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Research Article

SYNTHESIS AND CHARACTERIZATION OF UREA–FORMALDEHYDE ECO-FRIENDLY COMPOSITE BASED ON NATURAL FIBERS

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ABSTRACT

Present work explains the synthesis of urea–formaldehyde composites with Allo (*Girardinia diversifolia*) and cotton (*Gossypium arboreum*) fibers. Urea–formaldehyde resin was synthesized by condensation polymerization of urea and formaldehyde monomers. Cellulose fibers were extracted by various chemical treatments of natural fibers. Composites were prepared with neat and extracted cellulose from Allo and cotton fibers by solution casting method. Fibers and composites were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), optical microscopy (OM), thermo-gravimetric analysis (TGA) and micro-indentation tests. Results showed that composite with treated Allo fibers had better morphological, mechanical and thermal properties than untreated Allo and cotton fibers.

Keywords: Reinforcement, Natural fiber composites, Urea–formaldehyde resin, Morphology, Thermal properties

INTRODUCTION

Natural fibers are emerging and superior alternatives compared to glass and other inorganic fiber-based fillers for reinforcement in polymer composites from economic and ecological points of view. Environmental awareness has aroused massive interest in the research and the development of biodegradable and high-performance materials (Adhikari *et al.* 2012, Mohanty *et al.* 2002). Natural fiber (NF) composites are claimed to offer environmental advantages such as reduced dependence on non-renewable energy/material sources, lower pollutant emissions, lower greenhouse gas emissions, enhanced energy recovery and biodegradability of components (Christjanson *et al.* 2006). Cellulose extracted from natural fibers can be used to reinforce thermoplastics and thermosetting polymer matrixes (Satyanarayana *et al*. 2009).

Over the past decades many researches has been carried out using thermosets, thermoplastics and biodegradable plastics as matrixes and natural fibers as reinforcements for preparation of composites. The major thermosets include phenol formaldehyde, resorcinol formaldehyde, epoxy and urea–formaldehyde resins (Lee *et al.* 2014). The uses of thermosets as matrix in preparation of composites with natural fibers have been proven to enhance the thermal and mechanical properties (Li *et al.* 2007). Urea–formaldehyde (UF) resins are the class of thermosetting resin which is polymeric condensation product of chemical reaction between urea and formaldehyde. Wood-based industries are major consumers of UF resins (Lu *et al*. 2008, Aziz & Ansell 2004). Even though, many investigators have studied the chemical structure of UF resin prepared by different techniques, the work on *in situ* polycondensation for preparation of UF is very limited.

The aim of this research is to prepare crystalline and transparent UF resin by *in situ* polycondensation and use it in preparation of composites with cellulose extracted from Allo fibers by solution casting method. The composites were analyzed by FTIR, OM, SEM and TGA techniques. The morphological and mechanical properties were studied using compressive and micro-indentation tests (Chattopadhyay *et al.* 2010, Fan *et al.* 2012, Oza *et al.* 2011). The combination of Allo fibers and urea–formaldehyde resin has shown to improve thermal and mechanical properties; thus, it would provide some potential applications in designing tougher and thermally stable materials mainly suitable for house insulation as well as to make electric and electronic devices.

MATERIALS AND METHODS

Sodium hydroxide (NaOH), formic acid (HCOOH), hydrogen peroxide (H_2O_2), urea ($H_2N–CO–NH_2$), formaldehyde (HCHO), sulfuric acid (H_2SO_4), paraffin oil, distilled water were collected from commercial chemical suppliers. All the chemicals were of laboratory grade and used without further purification. Natural fibers such as Allo fibers and cotton fibers were collected from local suppliers.

Formaldehyde was heated in a beaker at 60° C for 10 minutes and 1 gram of urea was added at the interval of 1 minute on continuous stirring making the final U/F ratio 1:3. The viscous mass obtained on addition of concentrated H_2SO_4 was poured on mold and subjected to cure in hot air oven (Park *et al.* 2003).

Finely powdered and oven-dried Allo (*Girardinia diversifolia*) fibers were dipped in 4 % (weight/volume) aqueous sodium hydroxide solution keeping the fiber-to-solution ratio 1:15 (weight/volume) and warmed at 60° C for 4 hours. The solution was neutralized by 10 % (volume/volume) aqueous formic acid solution and washed several times with distilled water (Salam 2006, Abdul Khalil *et al*. 2015).

Clean and dried fibers were treated with 2 % (mass/volume) of hydrogen peroxide (H_2O_2) at 90° C for 2 hours with fiber-to-liquor ratio of 1:7 (weight/volume). The fibers were then neutralized with 10 % (volume/volume) formic acid, washed several times with distilled water and oven dried at 80° C for 24 hours (Zhong *et al*. 2007).

