

Preparation and Characterisation of Multipurpose Adhesives based on Biopolymers Blends

Neetha John¹, B.Srinivasulu², Rameesa³, Mehsana³ and Shilpa Santhosh³

¹Assistant Professor, CIPET IPT-KOCHI, India

²Principal Director & Head, CIPET IPT-KOCHI, India

³Students, SNDPYSS College, Perinthalmanna, Malappuram Kerala, India

Abstract - The objective of polymer blending is a practical one of achieving commercially viable product through either unique properties or lower cost than some other means might provide. The current study proposes the preparation of adhesives based on PLA/starch, PLA/CMC and PLA/Chitosan polymer blends. Various ratios of base polymers were prepared and analyzed. The properties like lap shear strength, resistance to water, acid resistance, base resistance, and heat resistance were studied. The biopolymer blends were also evaluated for FTIR. Surface hydrophobicity of the samples was examined.

Key Words: Biopolymers, adhesives, PLA, lap shear strength etc.)...

1. INTRODUCTION

Adhesives are materials with excellent properties and simple curing mechanisms widely used in different areas. Petroleum-based products create negative environmental impact, biopolymers are the best alternative. Biopolymers, such as cellulose, starch, lignin, or proteins, emerge as good alternatives. There are large amount of improvements and developments are still required to switch over from the synthetic routes to these new bio-based adhesive formulations. This is an environmentally friendly method can lead to the future partial or even total replacement of non-renewable petroleum-based source materials. [1].

Starch is a polysaccharides with linkages of anhydroglucose units. Starch consists of two types of molecules amylose and amylopectin. This conformational makes starch less crystalline than cellulose but also more easily solubilized. Ceseracciu et al biodegradable composites with high robustness and elastic properties based on corn starch and PDMS [2]. It is reported method for preparing a biodegradable elastomer incorporating large amounts of unmodified corn starch about 80% by volume in acetoxypolyorgano siloxane thermosets. All the developed bio-elastomers have hydrophobic surfaces with low friction coefficient and much less water uptake capacity than thermoplastic starch. The bio-elastomers are biocompatible and estimated to biodegrade rapidly even in an aquatic environment, thus it is not making the drawbacks of standard silicones [2]. Lignin is another material studied

which one of the most abundant biopolymers on earth and makes up 15% to 30% of the cell walls of the plants. It is very cheap renewable resource which have large numbers of properties. They are high thermal stability, biodegradability, high carbon content, antioxidant activity and very good stiffness. Lignin is used in various applications by many researchers [3, 4].

Vegetable oils are having reactive sites is also a better options for different applications as it contain ester groups, double bonds, and allylic hydrogens [5-7]. Vegetable oils as a raw material give many advantages. It is readily available with low price, have sustainability, physico-chemical properties and ecological advantages. Rapeseed is an oil seed and widely used for the preparation of biodiesel [8]. Poly lactic acid (PLA) is a biodegradable polymer and a promising material for use in biomedical applications. PLA had the second highest consumption volume of any bioplastic of the world [9].

According to mechanical theory, adhesion occurs by the penetration of adhesives into pores, cavities, and other surface irregularities of the surface of the substrate or adherent [10]. The adhesive displaces the trapped air at the interface. Therefore, it is concluded that an adhesive penetrating into the surface roughness of two adherents can bond the two. A positive contribution to the adhesive bond strength results from the mechanical interlocking of the adhesive and the adherents. [11].

Electrostatic forces in the form of an electrical double layer are thus formed at the adhesive-adherent interface. These forces account for the resistance to separating. This theory gains support from the fact that electrical discharges have been observed when an adhesive is peeled from a substrate are known as electrostatic adhesion [12].

The current work proposes the use of biopolymer based blends for making multipurpose adhesives. Biopolymer blends are to be prepared in various ratios and applied on various adherents like plastics, metal and leather. The lap shear strength of the adhesive joints were to be evaluated and also the retention of the properties under various environment to be studied.

2. Experimental

BPoly(lactic acid) (PLA) pellets (INGEO 3052D) of make Nature works LLC, (Minnetonka MN, USA). Carboxy methyl cellulose (CMC) and solvent chloroform are laboratory grade.

Chitosan (CS) Shrimp source chitosan (CS) was purchased from a local company with a deacetylation percentage (DD) of 88.1%. This chitosan is acid-soluble and white colored flakes. The metal GI sheet was cut in to pieces with length of 12cm and width of 2.5cm and leather pieces are cut into pieces with 12cm length and 2.5cm width and also the plastics sheets.

