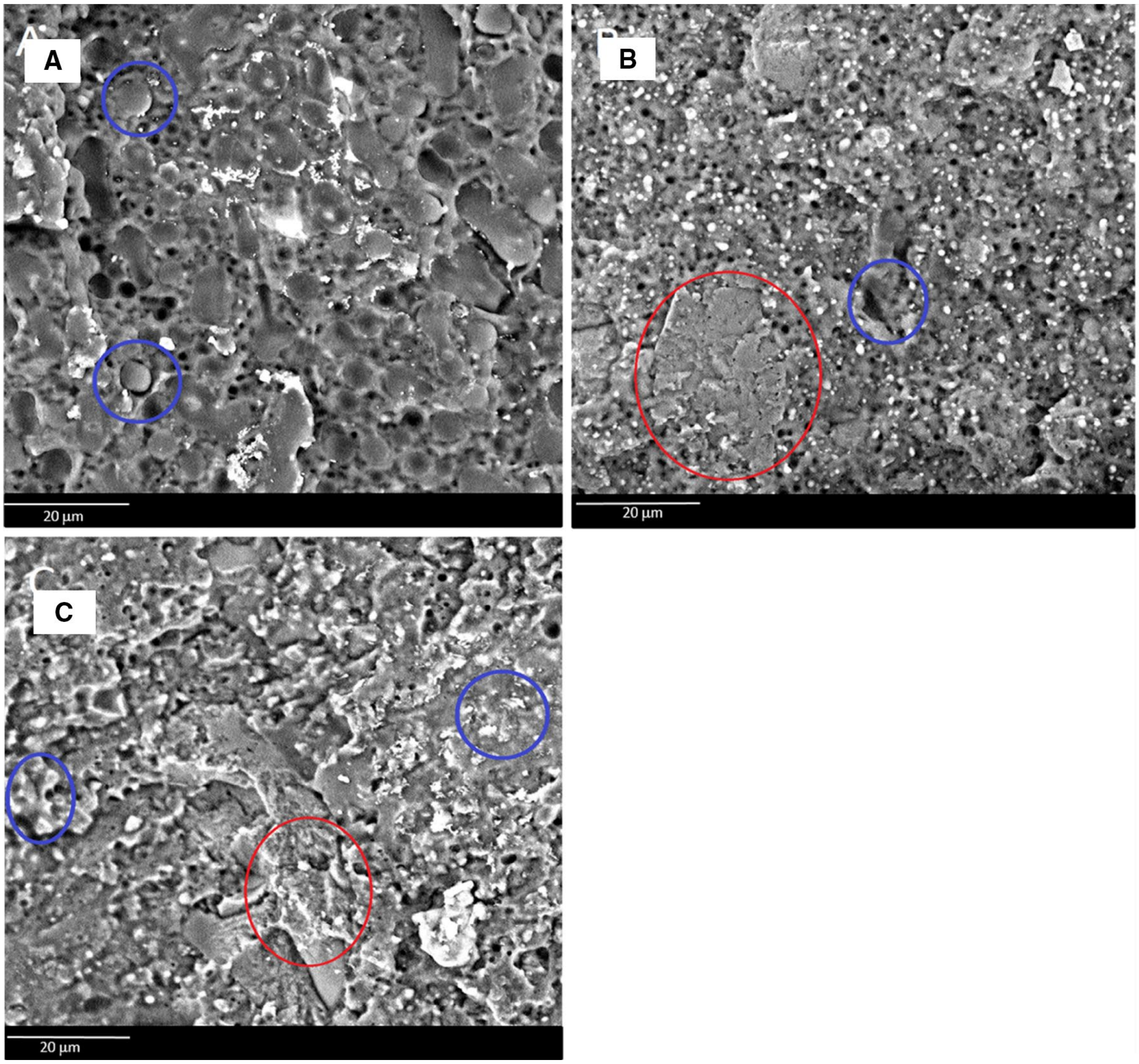


Fig. 2 Scanning electron microscope images of: **A** 30/70 PHBV/PCL, **B** 80%(PHBV–PCL)/20% Lignin, **C** 77%(PHBV–PCL)/20% Lignin/3%ENR at ×3000 magnification (blue circles mark PHBV phases in PCL Matrix). (Color figure online)