Composites were prepared using solution casting method. Firstly, fiber was chopped into size of about 0.5 mm and oven dried at 80° C for 8 hours. The composites of different compositions *viz*, 0 % 5 %, 15 %, 30 % and 45 % (by weight) of fiber were prepared. Three different composite samples were prepared with UF resin using neat and bleached Allo (*Girardinia diversifolia*) fiber as well as alkali-treated cotton fiber with similar UF/fiber ratio using similar procedure mentioned above. After this, final test samples were prepared prior to characterization.

The composite samples were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), optical microscopy (OM), thermogravimetric analysis (TGA) and micro-indentation tests. FTIR spectra of solid samples were obtained in transmittance mode using IRTracer-100 (SHIMADZU) at Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur, Nepal. SEM analysis was carried out at Fraunhofer Institute for Microstructure of Materials and Systems (IWMS), Halle (Saale), Germany using JSM6300 scanning electron microscope (JEOL). Thermal characterization of sample were carried out using thermogravimetric analysis (TGA) at Leibniz Institute for Polymer Research, Dresden, Germany and microindentation test was carried out at Polymer Service GmbH Merseburg, Germany, using Fischerscope H100C microindenter(FISCHER) with Vickers diamond indenter and maximum applied load of 1000 mN.

RESULTS AND DISCUSSION

Structural and morphological characterization

Figure 1a shows an optical image of urea–formaldehyde resin which is transparent and brittle in nature. FTIR spectrum of UF matrix (Fig. 1b) showed characteristic peak at 3290 cm^{-1} (N–H stretching peak of primary amines), 2926 cm^{-1} and 2854 cm^{-1} (C–H stretching of UF), 1656 cm^{-1} (C=O stretching vibration), 771 cm^{-1} (N–H bending of secondary aliphatic amines). The absorption band at 1381cm^{-1} and 1028 cm^{-1} is due to N–C–N and C–N stretching of methylene linkage (NCH_2N) of amides in resin (Christjanson *et al.* 2006, Park *et al.* 2003).

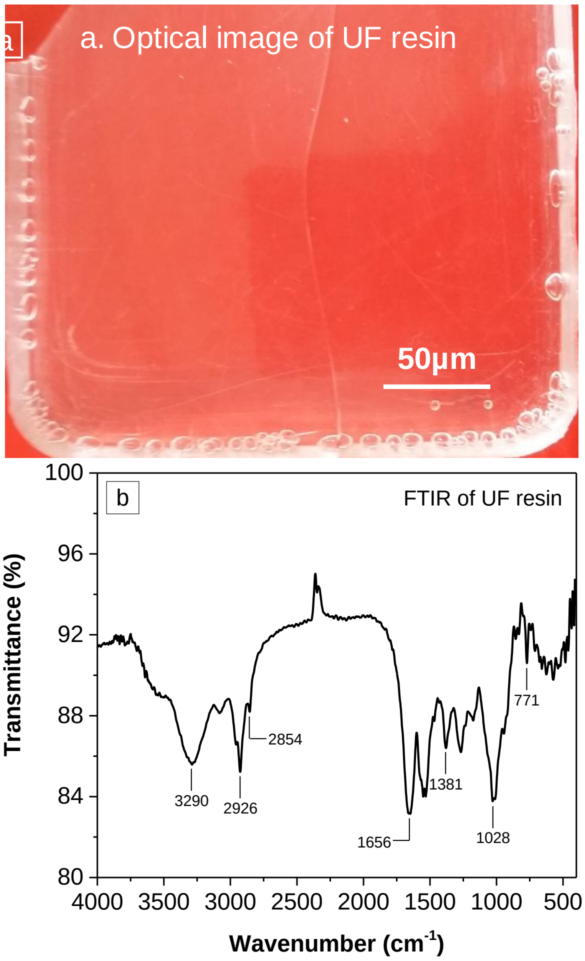

Fig. 1. (a) Optical image and (b) FTIR spectrum of urea–formaldehyde resin prepared at laboratory by *in situ* polymerization

Fibers were characterized before and after the chemical treatments. Figure 2 is the FTIR spectrum of neat Allo fibers compared with cotton fibers. Components of natural fibers are the cellulose, hemicellulose and lignin. Their characteristic peaks were observed in the respective spectra. The broad band at 3400 cm^{-1} and 2920 cm^{-1} are the O–H stretching and C–H stretching peaks of methyl and methylene of cellulose, respectively. Strong absorption band about 1050 cm^{-1} is the characteristics of cellulose (Fan *et al.* 2012, Suryanto *et al.* 2014, Hospodarova *et al.* 2018). Further, untreated Allo fiber showed characteristic lignin peak at 1240 cm^{-1} which were rudimentary in cotton fibers.