Dissolved the PLA in chloroform by the continuous shaking, blends were prepared with CMC in different ratios and make it uniform by stirring and kept it in airtight containers. The prepared adhesives were applied on different adherents like metal to metal, leather to leather and plastics to plastics.

The adhesive blends with different ratios are applied in between two metal pieces and jointed. Adhesive joint has an area of 2.5cm x 2.5cm. The joints were kept under load to get strong adhesion between the joints and allowed to dry. These joints were tested for acid resistance (1N HC and lap shear strength of samples are evaluated using universal testing machine (UTM). This procedure is repeated by using base (1N NaOH), cold water and by heating in an oven at 70°C and lap shear strength of these samples are calculated using UTM.

3. Results and Discussion

Figure 1 shows the FTIR of the biopolymer blends PLA/starch, PLA/CMC and PLA/CS

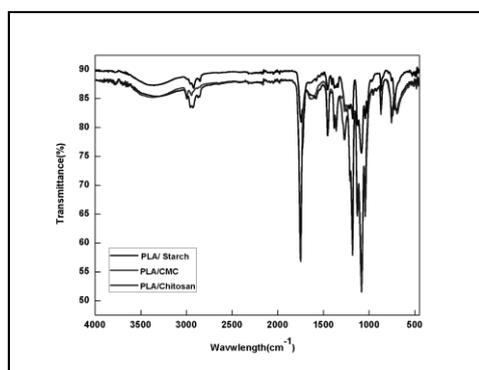


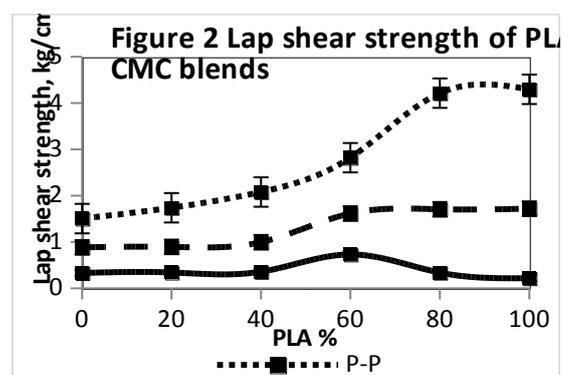
Figure 1 FTIR of biopolymer blends used as adhesives

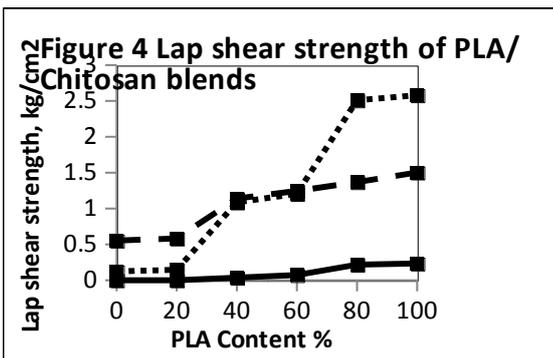
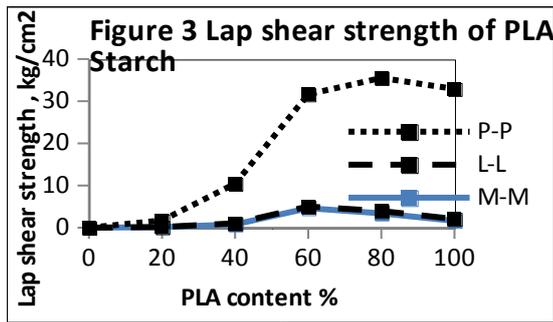
Peaks specific for PLA The peaks located at 2998, 2947 and 1751 cm⁻¹ of PLA were assigned to the stretching vibration of -CH₂ and vibration of -C = O bonds, respectively; while in the blend materials these peaks were found in the neutralized regions of 2995, 2944 and 1749 cm⁻¹.

Peaks specific for Chitosan: The band at 3357-3290 cm⁻¹ could be assigned to ν (N-H), ν (O-H) and ν (NH₂) which present in chitosan in different amounts among which NH₂ groups being the least. The small peak around 2873 cm⁻¹ is ascribed as -CH₂- and -CH₃ groups. However, the amide I band is observed around 1647 cm⁻¹, the peak observed around 1586 cm⁻¹ is attributed to N-H bending of the amide II bands and finally the peak at 1420 cm⁻¹ indicates the C-H bending vibrations of -CH₂.