complexity, lignin also characteristically degrades differently than neat PHBV and PCL polymers. In Fig. 4, it can be observed that thermoplastic polymers and their blends tend to degrade very steeply once their thermal degradation onset point is reached, whereas lignin can be seen to begin its thermal degradation process at a temperature below that of either thermoplastic biopolymer. For example, from Fig. 4, it is observed that neat PCL commences degradation at 334 °C and reaches a plateau at 428 °C. However, the degradation of lignin commences at 222 °C and begins to plateau after 500 °C. This contrast in behavior can be attributed to the fact that lignin is a polymer that is made up of a number of different chemical bonds that require differing levels of thermal energy to initiate radicalization and subsequent degradation [30, 35]. Similar patterns of thermal degradation have been observed by Sahoo et al. [36]. This experiment characterized 11 lignin samples, which were observed to possess a wide range of thermal degradation patterns depending on the processes that are used to produce lignin. One consistent feature of the TGA curves studied was the similarity between the visible degradation steps to those in Fig. 4 [36]. This similarity is important, because different varieties of lignin are often chemically different and can be expected to experience different chemical reactions during degradation [34, 36]. This phenomenon can be partially understood by the remaining mass at the end point of the experiment. At 600 °C, approximately 50% of mass on the lignin curve remains. This can be understood based on the work of Faravelli et al. [35] that during degradation, the cleavage of bonds in the lignin molecule forms a large number of species, which manifest in solid form as ash residue. This

