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Research article

Aluminium/iron reinforced polyfurfuryl alcohol resin as advanced biocomposites

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Abstract: Aluminium and iron are widely used in construction sectors for the preparation of advanced composites with epoxy resins as matrices. In recent times, there are several reports on the polymerization of polyfufuryl alcohol (PFA) a thermoset bioresins from furfuryl alcohol (FA). FA is obtained from waste of sugarcane bagasse. In this work, first the possibility of curing PFA from FA in the presence of aluminium or iron has been explored. Absorbance results from colorimeter/spectrophotometerindicated that the curing of FA to PFA in presence of aluminium started easily while in presence of iron the curing of FA to PFA could not start. Based on the above results, aluminium wire reinforced composites were successfully prepared with three different weight fractions (0.13, 0.09 and 0.07) of aluminium wire. The mechanical properties of these composites were determined theoretically and reported.

Keywords: polyfurfuryl alcohol; aluminium; curing; composites

1. Introduction

Among thermoset resins, epoxies and phenolics are matrix materials commonly used in the development of advanced composite materials. There is development of large volume of materials based on epoxies and phenolics. Epoxy resins currently dominate the market due to their superior thermal, mechanical and electrical properties, dimensional stability and chemical resistance [1].

Biobased thermoset polymers are attracting increased attention due to environmental concerns and therealization that global petroleum resources are finite.In the last 15–20 years, the research and development of composite materials from polyfurfuryl alcohol (PFA) polymers derived from renewable resources have gained momentum [2–7]. Kumar et al. has reported in their patents the ways to cure PFA in controlled manner by subjecting acid catalysedfurfuryl alcohol (FA) at 50 °C for 96 h followed by 2nd step curing of 1 h at 100 °C and 30 min at 150 °C [8,9]. There are several reports which showed the fabrication of cured PFA that can be used as bioplastics or biocomposites [10,11,12]. We have reported earlier the FTIR spectra (vibrational spectroscopy) of cured (after 3 days of curing) and uncured PFA [10]. In FTIR spectra, we could observe the change in the peak after curing. Sometimes, it is difficult to notice the small change in FTIR spectra due to overlapping of the bands. So in this paper, we have used the techniques where clear increase or decrease in absorbance is observed.

Aluminium and iron are widely used in construction sectors. Both the materials have very high mechanical strength. Aluminium is characterised with high corrosion resistance, excellent machining properties, high thermal and electrical properties, and wear resistance [13]. Iron based materials have low corrosion resistance but are widely used in construction sectors. A study of the adsorption of an epoxy acrylate resin on aluminium alloys relevant to aerospace industry has been undertaken by Grilli et al. [14]. There are several reports which showed good interactions of aluminium with epoxy resin attributed to hydrogen bonding of alcoholic group of epoxy [15,16]. Similarly, iron/steel reinforced epoxy composite has also been fabricated [17,18,19]. However, there are not a single report where fabrication of iron or aluminium reinforced PFA composites have been discussed.

From a conceptual point of view, the reinforcement of PFA with aluminium or iron seems very realistic for the development of advanced composites with low environmental impact. In the on-going research work, we have tried to answer the question whether a composite material can be developed from PFA resin with aluminium or iron as reinforcement materials. Further, we have tried to analyse colorometry/spectrophotometrically the interactions of iron and aluminium with acid catalysed FA resin during curing process so as to have an idea how aluminium or iron form composites with PFA. Spectroscopic method or colorometric method is a simple way to observe the change in colour and report the change of colour in terms of absorbance. Since there is change in colour for FA in presence of metal during curing and its absorbance fall in the visible range so we have found the absorbance from colorimetry/spectrophotometry to study the curing of PFA from FA.