Peaks specific for starch :The bands in the region between 3300 cm⁻¹ and 3000-2800 cm⁻¹ characterize the stretches of the OH and CH bonds, respectively, then the triple bonds region (2500-2000 cm⁻¹), followed by the region of double bonds (2000-1500 cm⁻¹) and the so-called fingerprint region (1500-600 cm⁻¹). The results show a wide and strong absorption band with transmittance between 3520 and 3217 cm⁻¹ corresponding to the stretches of the OH groups. The amplitude of the band indicates the presence of inter molecular hydrogen bonds. The transmittance between 2920 and 2930 cm⁻¹ correspond to the extension vibrations C-H. At 1643 cm⁻¹ there is a band of flexion of the OH of the water, which indicates that the polymer is hygroscopic. At 1459 and 1350 cm⁻¹ are the C-H bending vibrations and the transmittance band between 1060 and 990 cm⁻¹, is characteristic of the polysaccharides and is attributed to the strain deformations of the C-O-C and flexion of the OH. The results showed a representation of amylose and amylopectin, characteristic molecules of starches. The ratio of the absorbance to 970 cm⁻¹ represents the order of the starches and the band of 1020 cm⁻¹ is related to the amorphous component.

Peaks specific for CMC: The band at 2924 cm⁻¹ is due to C-H stretching of the -CH₂ groups. The band due to ring stretching of glucose appears at 1611 cm⁻¹. The bands in the region 1350-1450 cm⁻¹ are due to symmetrical deformations of CH₂ and COH groups. The bands due to primary alcoholic -CH₂OH stretching mode and CH₂ twisting vibrations appear at 1078 and 1021 cm⁻¹, respectively. The weak bands at around 770 cm⁻¹ are due to ring stretching and ring deformation of α -D-(1-4) and α -D-(1-6) linkages.





Lap shear strength test. Figure 2, Figure 3 & Figure 4 shows the results for the lap shear strength of adhesive joints prepared by PLA /CMC, PLA / Chitosan and PLA/starch blends respectively. It is shown for the three types of adherents plastics to plastics joints, leather to leather and metal to metal. The results show that there is an increase trend initially and reaches a maximum and shows a decrease in lap shear strength. This may be due to the lack of surface polarity and less chance of mechanical or physical bonding on metal substrates. The results are promising so that the adhesives can be easily adopted which does not make any toxins or non-degradable components which can be harmful to the environments.

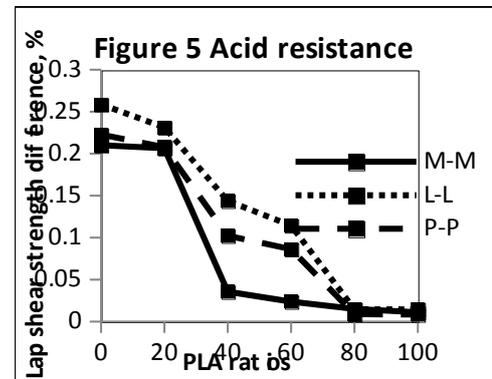
Starch based adhesive shows highest strength and makes the overall the adhesive bond quite mechanically robust. The naturally adsorbed moisture on the starch surface enables higher polar bonds, starch granules have also excellent compatibility with the addition chemistry.

The forces required for separating the samples increased with increasing % of PLA and thus lap shear strength also.

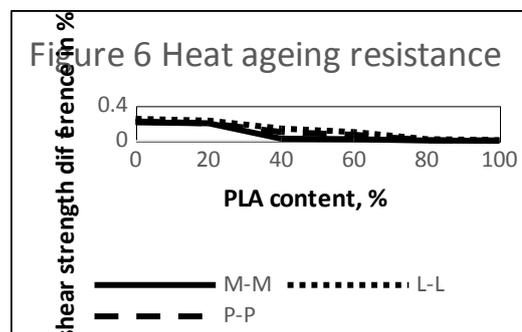
(Acid resistance for the all types of blends were tested and found identical, therefore only PLA /starch blend results are shown in this report which is having the highest lap shear strength).

Acid resistance of the lap joints are shown in figure 5. There is a decrease in lap shear strength as shown which is almost same for all types substrates. When the adhesives are of starch based the loss in strength is maximum as it does not have acid resistance, as PLA is added to the

adhesives the reduction in joint strength decreases and reaches to very lower values.



In M-M samples the ratio with low % of PLA (4:6) and also in P-P and M-M samples with starch only (0:10) were separated. Figure 5 shows the lap shear strength differences happening to the joints when subjected to acid attack. As in the case of weight loss, when starch is higher the strength is lower and retention also lower. When the blend is prepared with PLA the strength increases and retention also. The presence of acid decreases the adhesive strength and then the lap shear strength is decreased when compared with standard values.