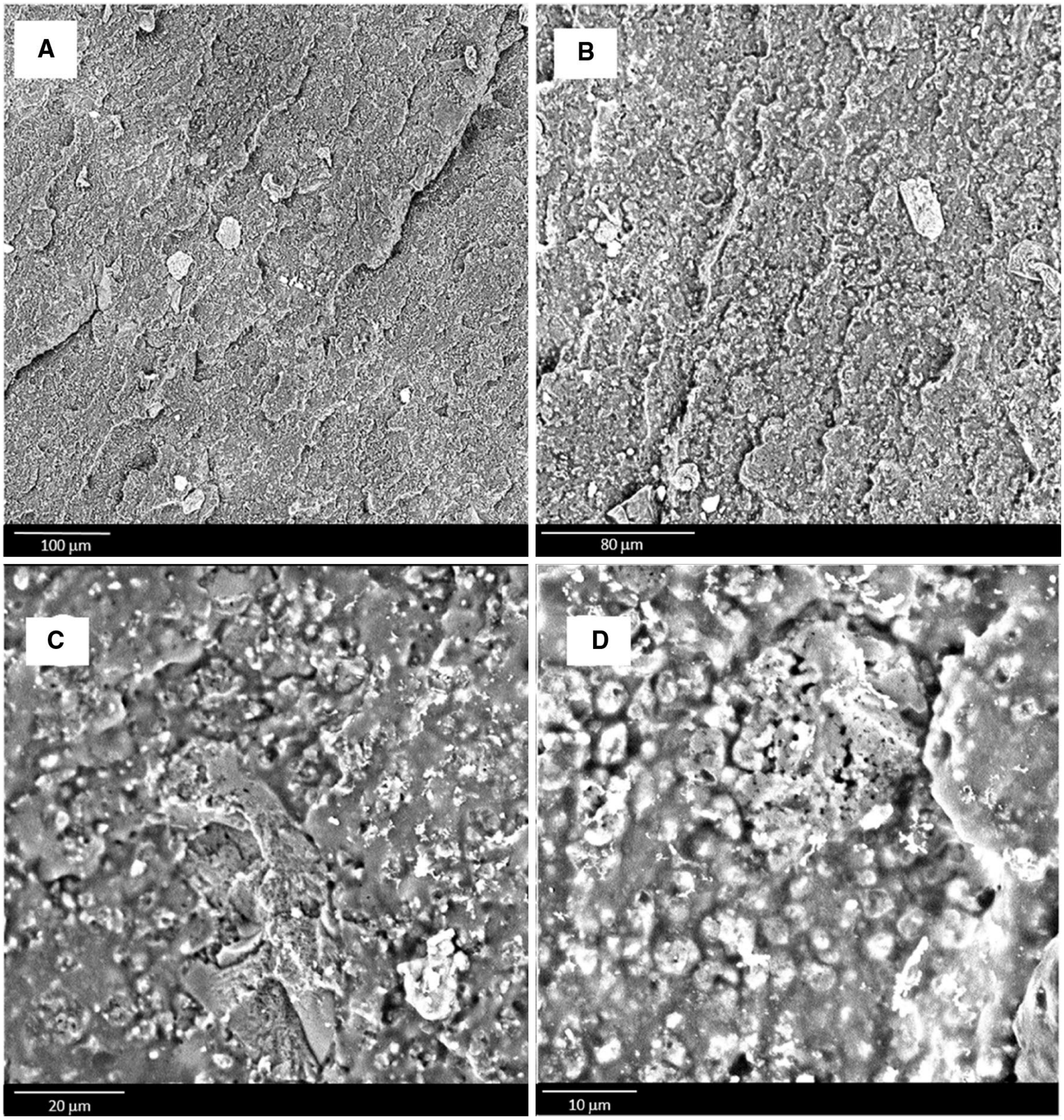


Fig. 3 Magnifications of 77%(PHBV–PCL)/20% Lignin/3% ENR. **A** ×500, **B** ×1000, **C** ×3000, **D** ×5000

property can account for the increase of remaining mass in both the neat lignin sample, as well as polymer blends involving lignin.

Blends of PHBV and PCL in Fig. 4 can be seen to display two independent thermal degradation curves. This behavior indicates that there are two polymers that are present in the system, as expected. This also suggests that the phase remains separate, because two onsets of degradation temperatures represent the phases that undergo separate degradation mechanisms [35]. Furthermore, it can be seen that the addition of lignin to this blend results in an improvement of thermal stability between these two polymers despite the fact that lignin is noted to be less thermally stable than both the component polymers. This apparent improvement of thermal stability can be attributed to lower overall concentrations of PHBV in this blend, because PHBV is less thermally stable than PCL, as well as the slow post-onset thermal degradation of lignin. Lastly, the addition of ENR does not appear to compromise the thermal stability of untoughened bioblend. ENR-25 has sometimes been noted to improve thermal stability of blends in which it is involved [25, 30]. However, in this study, little to no improvement of thermal stability is expected, because the concentration of ENR-25 in the blend is very small.

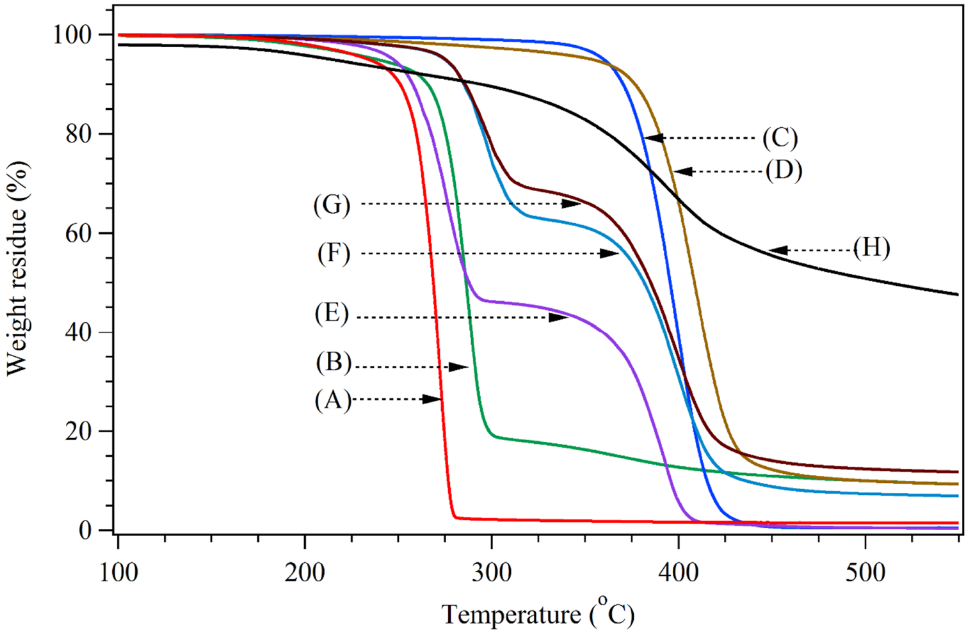


Fig. 4 Thermal degradation behaviour of polymer blends: **A** Neat PHBV, **B** 80% PHBV/20%Lignin, **C** Neat PCL, **D** 80% PCL/20%Lignin, **E** 30/70 PHBV/PCL, **F** 80%(PHBV-PCL)/20%Lignin, **G** 75%(PHBV-PCL)/20% lignin/5%ENR, **H** Lignin

