

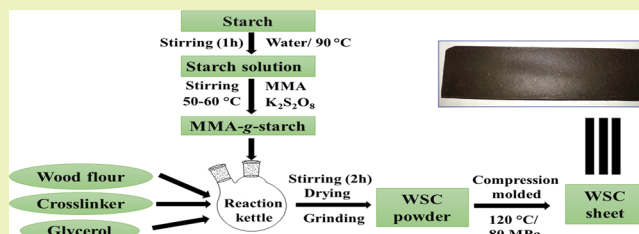
# Studies on Effects of Different Cross-Linkers on the Properties of Starch-Based Wood Composites

Prasanta Baishya and Tarun K. Maji\*

Department of Chemical Sciences, Tezpur University, Assam, 784028, India

**ABSTRACT:** A green route is demonstrated to prepare biobased composites from renewable resources like starch and soft wood with engineering aspects. In this process, three different cross-linkers such as glutaraldehyde (GA), dimethyloldihydroxyethyleneurea (DMDHEU), and *N*-methylol acrylamide (NMA) have been used to cross-link methyl methacrylate-grafted starch with wood flour. Water is used as a solvent and glycerol as a plasticizer in the preparation of wood starch composites. Effects of these cross-linkers on different properties of the composites have been investigated through a limiting oxygen index test and mechanical, dynamic mechanical, and thermogravimetric analysis. DMDHEU cross-linked composites show the least water uptake capacity compared to NMA- and GA-based cross-linked composites due to their better cross-linked structure as DMDHEU contains a higher number of functional groups. The interaction among polymer, cross-linker, and wood has been found to be the maximum in DMDHEU cross-linked composites as revealed by FTIR and SEM studies. DMDHEU cross-linked composites also exhibit higher mechanical and thermal properties.

**KEYWORDS:** Water-soluble polymers, Soft wood, Grafting, Dynamic mechanical analysis, Thermal properties, Mechanical properties, Hardness



## INTRODUCTION

Numerous studies are underway on the preparation and application of wood polymer composites due to their superior features such as ease of processing, productivity, and cost reduction.<sup>1</sup> They have various applications in different fields such as the automotive, construction, marine, electronic, and aerospace industries.<sup>2</sup> However, one of the major drawbacks of such composites is their low biodegradability resulting from the use of petroleum-based solvents and polymers during their preparation causing environmental pollution. Therefore, the concept of natural polymer-based composites have emerged that are not only biodegradable but can also be processed by using environmental friendly solvents. Water-soluble/dispersed polymers such as starch, gluten, soya flour, etc. can be used as the polymer matrix for preparing such composites. Recently, the use of starch polymers has gained much interest due to several advantages over petroleum-based polymer composites. The benefits of using starch polymers are their easy availability, low cost, and biodegradability. The main advantage for preparing starch composites is that water can be used as the solvent, which reduces the hazardous impact of organic solvents and follows the principles of green chemistry. However, modification of the starch is necessary to get better results because of its poor physical properties such as high hydrophilicity, high recrystallization behavior, and low decomposition temperature.<sup>3</sup> The brittleness of starch can be decreased by the use of plasticizers.<sup>4,5</sup> Chang et al. have prepared glycerol-plasticized wheat starch/cellulose nanoparticle composites using cellulose nanoparticles as filler by a casting process.<sup>6</sup>

The dimensional stability and mechanical properties of starch composites are reported to be poor due to the hydrophilic nature of starch.<sup>7</sup> The hydrophilicity of starch can be decreased by grafting with hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile, etc.<sup>8,9</sup> Ge et al. have reported that grafting of methyl acrylate onto starch has improved the stiffness, tensile strength, and thermal stability of the starch composites significantly.<sup>10</sup> The biodegradability of starch may remain almost unchanged if it is grafted with a limited percentage of synthetic monomers. Further, the interaction between wood and modified starch can be enhanced by the use of cross-linkers.<sup>11,12</sup>