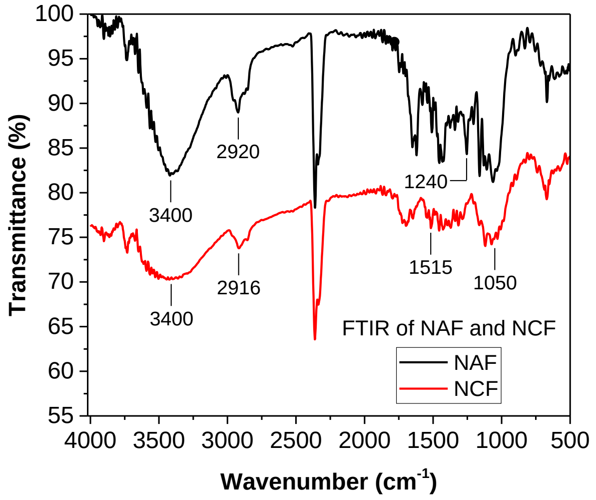

Fig. 2. FTIR spectra of neat (untreated) Allo fibers (NAF) compared with neat cotton fibers (NCF)

The comparable band intensities and peak positions in FTIR spectra of Allo and cotton fibers suggest the similar chemical composition and significantly high cellulose content in both of the fibers. The influence of chemical treatments (i.e. alkali treatment or mercerization and bleaching) was demonstrated by analyzing the FTIR spectra and SEM micrographs of fibers. Figures 3(a) and 3(b) are the SEM images of neat and alkali-treated Allo fibers. In neat Allo fibers, cellulose microfibers were compactly held and regularly aligned to each other in the form of bundles. The occurrence of compact bundles attributed to presence of hemicellulose and lignin as binder between the fibers. Alkali-treated fibers showed separate micro fibrils with smoother surface than untreated Allo fibers indicating sufficient delignification of fibers after alkali treatment (Sgriccia *et al.* 2008, Aziz & Ansell 2004). These observations were further supported by comparative study of the FTIR spectra of untreated and alkali-treated fibers.

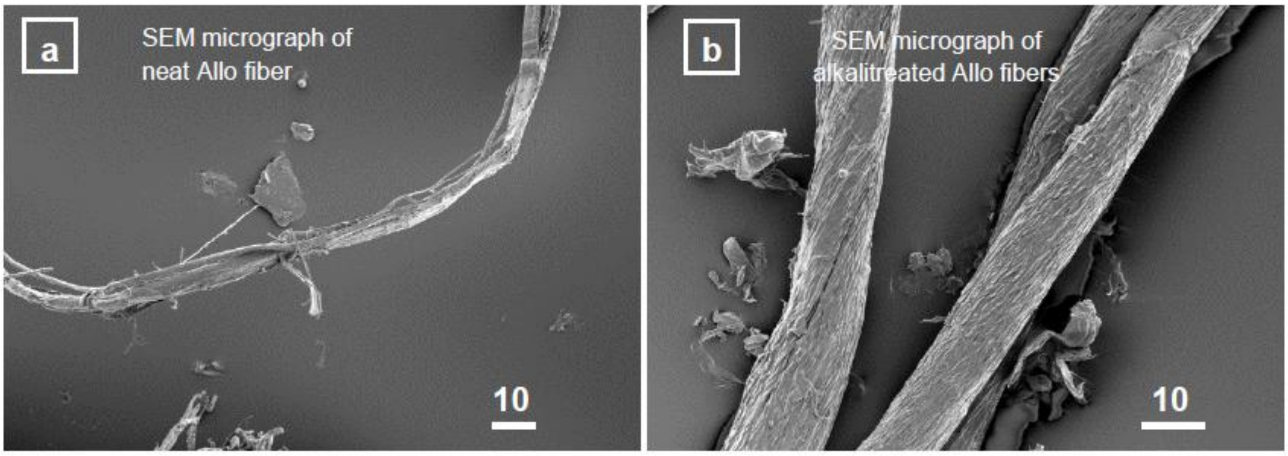

Fig. 3. SEM micrographs of (a) neat Allo fibers and (b) alkali-treated Allo fibers