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was conducted to determine whether the impact modification that is provided by ENR can be associated with any chemical reactions that take place in the system. The full spectra of the 80%(PHBV–PCL)/20% lignin blend, 80%(PHBV–PCL)/20% lignin/3% ENR blend and neat ENR can be seen in Fig. 5. If interactions were taking place between the ENR and other components of the blend, the presence or absence of these peaks in the spectra may provide clues as to what type of interactions occurred between ENR and the polymer matrix. This would indicate that a reaction was taking place that did not involve the epoxide ring [37]. Important peaks for epoxy groups occur at 878 and 1250 cm^{-1}, which correspond to symmetric and asymmetric vibrations of the epoxy ring, respectively [37, 38]. In Fig. 5, it can be seen that these peaks are present in the ENR spectra; however, they are not apparent in the 77%(PHBV–PCL)/20%Lignin/3%ENR blend. While the disappearance of these peaks can be attributed to the low concentration of ENR in the blend, it may also be indicative of a reaction taking place, as shown in Scheme 1. Together,

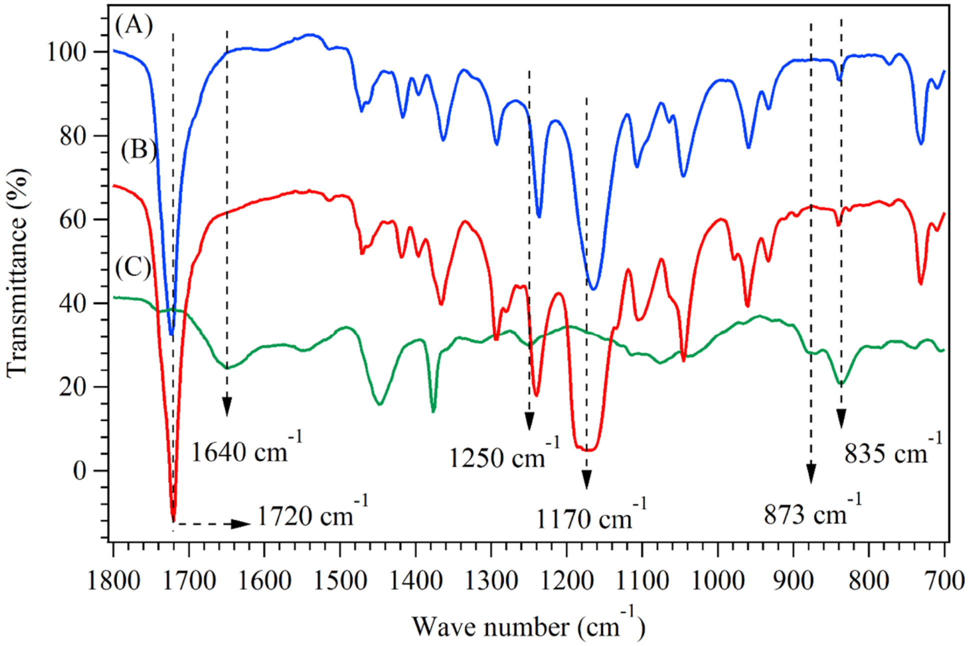
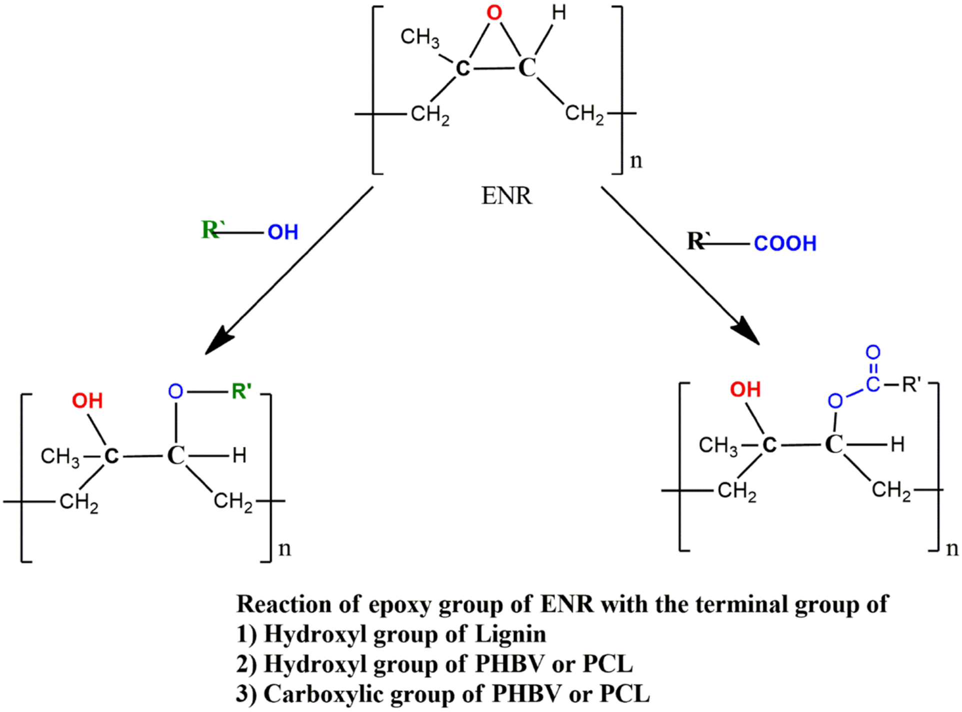