Varieties of cross-linkers are reported to be used for enhancement of properties of the composites. Duanmu et al. has used ethylene glycol dimethacrylate to cross-link allylglycidal ether-modified starch with softwood fibers.<sup>13–17</sup> Among the water-soluble cross-linkers, the use of DMDHEU, GA, and NMA have been cited in the literature for improvement of various properties of wood polymer composites.<sup>18–20</sup> Compared to the untreated composites, water uptake and dimensional swelling of the GA- and DMDHEU-treated wood composites were decreased, whereas flexural and tensile properties were improved.<sup>19</sup> Improvements in water resistance, thermal resistance, and mechanical properties of wood starch composites are required in order

Received: November 26, 2013

Revised: May 16, 2014

Published: May 20, 2014

to use it in outdoor applications. Various reports regarding the water absorption of wood polymer composites are available in the literature.<sup>21,22</sup>

The cross-linking reaction of DMDHEU is favored in acidic condition. The use of conventional catalysts in the cross-linking reaction may degrade or hydrolyze the hemicellulose and lignin of wood, which reduces the tensile strength of the composites. The use of different acids or metal salts like  $MgCl_2$ ,  $ZnCl_2$ , ammonium sulfate, and sodium or potassium bisulfate as catalysts is reported.<sup>23,24</sup> The use of potassium persulfate as initiator makes the system acidic and thus may favor the cross-linking reaction.

Most of the literatures pertaining to wood polymer composites have reported the use of at least one water-insoluble component in the composites.<sup>13–20</sup> There are a few reports of using modified starch and water-soluble initiators for the preparation of wood starch composites. To the best of our knowledge, there is neither any detailed investigation nor any comparison among different cross-linkers used for improving the properties of wood starch composites. It is envisaged that a thorough study may provide some important basis for the development of wood starch biodegradable composites. With all these ends in view, this work has been undertaken.

Wood is a cellular polymeric material widely available in nature. Kalmou (*Ipomoea carnea*), a type of soft wood, is found in abundance and does not have any structural applications due to its poor mechanical properties. These are mainly used for fuel purposes or remain as biowastes. These materials can be made value-added by using them as reinforcing agents for preparing composites with polymers.

In this study, an eco-friendly approach has been adopted for preparing wood starch composites (WSC) by using water as a solvent. In this process, soft wood from Kalmou (*Ipomoea carnea*) has been used as a cheap reinforcing agent. Methyl methacrylate (MMA) has been grafted onto starch using potassium persulfate ( $K_2S_2O_8$ ) as initiator. Modified starch and glycerol have been used as the polymer matrix and plasticizer. The effects of different cross-linkers on various properties of WSC have been studied and compared by employing three cross-linking agents: DMDHEU, NMA, and GA.

## MATERIALS AND METHODS

**Materials.** Starch (soluble, extra pure), glutaraldehyde, methyl methacrylate (MMA), and glycerol were obtained from Merck India, Ltd., Mumbai. The cross-linker DMDHEU and NMA were synthesized as discussed below. Glyoxal, urea, formaldehyde, and acrylamide were supplied by Merck India Ltd., Mumbai. The wood sample Kalmou (*I. carnea*) was collected from the local forest of Assam.

**Preparation of Wood Samples.** The collected nonconventional woods were chopped into small strips and washed with 1% soap solution followed by washing with 1% NaOH solution. Finally, the wood samples were washed with distilled water. After that, they were oven-dried at  $105 \pm 5$  °C and grinded. The grinded samples were sieved through a 70 mesh-sized sieve and kept ready for subsequent experiments.

**Synthesis of DMDHEU.** DMDHEU was synthesized by using the procedure as described in the literature.<sup>20</sup> The molar ratio of  $n(\text{glyoxal}):n(\text{urea}):n(\text{formaldehyde})$  was used as 1:1.10:1.95 for the preparation of DMDHEU. To an aqueous solution of glyoxal, urea was added under a nitrogen atmosphere. The pH of the reaction mixture was adjusted to 5.5 and stirred for 24 h by maintaining the temperature of the mixture at 50 °C. The mixture was then brought to room temperature, neutralized, and evaporated to dryness to get crude 4,5-dihydroxy ethylene urea (DHEU). DHEU was added slowly

to an aqueous formaldehyde solution, and pH was adjusted to 8.2–8.5. The reaction mixture was then heated to 50 °C and stirred for 24 h. The mixture was then allowed to cool to room temperature and was neutralized and kept for subsequent uses. However, a part of the DMDHEU was purified and used for characterization.

