

Fabrication of biodegradable composite – An Implication of plasticizer

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Abstract

This paper aims on the fabrication of fully biodegradable composite with the addition of plasticizer. For the fabrication of biodegradable composite, a twin screw extruder was used which provides a good blending of matrix, fiber and plasticizer. The percentage is varied from 5% to 40% for fiber and for plasticizer it is 5% to 20%. Higher percentage of plasticizer shows more difficulty during fabrication process of bio-composite. The results also showed that the addition of plasticizer reduces the melting and glass transition temperature of the composite which affects the processing parameter such as, temperature of different zones, rotation of the extruder screw, feed rate and production rate of the extruder. This paper also discussed on the suitable processing parameters for production of plasticized biodegradable composite.

Keywords: Biodegradable, Plasticizer, processing parameters.

Introduction:

On an average in USA every person wastes 1500 pounds of trash per year. Among these waste 20% is plastic polymer. So, sooner or later we will run completely out of space to dispose our trash. Now scientists are very much concern about the environment and try to improve biodegradable polymer. The query for the biodegradable polymer makes us familiar with poly lactic acid (PLA), poly(ϵ -caprolactone) (PCL), poly(*p*-dioxanone) (PPDO), poly(butylenes succinate) (PBS), poly (hydroxyalkanoate) such as poly(β -hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), and natural renewable polymers such as starch, cellulose, chitin, chitosan, lignin, and proteins [1-3]. Previous research was done on PLAs for drug delivery, sutures and orthopaedic implant applications [4–12]. Recently, considerable efforts have been made to extend the application of PLA to the packaging field [13–18].

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PLA represents a good candidate to produce biodegradable packaging because of its good mechanical properties and processability using most conventional techniques and equipment [19, 20]. However, low elongation at break and high modulus have limited its application only to the rigid thermoformed packaging industry while for flexible packaging new grades of PLA with specific end-use performances are required. The most important requirements for packaging materials such as films include a high tensile strength, ductility and flexibility at room temperature, transparency, barrier properties, etc.

Attempts have been made to improve the mechanical properties of PLA by copolymerization with other monomers but none of these copolymerization processes is yet economically viable and none is known to produce copolymers on an industrial scale for packaging applications [21–24]. Blending PLA with other polymers/copolymers has also been investigated and only moderate improvement in mechanical properties was achieved [25–34].

Another way to improve the processability, flexibility and ductility of PLA is the use of plasticizers as for glassy polymers in the plastics industry. The choice of plasticizers to be used as modifiers for PLA is limited by the requirement of the application. Only non toxic substances approved for food contact can be considered as plasticizing agents in food packaging materials. The plasticizer should be compatible with PLA and stable at the elevated temperature used during processing. The PLA/plasticizer blends should be stable over time because the migration of the plasticizer to the surface could be a source of contamination of the food or beverage in contact with the packaging or may possibly regain the initial brittleness of pure PLA.

In the past decade, a large amount of research was devoted to the plasticization of PLA to produce flexible films [35–37]. Candidates included poly(ethylene glycol) (PEG), citrate esters, glyceryl triacetate, glucosemonoesters, (partially) fatty acid esters, Oleic acid, Glycerol, lactide monomer, lactic acid oligomers, etc. have been widely attempted to plasticize PLA [38–48]. Plasticization by lactide monomer has shown a significant increase in the PLA thermal degradation during processing and a rapid migration to the end-product surface [35, 48]. The PEG was found to be a good plasticizer, but phase separation and its migration to the surface over time results in an unstable PLA/PEG blend [44–47]. Blending PLA with 20–25% of citrates resulted in a material with a glass transition temperature (T_g) well below room temperature and produced a higher elongation at break. For these materials the tensile strength was significantly decreased which makes the material unsuitable for the packaging applications where high stress performances are needed [37–40]. On the other hand, the processing conditions usually require an advanced thermal stability of the PLA-plasticizer compositions and in this context improved formulations are sought.