Fig. 5 FTIR spectra of blends of: **A** 80% (PHBV–PCL)/20% Lignin, **B** 77% (PHBV–PCL)/20% Lignin/3% ENR, **C** ENR



Scheme 1 Schematic reaction between the functional group present in PHBV, PCL, and Lignin with ENR during reactive extrusion

the disappearance of these peaks may indicate that interactions have taken place between ENR and the polymer matrix via the opening of the epoxy ring. However, it should be noted that the 1250 cm^{-1} peak may have been absorbed by the larger peak at 1240 cm^{-1} [39] (Fig. 5B). Because both PHBV and PCL are polyesters, this peak is already present in the spectra of the blends. Lee et al. [28] experimented on the PHB/ENR blend and determined that with a proper thermal treatment, the epoxide ring was not present in the PHB composite despite the 30/70 ratio of PHB/ENR. This, coupled with a change in the behavior of the peak associated with the carbonyl group present in the PHB matrix, suggested that interactions were taking place between this group and the opened epoxy ring [28]. It can be seen in Fig. 5 that in this experiment, there is a modification of the behavior of the peak that correlates with the C=O group found at 1720 cm^{-1}. Lee et al. [28] report a similar behavior correlating the modification that takes place at 1640 cm^{-1} with the C=C bond that is found in the natural rubber section of the ENR molecule. In Fig. 5, it can be noted that there is a widening of the C–O peak at 1170 cm^{-1} [28]. From this, it can be reasoned that the epoxide ring potentially opens during the reaction to react with either the side chain –OH bonds or the terminal –OH component of the polymer chain [28]. These details can be correlated with an increase in notched Izod impact strength with the presence of ENR in the toughened blend. This behavior is indicative of better dispersion of the rubbery phase within the polymer matrix due to reaction with various phases of the matrix. In Figs. 3C and 7D, it can be seen that PHBV and PCL still exist as discrete phases in the polymer matrix. This finding suggests that the compatibility of these polymers has not been achieved.

Rheology

In addition to other properties, the rheological properties of the blending system in its molten state are helpful for identifying the applicability of the material under processing conditions [32]. In this experiment, the material was measured using an oscillatory rheometer. Experimentation was conducted to determine the LVE of the studied materials. Based on this, the 1% strain during the frequency sweep experiments is outlined in this section. Figure 6 demonstrates the frequency dependency of the complex viscosity of the various blends. In Fig. 6, it can be seen that the PCL and PCL/20% lignin blends follow the same trend. The primary difference between these blends relates to the fact that the absolute value of the plateau decreases with the addition of lignin. Both of these polymer systems exhibit a more pronounced Newtonian plateau compared with the 30/70 PHBV/PCL blend, which suggests that the implementation of an immiscible polymer blend has modified the viscosity behavior of this material. This effect has been observed in other immiscible polymer systems by Elias et al. [32] in their study of blends of polypropylene and polystyrene. This occurs due to the dispersed phase of the secondary polymer, which impacts the flow characteristics of the matrix phase of the material. This is similar to what the filler material does within the matrix [40]. The 80%(PHBV–PCL/20%) and 77%(PHBV–PCL)/20%Lignin/3% ENR blends do not