2. Materials and Method

2.1. Materials

Furfuryl alcohol (FA) and p-toulenesulphonic acid (PTSA) monohydrate were purchased from Sigma-Aldrich, and were used as received. The density of FA as mentioned in the manufacturer's data sheet is 1.135 gm/mL. Aluminium in form of wire and sheet and iron in form of mesh were purchased from local market. Circular silicon based mold of 10 cm diameter was used for molding the products. The area of the silicon mold was 78.5 cm^2.

2.2. Methods

A solution of PTSA monohydrate (0.3 phr with respect to the resin) prepared in 5 ml water was added drop-wise to FA at room temperature in order to catalyse the FA.

Five test tubes were taken. In the first test tube, 10 ml of FA was taken. PTSA was added drop-wise to FA in the second test tube designated as AcFA. About 1 g of iron mesh, aluminium sheet and aluminium wire were put in 3rd, 4th and 5th test tube containing acid catalysed FA designated as

AcFA-IrW, AcFA-AlS and AcFA-AlW, respectively. The absorbance of all the liquids present in the five test tubes was determined immediately. After that the test tubes were kept in freeze (12–14 ^{o}C) so that slow curing of acid catalysed FA in presence and absence of iron and aluminium metal takes place.

2.3. Curing of Acid Catalysed FA in Presence of Aluminium and Iron

Three different weight fractions of aluminium wire (0.13, 0.09 and 0.07) were arranged manually by hand in the circular silicon based mold. In the first, second and third cases the spacing between two wires were maintained as 1 cm, 1.5 cm and 2 cm, respectively. About 56.75 gm of acid catalysed FA was poured in the silicon mold containing three different weight fraction of aluminium wire. Aluminium sheet of 0.09 weight fraction was also placed in the circular silicon based mold and about 56.75 gm of acid catalysed FA was poured in the silicon mold. The material was cured as per the process described in world patent filed by us [9]. However, keeping all the conditions same curing of FA could not take place in presence of iron.

3. Results and Discussion

3.1. Visual Inspection of Curing

Figure 1 shows the colour of all the liquids present in the five test tubes after 5 days. By visual inspection, it looks that colour of FA in presence of aluminium wire is similar to that of acid catalysed FA.

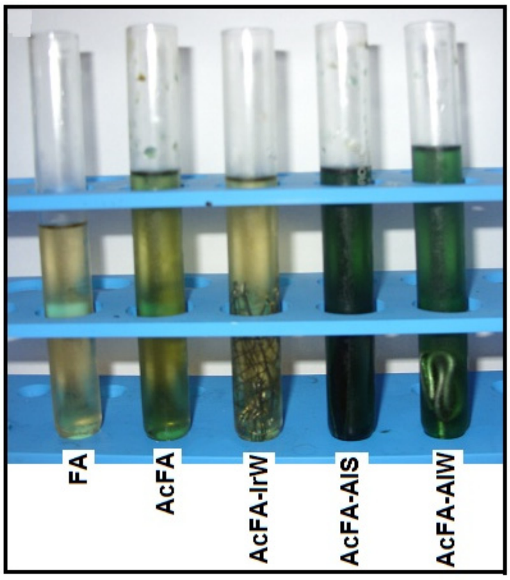

Figure 1. Colour of furfuryl alcohol (FA) and acid catalysed furfuryl alcohol (AcFA) in presence and absence of aluminium and iron metal after 5 days. In this Figure, AcFA-IrW, AcFA-AlS and AcFA-AlW represent presence of iron mesh, aluminium sheet and aluminium wire, respectively in acid catalysed furfuryl alcohol.

On the other hand, the colour of FA in presence of iron wire is similar to that of neat FA. This indicates that slow curing of FA has started in presence of aluminium metal but in presence of iron metal it has not started.

3.2. Effect of Metal on the Curing Characteristics PFA with Respect to Absorbance at Different Intervals of Days

(a) Furfuryl alcohol (FA)—Three prominent peaks at 457 nm, 519 nm and 588 nm are observed in FA (Figure 2). The absorbance at 457 nm and 588nm are 0.56 and 0.49, respectively. The absorbance at 519 nm is quite low (0.15), so we will not discuss this wavelength to monitor the cure process. As expected, there is no increase in absorbance because of absence of acid catalyst which is necessary to initiate curing process in FA.