**Synthesis of NMA.** NMA was synthesized using the procedure as reported.<sup>25</sup> In 200 mL of distilled water, 48 g of acrylamide and 42 g of formaldehyde were added and stirred mechanically. The stirring was done at 23–25 °C under a  $N_2$  atmosphere. After dissolution of the reagent in water, the pH was maintained between 8.0 and 9.0 by adding NaOH solution. This reaction mixture was further stirred for 2 h, and pH was adjusted to 5.0–6.0 by adding formic acid. A portion of the NMA was purified for characterization.

**Preparation of Methyl Methacrylate-Grafted Starch (MMA-g-Starch).** A total of 50g of starch was dissolved in 100 mL of deionized water and stirred at 90 °C for 1 h. The temperature of the solution was decreased to 50–60 °C, and MMA (5 mL) was added to the solution. Now, a known amount of  $K_2S_2O_8$  solution (3% w/v of starch) was prepared, and 2/3 of it was added to the solution. The temperature of the solution was increased to 70 °C. The whole mixture was stirred for 3 h at 70–80 °C. Then again, the remaining part of the  $K_2S_2O_8$  solution was added to the mixture and stirred for another 1 h in order to ensure the complete reaction. The pH of MMA-g-starch solution was checked and found acidic due to the presence of  $K_2S_2O_8$ . The pH value of the system was approximately 2.5. The cross-linking reaction of DMDHEU with polyols can take place efficiently in the pH range of 1.0 to 6.0.<sup>26</sup> Thus, addition of further catalyst is not required to drive the cross-linking reaction for preparation of the wood starch composites. The amount of homopolymer, PMMA, formed in this process was negligible. In view of that, the mixture was kept as such for subsequent use in the preparation of wood starch composites.

**Preparation of Wood Starch Composites (WSC).** A total of 27.5 g of oven-dried wood flour samples were added in the entire mixture of MMA-g-starch solution and stirred for 1 h at 70 °C. The temperature of the solution was decreased to 35 °C, and the required quantity of cross-linker (50% of starch, w/w, and approximately 25% of composites, w/w) was added to the mixture and stirred for 1 h. After that, glycerol (5%, v/w of starch) was added to the mixture as a plasticizer and stirred for another 30 min. The mixture was then transferred to a tray, dried, and grinded. From the grinded mixture, 27 g was transferred to a mold. The composite sheets were obtained by the compression molding press (Santec, New Delhi) at 120 °C under pressure of 80 MPa. WSC thus treated with GA, NMA, and DMDHEU were designated as W/MMA-g-starch/GA, W/MMA-g-starch/N, and W/MMA-g-starch/D.

The FTIR, NMR, and XRD characterizations of the composite samples were done without removing the unreacted chemicals. The probability of existing unreacted chemicals in the final composites is very low as high temperature and pressure are applied during composite preparation. The removal of trace amounts of chemicals, if any, is difficult due to the cross-linked structure. If the composite is treated with solvent, the cross-linked structure may breakdown, which gives an incorrect interpretation. Also, a massive amount of solvent is required to remove such impurities, which limits the laws of green chemistry.

## CHARACTERIZATIONS

**NMR Study.** NMR spectra of DMDHEU, NMA, and MMA-g-starch were recorded by using a 400 MHz FTNMR (JEOL, JAPAN) spectrophotometer using DMSO as solvent and TMS as internal standard.

**Fourier Transform Infrared Spectroscopy (FTIR) Studies.** FT-IR spectra of wood flour, starch, MMA-g-starch, and WSC cross-linked with DMDHEU, NMA, and GA were recorded in FTIR spectrophotometer (Impact-410, Nicolet, U.S.A.) using a KBr pellet.