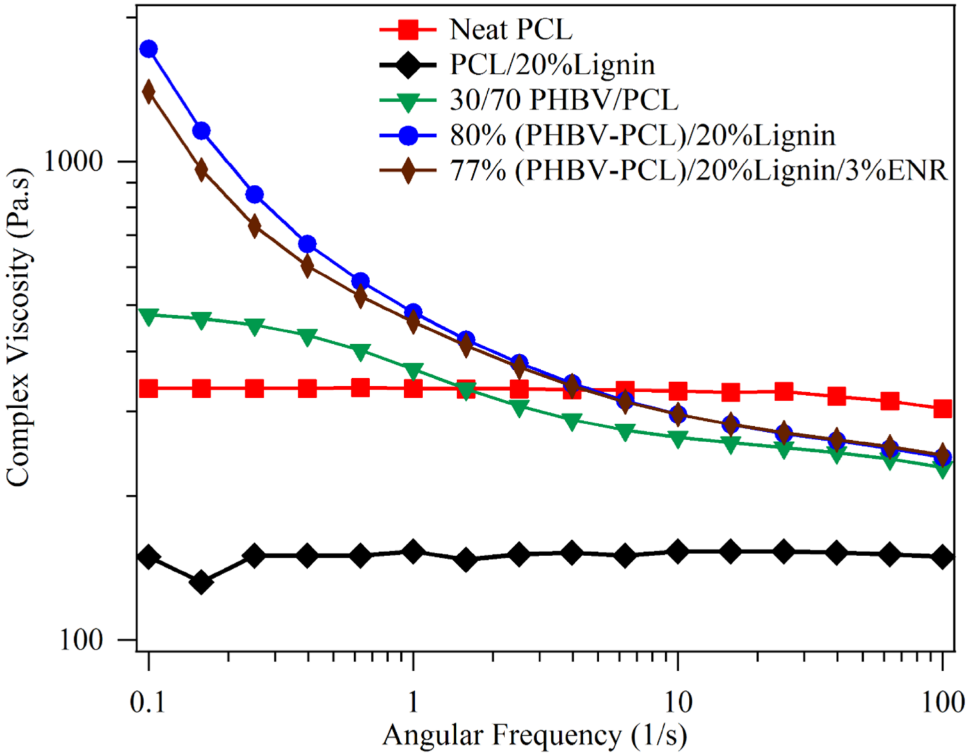


Fig. 6 Complex viscosity of blends of PHBV, PCL and Lignin toughened by ENR. **a** Neat PCL, **b** 30/70 PHBV/PCL, **c** 80%(PHBV–PCL)/20% Lignin, **d** 77%(PHBV–PCL)/20% lignin/3% ENR