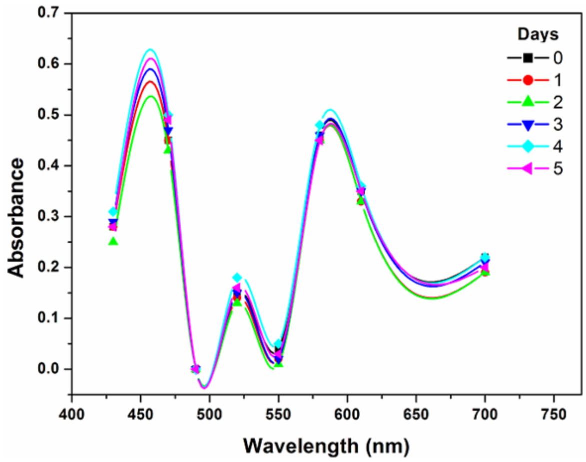

Figure 2. Absorbance of furfuryl alcohol from 0 to 5 days.

(b) Acid catalysed furfuryl alcohol (AcFA)—Figure 3 shows the absorbance of AcFA at different days. On 1st day, the absorbance at 457 nm and 588 nm are 0.50 and 0.49, respectively. Till 2nd day absorbance increases slightly but after that increase is prominent.

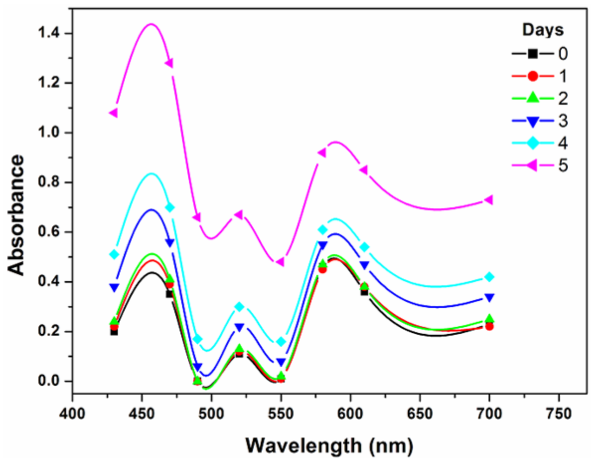

Figure 3. Absorbance of acid catalysed furfuryl alcohol from 0 to 5 days.

The absorbance at 457 nm increases to 0.83 and 1.44 for 4th and 5th day, respectively. Similarly, the absorbance at 588 nm increases to 0.65 and 0.96 for 4th and 5th day, respectively. The increase in absorbance indicates that curing process in FA has started due to presence of an acid catalyst.

(c) AcFA-AlS and AcFA-AlW—First we will discuss about the absorbance of aluminium wire in AcFA. Figure 4a shows the absorbance of AcFA in presence of aluminium wire on different days. On 1st day, the absorbance at 457 nm and 588 nm are 0.62 and 0.58, respectively. Absorbance increases significantly from 2nd day.The absorbance at 457 nm increases to 1.2 and 1.78 for 4th and 5th day, respectively. Similarly, the absorbance at 588 nm increases to 1.13 and 1.67 for 4th and 5th day, respectively. Figure 4b shows the absorbance of AcFA in presence of aluminium sheet on different days. On 1st day, the absorbance at 457 nm and 588 nm are 0.54 and 0.56, respectively. Absorbance increases significantly from 2nd day. The absorbance at 457 nm increases to 1.51 and 2.01 for 4th and 5th day, respectively. Similarly, the absorbance at 588 nm increases to 1.44 and 1.83 for 4th and 5th day, respectively. In the presence of aluminium metal, the absorbance increases considerably and there is also a shift in wavelength towards longer wavelength termed as Bathochromic shift. This indicates that curing process increases in the presence of aluminium.