In this present work, attention was paid on PLA because it is one of the most studied polymers, like sugar beets or corn starch by adding plasticized. After producing plasticized, kenaf fiber was added to produce a biodegradable composite.

Experimental

Materials

PLA was obtained from NatureWorks (USA). The characteristics of the sample of PLA are as follows: Grade-3051D, Its melting and glass transition temperature are 145-155⁰C and 55-65⁰C. Its yield strength is 7 kpsi and elongation is 2.5%. Its density is 1.42 g/cc. Kenaf fiber which is locally collected. Glycerol and Oleic Acid is collected from Sigma Aldrich. The properties of these two plasticizers are given in Table 1.

Table 1: Properties of plasticizers

<i>Properties</i>	<i>Glycerol</i>	<i>Oleic Acid</i>
Synonyms	Glycerine	cis-9-Octadecenoic acid
Molecular Formula	C ₃ H ₈ O ₃	C ₁₈ H ₃₄ O ₂
Formula weight	92.09	282.46
Density	1.261	0.89
Melting Point	18 °C (lit.)	13 °C (lit.)
Boiling Point	290 °C (lit.)	360 °C (lit.)
Flash Point	160 °C	189 °C

Besides these Heidolph MR-3001 hotplate and Thermo Hakke Rheomix Twin Screw Extruder was used to make the composite.

Production of Biodegradable composite with plasticizer

Biodegradable composite with addition of plasticizer was produced in two ways. The first way is, the pellets were first dried in a vented oven at 40⁰ overnight prior to processing. Varying amounts of each plasticizer (5, 10 and 20 in wt%) were then mixed together with PLA pellets by using Heidolph MR-3001 hotplate at 85⁰C for 15 minutes. After that this mixture is blended through twin screw extruder at various temperatures. By getting the plasticized PLA we mixed kenaf with that by using the same extruder to produce the composite. In the second way by using the twin screw extruder we made the composite (PLA+Kenaf) first and then the composite was pelletized by using pelletizer. Now the pelletized composite is mixed with plasticizer at 85⁰C in the hotplate for 15 minutes. After finishing the mixing the mixed was again extruded by using twin screw extruder. But during the extrusion process we have lots of variables, like temperature at different zones in the extruder, feed rate, and rotation of the screw. Each of the variables has a significant effect. During the production of the composite we have tried all possible combinations of the variables to get the best result.

Results and Discussions

Effect of Zone Temperatures on Fabrication of Biocomposite

The twin screw extruder has four different zones as shown in Fig. 1. The appropriate temperature was set in each different zone during extrusion. In Fig. 1 the lower numbers (1,2,3,4) indicates the four zones temperature which we can adjust where as the upper numbers (3,5,7) heaters are automatically adjusted and finally D1, D2 are for die which also we can adjust.