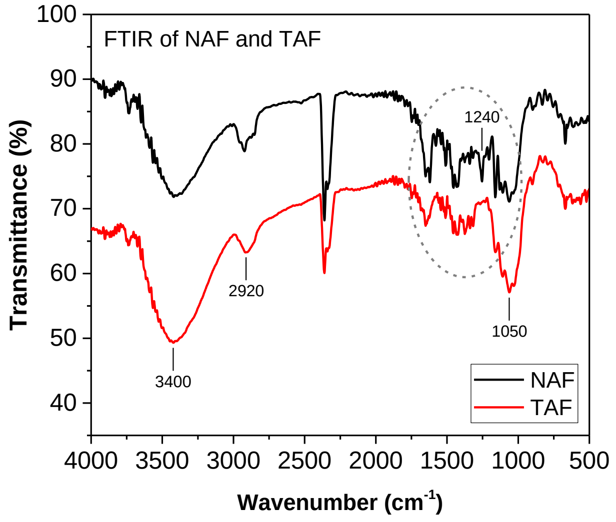

Fig. 4. FTIR spectra of neat Allo fibers (NAF) and treated Allo fibers (TAF)

Figure 4 shows FTIR spectra of treated Allo fibers (TAF) compared to neat Allo fibers (NAF). It is evident from the figure that there was significant change in morphology and chemical composition of the fibers after chemical treatments.

Major differences in pure and treated (delignified) Allo fibers were observed in the finger print region (1400–700 cm^{-1}). A group of complex IR absorbance of lignin in the finger print region might be due to the stretching of methoxy O–CH_3, ether C–O–C and C=C stretching of aromatic ring containing compounds. Small peaks at 1240 cm^{-1} for C–O–H and at 1050 cm^{-1} for C–O–C stretching vibrations of pyranose ring skeleton were the characteristic peaks of cellulose fibers. Peak at 820 cm^{-1} for C–H aromatic hydrogen and at 700–400 cm^{-1} for C–C stretching vibrations were the characteristics of hemicellulose, which were almost rudimentary in treated Allo fibers. The C=O peak at around 1750–1400 cm^{-1} was relatively broader and distinct in hemicellulose than in the cellulose, was rudimentary in treated fibers, indicating sufficient delignification after alkali treatment and bleaching. The peak at 1520 cm^{-1} was due to C=C stretching of the aromatic ring of lignin, the intensity of which decreased after chemical treatment (Chattopadhyay *et al.* 2010, Fan *et al.* 2012, Oza *et al.* 2011).

FTIR spectra of UF showed significant difference in absorption peaks than that of UF–NAF composites (Fig. 5). The absorption peaks corresponding to both UF and fibers observed in FTIR spectra of UF–NAF composite suggest the uniform distribution of fiber in the matrix in composite system. The absorption bands in composite at 3280 cm^{-1} was due to O–H stretching vibration. The shifting at 2926 cm^{-1} to 2960 cm^{-1} for C-H stretching peak suggests that $-CH_2$ group of the cellulose played significant role in fiber and fiber-matrix interfaces. Similar small peak shifts in FTIR spectra between 1000 cm^{-1} to 1750 cm^{-1} represents the weak chemical interaction in filler and matrix (Chiang *et al.* 2015, Zhong *et al.* 2007, Zorba *et al.* 2008).

Figures 6 (a) and 6 (b) represent SEM micrograph of UF composites with NAF and BAF of 70/30 composition by weight percent. Although the fibers are homogeneously distributed in the UF matrix, the appearance of dark voids and gaps around the fiber–matrix interface implies their incompatibility with polymer matrix.

The absence of voids and gaps at the fiber–matrix interface even with out the use of compatibilizer suggests the better compatibilty of bleached Allo fiber with UF matrix (Chattopadhyay *et al.* 2010, Bhandari *et al.* 2012).

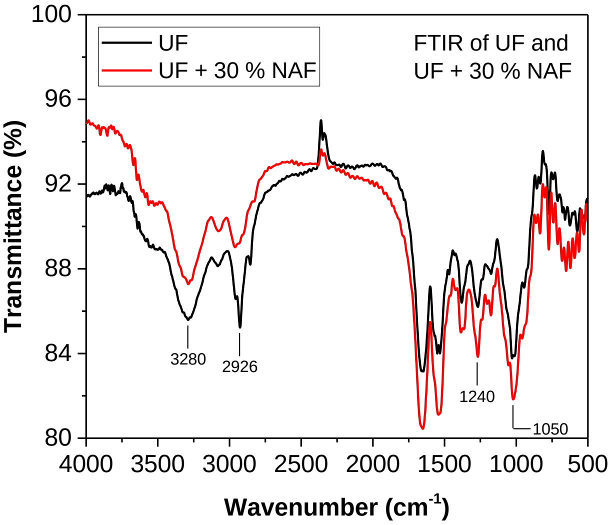

Fig. 5. Comparison of FTIR spectra of pure UF and UF–NAF composite of 70/30 composition