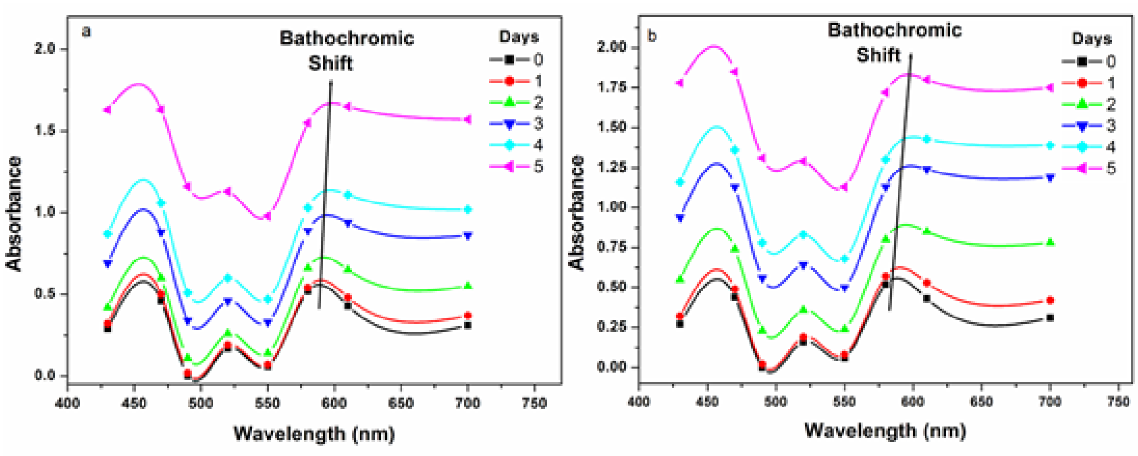

Figure 4. Absorbance of acid catalysed furfuryl alcohol in presence of aluminium wire (a) and aluminium sheet (b) from 0 to 5 days.

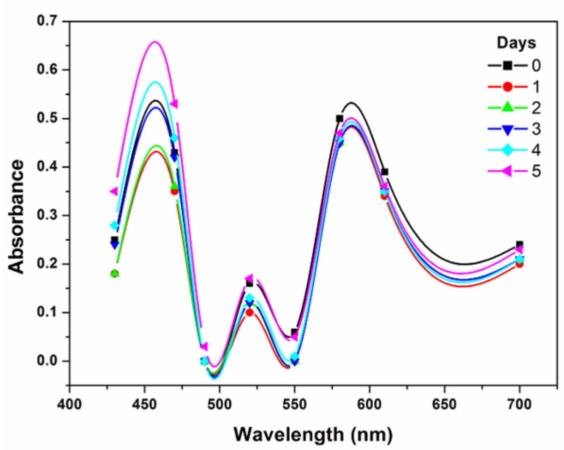

Figure 5. Absorbance of acid catalysed furfuryl alcohol in presence of iron from 0 to 5 days.

(d) AcFA-IrW—Figure 5 shows the absorbance of AcFA in presence of iron wire at different days. On 1st day, the absorbance at 457 nm and 588 nm are 0.43 and 0.48, respectively. Absorbance shows negligible increase till 3rd day. The absorbance at 457 nm increases to 0.57 and 0.65 for 4th and 5th day, respectively. Similarly, the absorbance at 588 nm increases to 0.49 and 0.50 for 4th and 5th day, respectively. In the presence of iron metal, the absorbance increases like FA and hence it looks that the presence of iron prevents the curing process.

3.3. Effect of Aluminium Wire and Aluminium Sheets on the Fabrication of PFA based Sheets

Figure 6 shows the fabricated PFA based sheets (thickness 0.5 cm) in presence of aluminium wire and aluminium sheets. The fabricated sheet is black in colour and the aluminium wire can easily be observed in the composites.