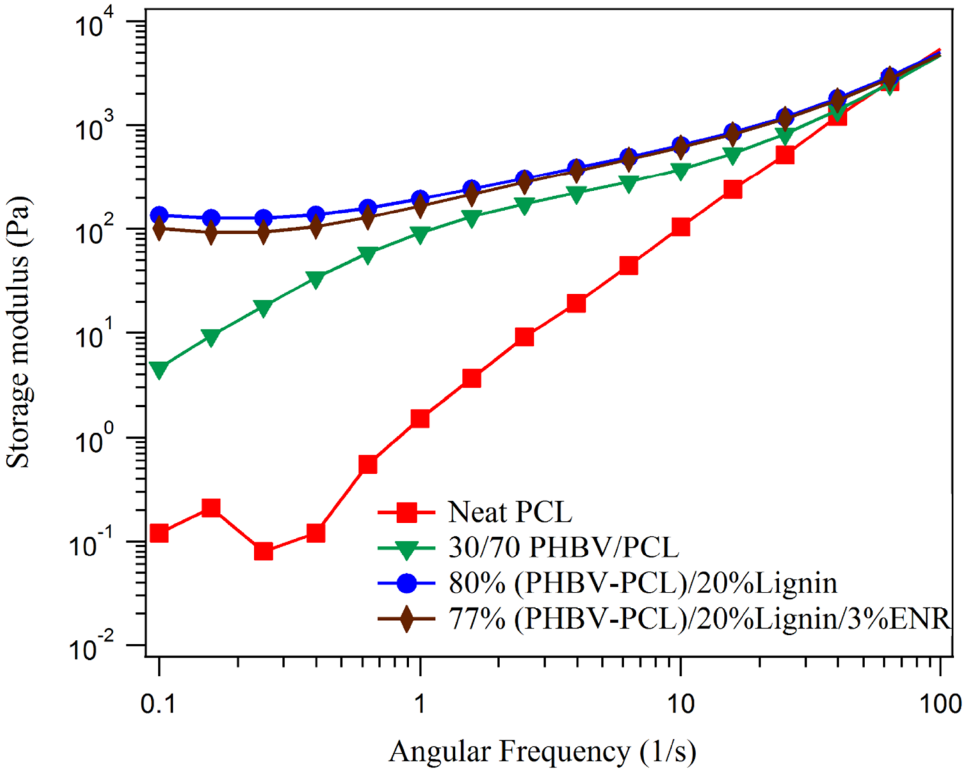


Fig. 7 Storage moduli of blends of PHBV, PCL and Lignin toughened with ENR. **a** Neat PCL, **b** 30/70 PHBV/PCL, **c** 80%(PHBV–PCL)/20% Lignin, **d** 77%(PHBV–PCL)/20% lignin/3% ENR

enter the terminal region in the range that is measured in this experiment. This suggests that shear thinning is more pronounced in blends that contain PHBV, PCL, lignin and ENR. Historically, shear thinning correlates with solid-like materials, such as the filler material, that are added to polymer composites [40, 41]. This occurs due to the presence of solid materials within the molten polymer matrix, such as lignin. In this case, the addition of ENR does not appear to have as large an impact on the complex restriction in the matrix as that caused by solid lignin particles or by the immiscible phases of PHBV and PCL. This explains why blending of PHBV and PCL causes an increase in viscosity and a shift out of the terminal zone to a small degree, where blends containing lignin and ENR shift even farther out of the terminal zone and demonstrate a higher value in complex viscosity. From a theoretical standpoint, the presence of ENR in the matrix should cause an increase in viscosity because it is an elastomeric material [26]. However, the quantity of ENR that is present in this particular bioblend is very low. Therefore, it is likely that at larger concentrations of material, there would be a more noticeable shift in viscosity with ENR.

Figures 7 and 8 show the frequency dependencies of the loss modulus (G″) and storage modulus (G′) of blends of PHBV, PCL, lignin and ENR. The loss modulus reflects the viscous response, where the storage modulus represents the elastic response of the material. In terms of storage modulus at frequencies above 50 rad/s, all formulations experience a similar behavior. However, at lower frequencies, the trends of these blends begin to diverge. This can be attributed to the presence of additional phases in the blend systems, which provides enhancements in storage modulus at low frequencies due to blend heterogeneity. Similar results can be seen in the work of Zhang et al. [42], who reported an increase in both high and low frequency behavior in the presence of a compatibilizing agent. Similarly, Al-Itry et al. [43] blended PLA and PBAT and reported that improved chain entanglement had resulted in an increase in lower frequency values of storage moduli. It can be seen in this plot that the storage modulus exhibits an upward trend as frequency decreases, which correlates with the addition of PHBV, Lignin and ENR. The behavior of the 30/70 PHBV/PCL blend can be understood as the interaction of the dispersed polymer phases of PHBV within the PCL matrix, which causes an enhancement of the low frequency behavior of the system [43]. The differing behaviors of the 80%(PHBV–PCL)/20% lignin and 77%(PHBV–PCL)/20% Lignin/3% ENR blends can be attributed to the presence of solid lignin phases that are dispersed within the polymer system. Unlike the thermoplastic PHBV and PCL phases, this material does not undergo melting, and, therefore, provides resistance to disturbances that occur at lower frequencies of this analysis [42]. This behavior of the systems in terms of storage modulus can also be correlated with the loss modulus, which demonstrates upward trends of these materials as frequency increases. This effect is not as pronounced as in the storage modulus. However, when the information from these plots is analyzed in parallel, it becomes apparent that the immiscible phases in the material are well dispersed,