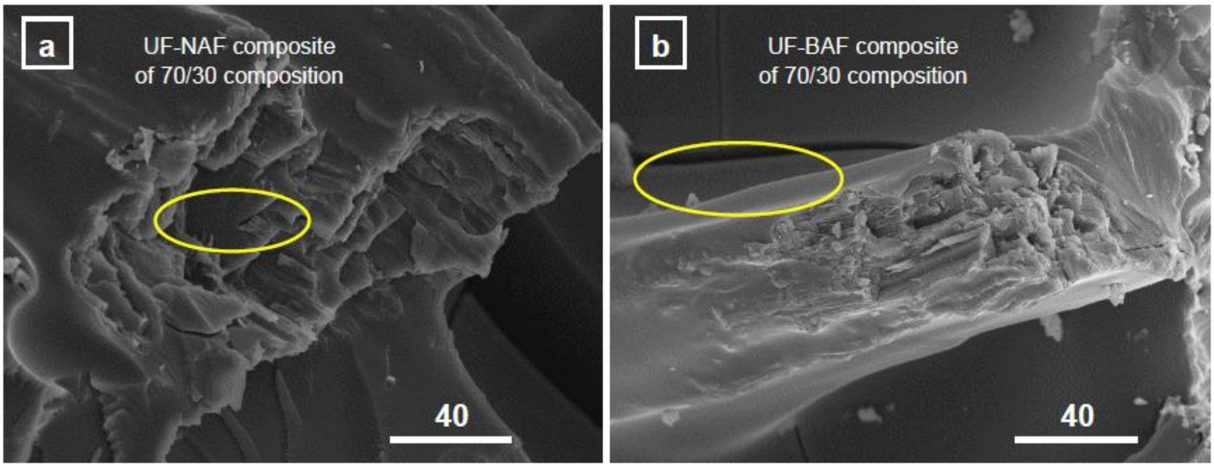

Fig. 6. SEM micrographs of (a) UF–NAF and (b)UF–BAF composites of 70/30 composition

Thermal Characterization

A thermal stability of the matrix, filler and composites was characterized using thermo-gravimetric (TGA) analysis. TGA thermogram of pure UF resin (Fig. 7) showed three distinct regions of UF pyrolysis. Small mass loss between 150- 200° C is attributed to slow release of free formaldehyde from UF and that between 220- 250° C is attributed to degradation of methylene ether bridges in the resins network. The major pyrolysis process of pure UF takes place between 270- 350° C, maximum being at 292° C. The last stage that occurs above 350° C is the further pyrolysis process of a thermally stable residues formed in the former stage with slight weight loss leading to about 15 % of final residual mass.

Similarly, Fig. 8 represents the derivative of TGA curve (the DTG curves) of untreated Allo and treated Allo fibers compared with pure cotton fibers. The curve shows that the thermal degradation of natural fibers is a two-step process, i. e., below 100° C was due to release of volatiles and moisture present in the fibers and other in between 250- 450° C was due to decomposition of lignin, hemicellulose and cellulose of the fibers. In specific, the weight loss between 250- 300° C was due to thermal decomposition of hemicelluloses and break of glycoside linkage in cellulose molecules. The maximum mass loss appeared between 350- 400° C. The low-temperature degradation process was associated with degradation of hemicellulose whereas the high-temperature process was due to lignin (Fan *et al.* 2012, Suryanto *et al.* 2014). Lignin being amorphous in nature has no sharp degradation temperature but degrades gradually from 230° C to 800° C (Chattopadhyay *et al.* 2010, Lette *et al.* 2018). It showed that treated Allo fibers were found to be stabilized by 15° C than raw Allo fibers and about 25° C than cotton fibers.