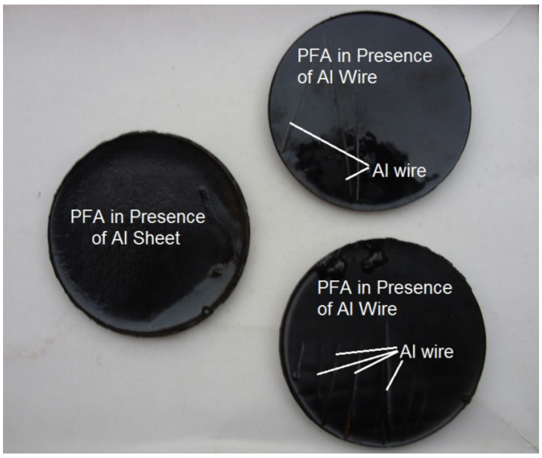

Figure 6. Polyfurfuryl alcohol based bioplastics in presence of aluminium metal.

3.4. Theoretical Calculation of Tensile Strength of Aluminium Wire Reinforced PFA Composites

Based on the literature review, the ultimate tensile strength of aluminium wire has been reported around 90 MPa [20]. We have observed that the tensile strength of neat PFA based sheet is around 20 MPa [8,9,11]. In this study, we have taken three volume fractions of aluminium wire (Section 2.3) to prepare the composites. Theoretical tensile strength is calculated by the following formula considering the fact that the ultimate tensile strain of the PFA is lower than that of the aluminium wire. Theoretically the composite will fail when its longitudinal strain reaches the ultimate strain of the PFA. The longitudinal tensile strength of the composite is calculated with relation

$$f_{Lt} = f_{ft}V_f + \sigma_m(1 - V_f) \quad (1)$$

Here f_{Lt} = Theoretical longitudinal tensile strength of composites, f_{ft} = Theoretical longitudinal tensile strength of aluminium, V_f = Volume fraction of aluminium, $\sigma_m(1 - V_f)$ = Theoretical tensile strength of PFA, $(1 - V_f)$ = Volume fraction of PFA.

The longitudinal tensile strength of the aluminium wire reinforced composites as calculated theoretically is 29.1 MPa, 26.3 MPa and 24.9 MPa for 0.13, 0.09 and 0.07 volume fraction of aluminium wire, respectively.

In this paper, our focus was to show that in presence of aluminium curing of FA to PFA takes place while in presence of iron it does not take place. With aluminium wire, we were facing difficulty in getting good composites because of aluminium wire getting distributed non-uniformly in the mold. Hence, for finding tensile properties experimentally, we will have to use aluminium mat so that there will be equal distribution of aluminium wire in the composites and that will form separate work. That was the reason we could not report the experimental tensile strength.

3.5. Mechanism of Interaction between FA/PFA with Aluminium or Iron

In this study, we have used acid catalysed FA for the fabrication of aluminium or iron reinforced PFA advanced composites. To our surprise, we found that curing of FA to PFA in presence of iron could not take place and acid catalysed FA was in liquid state even though we have subjected FA in presence of iron wire to same curing conditions reported elsewhere [8–12]. On the other hand, curing of FA to PFA in presence of aluminium was clearly evident. We think that in case of iron, first iron reacts with moisture present in acid catalysed FA to form iron hydroxide which in turn undergoes hydrogen bonding with –OH group of FA. Due to this process, there is non-availability of free –OH groups of FA and hence the curing reaction of FA in presence of iron could not take place. It is also possible that iron may start undergoing corrosion in presence of moisture. On the other hand, Al in presence of moisture forms protective oxide film on its surface. Due to this –OH groups of FA are easily available for curing reactions. Also to be noted that aluminium does not undergo corrosion.