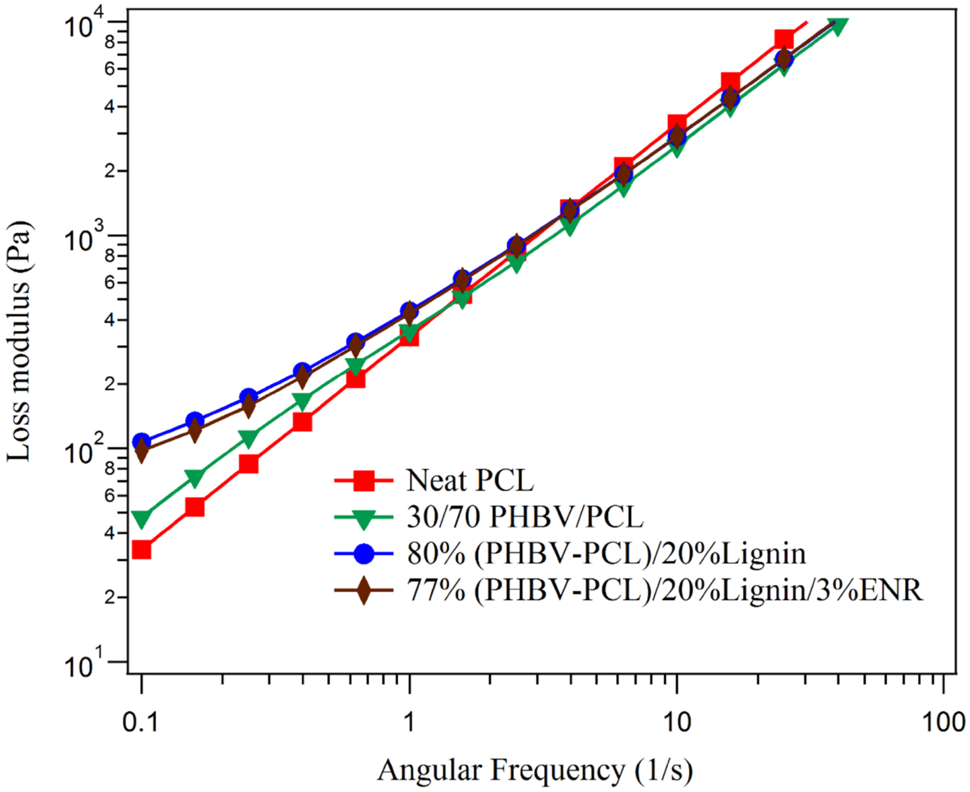


Fig. 8 Loss modulus of blends of PHBV, PCL and Lignin toughened by ENR. **a** Neat PCL, **b** 30/70 PHBV/PCL, **c** 80%(PHBV–PCL)/20% Lignin, **d** 77%(PHBV–PCL)/20% lignin/3% ENR

which causes the PCL chains to exhibit a lower degree of movement. It appears that the addition of lignin to the PHBV/PCL matrix causes both the loss and storage modulus to increase. This suggests that the presence of ENR causes a slight shift away from the solid-like behavior with its addition [40, 41]. This suggests that the addition of ENR improves the flowability of the matrix [32, 44].

Conclusions

In this study, it can be concluded that ENR is an effective tool to provide impact modification in blends of PHBV, PCL, and lignin. An improvement of 40–136% in terms of impact modification was demonstrated with only small quantities of ENR (1–5 wt%). To compensate for this increase in impact strength, there were losses in terms of stiffness-related properties such as tensile and flexural strength. The degree of loss associated with these properties increased with added content of ENR. In addition to providing impact modification, the presence of ENR in the polymer matrix yields some interesting morphological behaviors. Contact between the PCL matrix and the lignin particles that are embedded within improved. In addition, there is less evidence of pull-out in samples containing ENR. The presence of these morphological conditions in toughened blends suggests that this morphology provides improved stress transfer conditions between the phases. It should be noted that PHBV and PCL are still present as separate phases in this system, which demonstrates that these two materials have not been compatibilized by the addition of ENR. FTIR analysis indicates, through the formation of small peaks that correlate with epoxy functionality in the blend spectra, that a reaction has taken place. Similarly, the rheological behavior can be seen to increase in the PCL matrix with the addition of a PHBV phase, and further increased through the presence of a lignin phase. This shear thinning can be correlated with both incompatible polymer phases and processability. This experimentation suggested that ENR did not have a compatibilizing effect on the polymer system; however, it did not cause an increase in the absolute value of viscosity or in any other property associated with poor processability. In bioblends, the increase in impact energy can be associated with morphological changes that favor stress transfer.

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