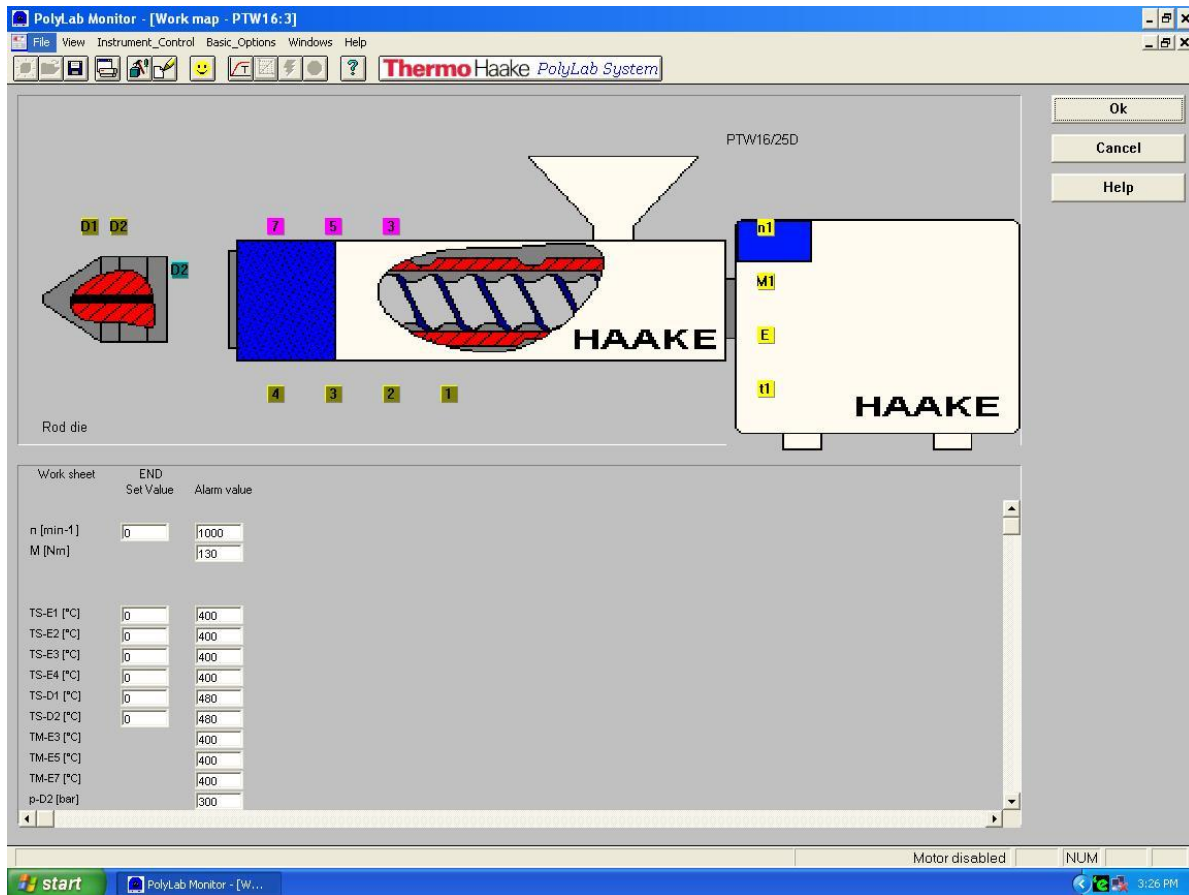


Figure 1: Schematic diagram of a Twin Screw Extruder.

But usually the die temperature remains same to the final zone (Zone-4) temperature. In this experiment first we set the same temperature for all four zones which helps to find the suitable temperature for that composite. After getting that temperature it was assumed that the initial zones (1, 2, 3) have comparatively lower temperature than zone-4. Usually the difference between zone-1 and zone-4 temperature is 10-15⁰C.

In the first experiment initially the temperature was fixed (i.e. 180⁰C) for all zones and the rotation of the screw was 100 rpm and raw materials were plasticized PLA (plasticizer mixed

with PLA first) and kenaf. This temperature is selected because the melting point of PLA is about 170⁰C. But with that temperature the fibers become totally burn as shown in Fig 2.



Figure 2: Biocomposite (PLA+Kenaf+Plasticizer) at 180⁰C which indicates the burning of fiber.

It can be concluded that the temperature is too high for the fabrication of biocomposite due to the addition of plasticizer which in turn decrease the melting point of PLA.

For the fabrication of successful biodegradable composite the next experiments were performed using 170, 160, 150, 140, 130⁰C temperatures by keeping other conditions remain same. At 170,160 and 150⁰C similar composite was obtained as 180⁰C. The Fig. 3 shows the fabricated PLA-plasticizer composites which clearly exhibits the burning of the fibers.