When heat is applied lap (Figure 6) shear strength of these samples were decreased when compared with the standard values. This shows that the adhesive strength decreased on exposure of heat. The weight loss due to heating may be the change in weight of the volatile matter which gets evaporated and which could result in lowering of lap joint strength.

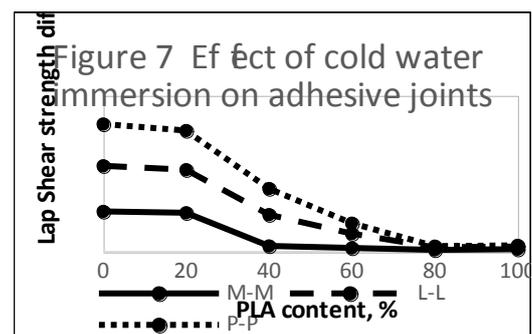


Figure 7: PLA /starch comparison of lapshear strength of samples with cold condition. The cold water condition decreases the strength of adhesives. In M-M the adhesive blends with low % of PLA were separated. The solubility of the components is water may be the reason for loss of weight, which is decreasing as the amount of PLA increases.

4. Conclusions

Biopolymer based adhesives were prepared based on PLA /CMC, PLA/ Starch and PLA / chitosan and tried on three different adhesives joints. PLA/starch blends are found to be superior among the adhesives. The blend with ratio of 6:4 and 8:2 are found to be stronger adhesives, because they have high lapshear strength value compared with other ratios. That is force required to separate the samples is more means adhesive is stronger. The blends with low % of PLA found to be less strong or some samples found as separated. The effect of acid, base, heat and cold condition affect the adhesive strength of these adhesive blends. Their lapshear strength is less when compared with the value of standard samples. Some of these adhesive blends can withstand the conditions of high temperature, acidity, basicity and cold conditions up to a limit. The PLA makes the adhesive blends stronger. So, when the % of PLA increased that blends become stronger.

REFERENCES

- [1] Solange Magalhães, Luís Alves, Bruno Medronho, Ana C. Fonseca, Anabela Romano, Jorge F.J. Coelho and Magnus Norgren, Brief Overview on Bio-Based Adhesives and Sealants Polymers 2019, 11, 1685.
- [2] Ceseracciu, L.; Heredia-Guerrero, J.A.; Dante, S.; Athanassiou, A.; Bayer, I.S. Robust and Biodegradable Elastomers Based on Corn Starch and Polydimethylsiloxane (PDMS). *Acs Appl. Mater. Interfaces* 2015, 7, 3742–3753.
- [3] Pizzi, A.; Mittal, K.L. (Eds.) *Wood Adhesives*; CRC Press: Boca Raton, FL, USA, 2011; pp. 1–451.
- [4] Norgren, M.; Edlund, H. Lignin: Recent advances and emerging applications. *Curr. Opin. Colloid Interface Sci.* 2014, 19, 409–416
- [5] De Haro, J.C.; Allegretti, C.; Smit, A.T.; Turri, S.; D'Arrigo, P.; Griffini, G. Bio-based polyurethane coatings with high biomass content: Tailored properties by lignin selection. *ACS Sustain. Chem. Eng.* 2019.
- [6] Szubert, K. Synthesis of organofunctional silane from rapeseed oil and its application as a coating material. *Cellulose* 2018, 25, 6269–6278. *Polymers* 2019, 11, 1685 20 of 20
- [7] Mohd Salleh, K.; Hashim, R.; Sulaiman, O.; Hiziroglu, S.; Wan Nadhari, W.N.A.; Abd Karim, N.; Jumhuri, N.; Zuin Ping Ang, L. Evaluation of properties of starch-based adhesives and particleboard manufactured from them. *J. Adhes. Sci. Technol.* 2015, 29.
- [8] Britz, W.; Hertel, T.W. Impacts of EU biofuels directives on global markets and EU environmental quality: An integrated PE, global CGE analysis. *Agric. Ecosyst. Environ.* 2011, 142, 102–109
- [9] Martin, O; Avérous, L (2001). "Poly (lactic acid): plasticization and properties of biodegradable multiphase systems". *Polymer.* 42 (14): 6209–6219.
- [10] William Andrew (2009), "Adhesive technology hand book (second edition) -classification of adhesives and compounds (chapter 4), published by Elsevier.inc.
- [11] Ebnesajjad .C.F (n.d)- 2006 "Surface treatment of materials for adhesion bonding assisted by, William andrew.inc
- [12] Sina Ebnesajjad (2011) "Handbook of adhesives and surface preparation" assisted by Elsevier.inc.