4. Conclusion

There is increase in absorbance with increase in no. of days for AcFA in presence of aluminium metal either in form of wire or sheet. The increase in absorbance for AcFA-AlS or AcFA-AlW is higher than that for AcFA. This shows that the presence of aluminium metal will increase the curing process. On the other hand, the absorbance for AcFA-IrW is similar to FA. Since FA does not contain acid curing catalyst so we can state that the presence of iron metal prevents the curing process of AcFA. In this paper, we have tried to correlate what we got from visual inspection (section 3.1) and what values we got from colorimetry/spectrophotometry (Section 3.2). PFA based sheets in presence of aluminium metals can be fabricated successfully. Further work is needed to characterise the advanced composites experimentally with respect to mechanical properties and also to study the extent of interaction between metal and polymers.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

References

1. Njjuguma J, Pielichowski K, Alcock JR (2007) Epoxy-based fibre reinforced nanocomposites. *Adv Eng Mater* 9: 835–847.
2. Klemm D, Heublein B, Fink HP, et al. (2005) Cellulose: fascinating biopolymer and sustainable raw material. *Ang Chem Int Ed* 44: 3358–3393.

3. Gandini A (2011) The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem* 13: 1061–1083.
4. Gandini A, Belgacem MN (1997) Furans in polymer chemistry. *Prog Polym Sci* 22: 1203–1379.
5. Gandini A (2008) Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules* 41: 9491–9504.
6. Wang H, Yao J (2006) Use of Poly(furfuryl alcohol) in the fabrication of nanostructured carbons and nanocomposites. *Ind Eng Chem Res* 45: 6393–6404.
7. Guigo N, Mija A, Vincent L, et al. (2010) Eco-friendly composite resins based on renewable biomass resources: Polyfurfuryl alcohol/lignin thermosets. *Eur Polym J* 46: 1016–1023.
8. Kumar R, Anandjiwala RD (2011) Polyfurfuryl alcohol products. *South Africa Patent Application* ZA2011/01976.
9. Kumar R, Anandjiwala RD (2012) Process for preparing polyfurfuryl alcohol products. *WIPO Patent Application* WO/2012/123902.
10. Kumar R, Kumar R, Anandjiwala RD (2012) Biofilms from polyfurfuryl alcohol adsorbed on soy protein isolate. *Plast Rubber Compos Macro Eng* 41: 1–7.
11. Kumar R, Anandjiwala RD (2013) Compression moulded flax fabric reinforced polyfurfuryl alcohol bio-composites: Mechanical and thermal properties. *J Therm Anal Calor* 112: 755–760.
12. Liganiso LZ, Kumar R, Anandjiwala RD (2014) Effect of agave americana microfiber content on poly(furfuryl) alcohol (PFA) based composites. *J Biobased Mater Bioe* 8: 299–307.
13. Bello SA, Agunsoye JO, Hassan SB, et, al. (2015) Epoxy resin based composites, mechanical and tribological properties: A review. *Tribol Ind* 37: 500–524.
14. Grilli R, Abel ML, Baker MA, et al. (2011) The adsorption of an epoxy acrylate resin on aluminium alloy conversion coatings. *Int J Adhes Adhes* 31: 687–694.
15. Kim HJ, Jung DH, Jung IH, et al. (2012) Enhancement of mechanical properties of aluminium/epoxy composites with silane functionalization of aluminium powder. *Compos Part B Eng* 43: 1743–1748.
16. Semoto T, Tsuji Y, Yoshizawa K (2011) Molecular understanding of the adhesive force between a metal oxide surface and an epoxy resin. *J Phys Chem C* 115: 11701–11708.
17. Segun MA, Modupe AO (2012) Tensile properties of iron ore tailings filled epoxy composites. *W Indian J Eng* 35: 51–59.
18. Makoto N (1994) Mechanism of adhesion of epoxy resin to steel surface. *Nippon steel technical report No 63.*
19. Drazic DM, Miskovic-Stankovic VB (1990) The effect of resin concentration and electrodeposition bath temperature on the corrosion behaviour of polymer coated steel. *Pro Org Coat* 18: 253–264.
20. Available from: http://www.azom.com/article.aspx?ArticleID=2863.