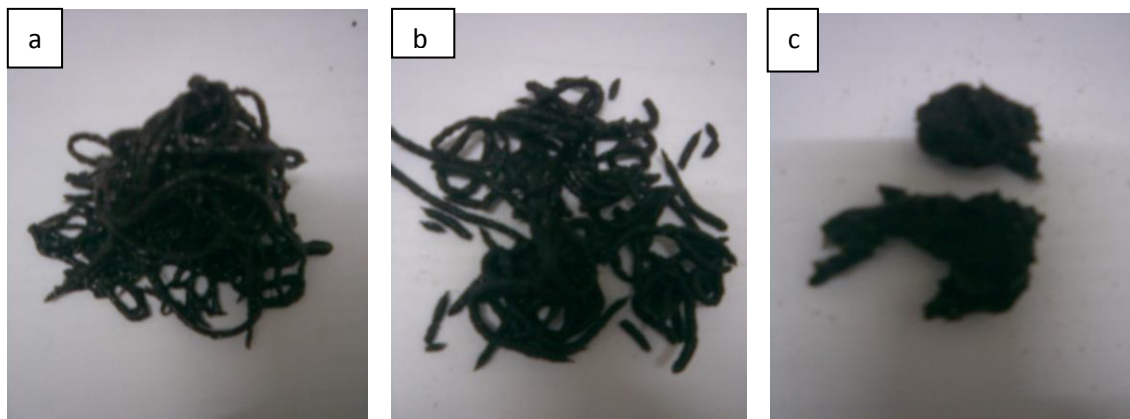


Figure 3: Biocomposite at a) 170⁰C b) 160⁰C c) 150⁰C temperatures.

However, at 140⁰C the fibers are not burn rather adhesion between the fibers and the matrix are found with very poor bonding (Figure 4).



Figure 4: Biocomposite at 140⁰C temperature.

At 130⁰C the fibers and matrix shows very good bonding and the fibers was not burnt which is shown in Figure 5. But the main problem is at 130⁰C the production rate is very slow and the product composite is very hard and brittle. But our desire is to increase the ductility of the composite by adding plasticizer. So this temperature is also not suitable.



Figure 5: Biocomposite at 130⁰C temperature.

Effect of Manual Mixing

The manual mixing concept was used to produce the biocomposite using same Twin Screw Extruder. For manual mixing first some PLA was taken in a beaker and by using hotplate it was melted at 250⁰C. Higher temperature was chosen so that PLA shows less viscosity and better flowness to get a good mixing. When the PLA become melt first plasticizer and then kenaf were added and continuously stirred for better mixing and bonding. However, the final product shows moderate adhesion of fiber with the matrix which is shown in the Fig 6.



Figure 6: Manual mixed Biocomposite.

Effect of Rotational Speed of the Screw

By making the screw speed 150 rpm we tried to produce composite (plasticized PLA and kenaf) at various temperature. However it did not show any desirable result on the biocomposite fabrication. Then we tried to make biodegradable composite (produced kenaf and PLA composite first then add plasticizer) at 150 rpm with various temperature such as 180, 170, 160 and 150⁰C. However, at 140⁰C we get a very good composite which is shown below. From the Figure 7 it can be seen that the fiber of the composite shows very good adhesion with matrix and the fibers resulting the good reinforcement action of the fibers.

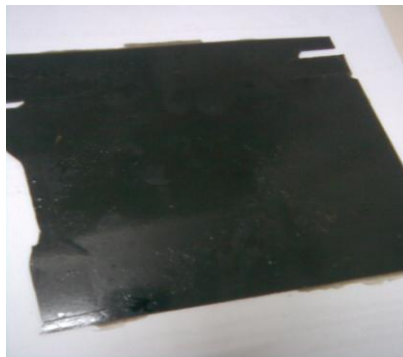


Figure 7: Hot pressed Biocomposite produced by 150 rpm screw speed.

Conclusion

Production of a biodegradable composite with addition of plasticizer is a tedious task. With addition of plasticizer (glycerol and oleic acid) the melting and glass transition temperature is decreased. For this 140⁰C is a suitable temperature for making composite. But we have to make

sure that the dwelling time is not long enough so that the fiber become burnt. At 140⁰C, the plasticized PLA and kenaf biocomposite showed moderate result. Because kenaf has very low density which takes time to pass in the extruder and make the fiber burn. However for the fabrication of optimum combination of composite first kenaf and PLA are blended and then plasticizer is added with higher speed which showed good yielding of the biocomposite fabrication.

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