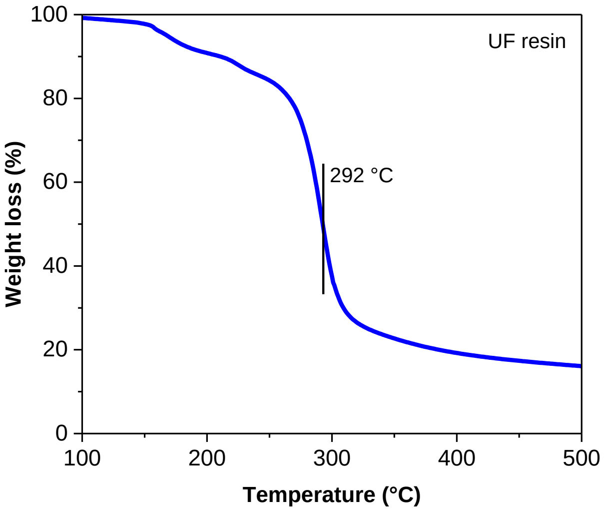

Fig. 7. TGA curve of pure UF matrix

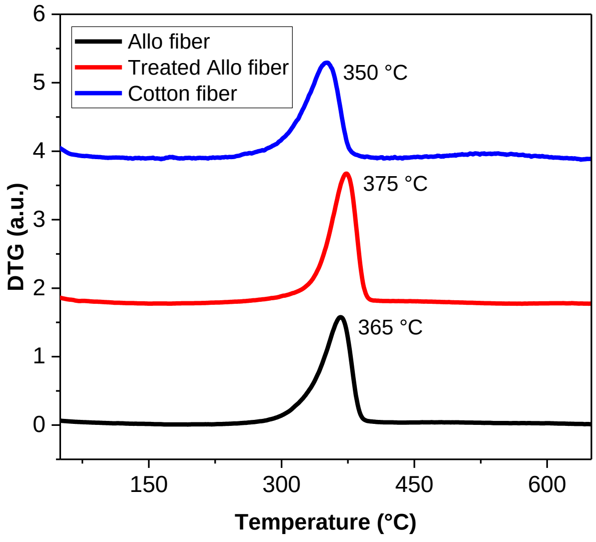

Fig. 8. DTG analysis of Allo and cotton fibers (the curves are vertically shifted for better visibility)

Figure 9 shows TGA curves of urea–formaldehyde composites with 30 wt% fiber loading of untreated Allo fibers (AF), treated Allo fibers (TAF) and cotton fibers (CF). These curves show that the thermal degradation of pure UF and neat Allo composite (UF–AF) is almost similar in which maximum pyrolysis occurs at 292° C and 291° C, respectively. The maximum pyrolysis in treated Allo fiber composite (UF–TAF) composite took place at 302° C and that of cotton fiber composite took place at 284° C. This shows that both neat and bleached Allo fiber composites to be thermally more stable than UF–CF composites with similar fiber loading. Compatibility of fibers with matrix is also an important factor that contributes to better thermal stability of the composites (Chiang *et al.* 2015). A higher thermal stability of UF–TAF composites can be attributed to a better compatibility with UF matrix.

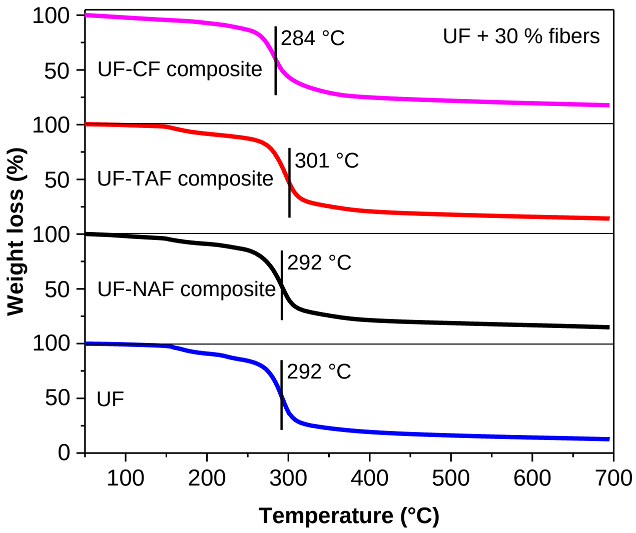

Fig. 9. TGA curves of UF, UF–NAF, UF–TAF and UF–CF composites of 70/30 composition

Micromechanical Characterization

Mechanical property of composites were evaluated by micro indentation hardness testing. The force (F)–indentation depth (h) curves of UF–NAF composites with 0, 5, 15, and 45 % of fibers are given in Fig. 10a. From figure 10a, it is evident that the curves progressively shifted towards left side with increasing fiber loading leading to an increase in the slope of initial part of unloading cycle suggesting an increase in hardness of UF–NAF composites up to filler content of 45 %.

Similarly, figure 10b shows variation of Martens hardness and maximum indentation depth of UF–NAF composites of different fiber loadings. There was drastic increase in Martens hardness almost by two folds compared to pure UF for composite with 45 % fiber loading. These results were further supported by decrease in indentation depth on increasing hardness thus proving fiber reinforcement acted as stress transforming medium (Lee *et al.* 2007, Shalwan & Yousif 2013, Van Landingham *et al.* 2001).

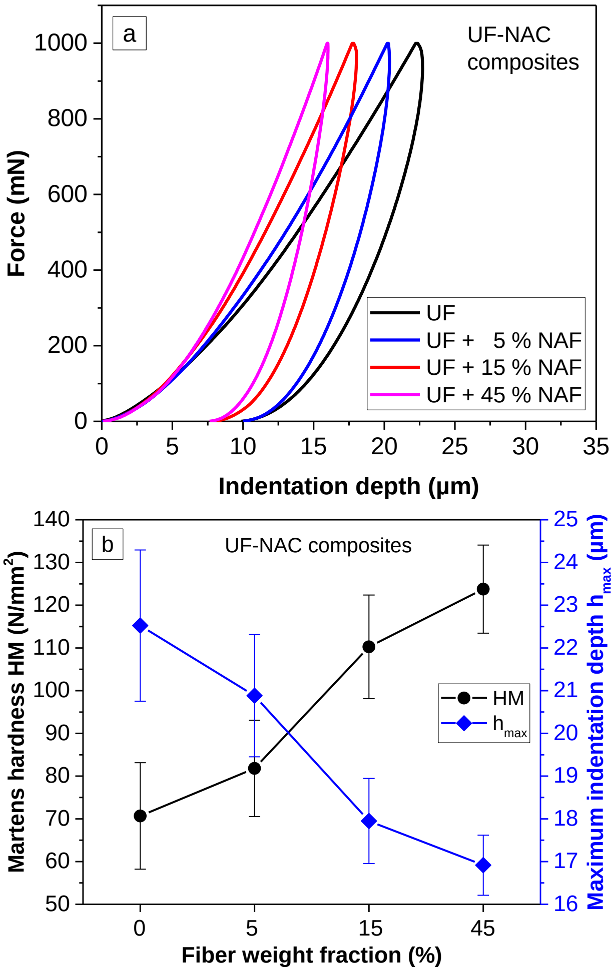

Fig. 10. (a) Force (F)–Indentation depth (h) diagram and (b) variation of Martens hardness (HM), maximum indentation depth (h_{max}) of UF–NAF composites of different composition

CONCLUSION

Urea–formaldehyde (UF) composites of different fiber loading were prepared with neat and bleached Allo fibers using solution casting method, characterized with FTIR, SEM, TGA and micro-hardness measurements and the results were compared with cotton fiber composites. The composites with treated Allo fibers were found to be more compatible with UF matrix prepared even without the use of compatibilizers and compared to neat Allo fiber composites. The composites with treated Allo fibers were found to be thermally 25° C more stable than the cotton fiber-loaded composites and about 15 °C than that of the neat Allo fiber-loaded composites. Further, micro-hardness of treated fiber composites is higher than that of neat fiber composites. Morphologically treated fibers were found to be more compatible than neat fiber composites which might be because of large number of cellulose microfibers exposed towards the surface in treated fibres and hence the UF resin finds more area for interaction with fibers. Thus, treated fibers were found to be better than neat fibers with polar matrix to prepare composites.

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REFERENCES

Abdul Khalil, H.P.S., Davoudpour, Y., Sri Aprilia, N.A., Mustapha, A., Hossain, M.S., Islam, M.N. and Dungani, R. 2015. Nanocellulose based polymer nanocomposite: Isolation characterization and applications. In: *Nanocellulose Polymer Nano-composites: Fundamentals and Applications*. Vijay Kumar Thakur (Ed.), Wiley, Chapter 11, pp. 273-310.

Adhikari, R., Bhandari, N.L., Le, H.H., Henning, S. and Radusch, H.-J. 2012. Thermal, mechanical and morphological behavior of poly(propylene)/wood flour composites. *Macromolecular Symposia* **315**: 24-29.

Aziz, S.H. and Ansell, M.P. 2004. The effect of alkalization and fiber alignment on the mechanical and thermal properties of kneaf and hemp fiber composites: Part 1–polyester resin matrix. *Composite Science and Technology* **64**: 1219-1230.

Bhandari, N.L., Thomas, S., Das C.K. and Adhikari, R. 2012. Role of compatibilizer on morphological and mechanical properties of low cost polypropylene/wood flour composites. *Journal of Nepal Chemical Society* **29**: 113-120.

Chattopadhyay, S.K., Khandal, R.K., Uppaluri, R. and Ghosal, A.K. 2010. Bamboo fiber reinforced polypropylene composites and their mechanical, thermal and morphological properties. *Journal of Applied Polymer Science* **119**: 1619-1626.

Chiang, T.C., Hamdan, S. and Osman, M.S. 2015. Urea formaldehyde composites reinforced with sago fibers; Analysis by FTIR, TGA and DSC. *Advances in Material Science and Engineering* **2016**: Article ID 5954636, 10 pages.

Christjanson, P., Pehk, T. and Siimer, K. 2006. Structure formation in urea formaldehyde resin synthesis. *Proceedings of the Estonian Academy of Sciences. Chemistry* **55**: 212-225.

Fan, M., Dai, D. and Huang, B. 2012. Fourier transform infrared spectroscopy for natural fibres.*Fourier*

Transform – Materials Analysis, Salih Salih (Ed.), Chapter 3, p. 45-68, IntechOpen.

Hospodarova, V., Singovszka, E. and Stevulova, N. 2018. Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials. *American Journal of Analytical Chemistry* **9**: 303-310.

Lee, K.Y., Aitomäki, Y., Berglund, L.A., Oksman, K. and Bismarck, A. 2014. On the use of nanocellulose as reinforcement in polymer matrix composite. *Composite Science and Technology* **105**: 15-27.

Lee, S.H., Wang, S., Pharr, G.M. and Xu, H. 2007. Evaluation of interphase properties in a cellulose fiber-reinforced polypropylene composite by nano-indentation and finite element analysis. *Composites Part A: Applied Science and Manufacturing* **38**: 1517-1524.

Lette, M.J., Ly, E.B., Ndiaye D., Takasaki, A. and Okabe, T. 2018. Evaluation of sawdust and rice husks as fillers for phenolic resin based wood-polymer composites. *Open Journal of Composite Materials* **8**: 124-137.

Li, X., Tabil, L.G. and Panigrahi, S. 2007. Chemical treatments of fiber for use in natural fiber-reinforced composites: A review. *Journal of Polymer and the Environment* **15**: 25-33.

Lu, J., Wang, T. and Drzal, L.T. 2008. Preparation and properties of microfibrillated cellulose polyvinyl alcohol composite materials composites. *Composites Part A: Applied Science and Manufacturing* **39**: 738-746.

Mohanty, A.K., Mishra, M. and Drzal, L.T. 2002. Sustainable bio-composites from renewable resources: opportunities and challenges in green materials world. *Journal of Polymers and the Environment* **10**: 19-26.

Oza, S., Wang R. and Lu, N. 2011. Thermal and mechanical properties of recycled high density polyethylene/hemp fiber composites. *International Journal of Applied Science and Technology* **1**: 31-36.

Park, B.D., Kim, Y.S., Singh, A.P. and Lim, K.P. 2003. Reactivity, chemical structure and molecular mobility of urea–formaldehyde adhesives synthesized under different conditions using FTIR and solid-state ^{13}C CP/MAS NMR spectroscopy. *Journal of Applied Polymer Science* **88**: 2677-2687.

Salam, M.A. 2006. Effect of hydrogen peroxide bleaching onto sulfonated jute fiber. *Journal of Applied Polymer Science* **99**: 3603-3607.

Satyanarayana, K.G., Arizaga, G.C. and Wypych, F. 2009. Biodegradable composites based onlignocellulosic fibers– An overview. *Progress in Polymer Science* **34**: 982-1021.

Sgriccia, N., Hawley, M.C. and Mishra, M. 2008. Characterization of natural fiber surfaces and natural fiber composites. *Composites Part A: Applied Science and Manufacturing* **39**: 1632-1637.

Shalwan, A. and Yousif, B.F. 2013. In state of art: Mechanical and tribological behavior of polymeric composite based on natural fibers. *Material and Design* **48**: 14-24.

Suryanto, H., Marsyahyo, E., Irawan, Y.S. and Soenoko, R. 2014. Morphology, structure and mechanical properties of natural cellulose fiber from mendong grass *(Fimbristylis globulosa). Journal of Natural Fibers* **11**: 333-351.

VanLandingham, M.R., Villarrubia, J.S., Guthrie, W.F. and Meyers, G.F. 2001. Nano-indentation of polymers: an overview. *Macromolecular Symposia* **167**(1): 15-44.

Zhong, J.B., Lv, J. and Wei, C. 2007. Mechanical properties of sisal fiber reinforced urea-formaldehyde resin composite. *Express Polymer Letters* **1**: 681-687.

Zorba, T., Papadopoulou, E., Hatjiissaak, A., Paraskevopoulos K.M. and Chrissafis, K. 2008. Urea-formaldehyde resins characterized by thermal analysis and FTIR method. *Journal of Thermal Analysis and Calorimetry* **92**: 29-33.