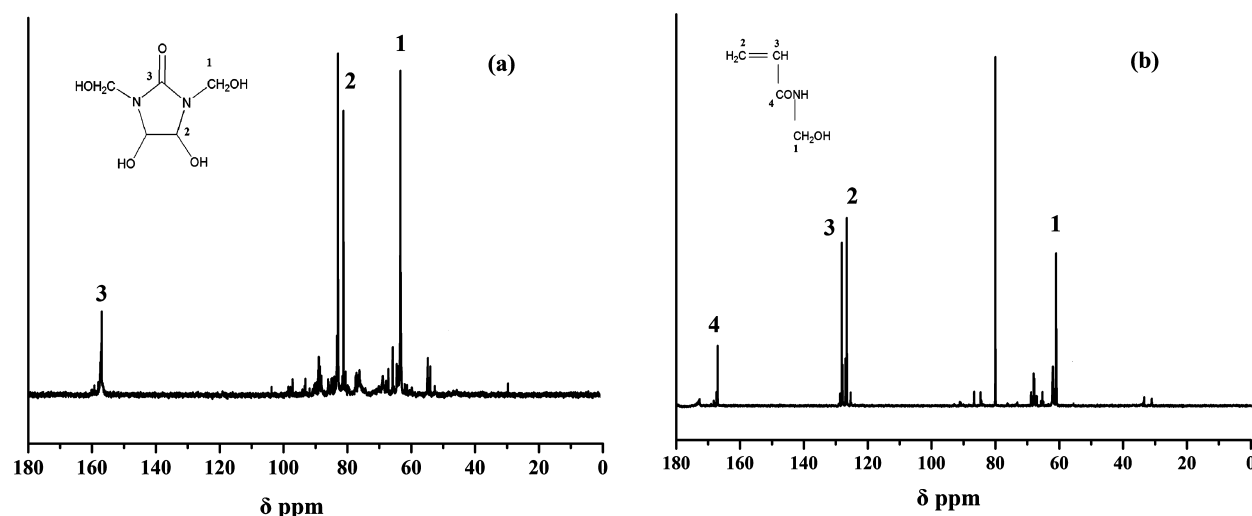


Figure 1.  $^{13}\text{C}$  NMR spectra of (a) DMDHEU and (b) NMA.

**X-ray Diffraction (XRD) Study.** The crystallinities of the WSC were evaluated by XRD analysis. They were carried out in a Rigaku X-ray diffractometer (Miniflux, UK) using  $\text{Cu K}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation at a scanning rate of  $1^\circ/\text{min}$  with an angle ranging from  $10^\circ$  to  $70^\circ$ .

**Mechanical Properties.** The tensile and flexural tests for WSC cross-linked with DMDHEU, NMA, and GA were carried out in a Universal Testing Machine (Zwick, model Z010) according to ASTM D-638 and D-790, respectively. A total of five samples of each composites were tested, and their average values were reported.

For tensile tests, the samples were cut into  $10 \text{ cm} \times 0.5 \text{ cm} \times 2 \text{ cm}$ , and for flexural strength measurements, the samples were cut into dimensions of  $1 \text{ cm} \times 1 \text{ cm} \times 10 \text{ cm}$  (radial  $\times$  tangential  $\times$  longitudinal).

**Hardness.** The hardness of the samples were measured according to ASTM D-2240 using a durometer (model RR12) and expressed as shore D hardness.

**Dynamic Mechanical Analysis (DMA).** The DMA was performed under tensile mode using a Universal Q800.0 TA Instrument. The dimensions of the specimens were  $5 \text{ cm} \times 1.25 \text{ cm} \times 0.35 \text{ cm}$ . The specimens were scanned over a temperature range of  $20\text{--}200^\circ\text{C}$ . Frequency of oscillation was fixed at  $1 \text{ Hz}$  and ramped at  $2^\circ\text{C}/\text{min}$  to  $200^\circ\text{C}$ . Storage modulus, loss modulus, and mechanical loss factor ( $\tan \delta$ ) were recorded and plotted against temperature.

**Thermogravimetric Analysis (TGA).** Thermal properties of wood, starch, and the WSC were measured in a thermogravimetric analyzer (TGA-50, shimadzu) at a heating rate of  $10^\circ\text{C}/\text{min}$  up to  $600^\circ\text{C}$  under a nitrogen atmosphere at a flow rate of  $30 \text{ mL}/\text{m}$ .

**Limiting Oxygen Index Test (LOI).** LOI of the samples was measured by a flammability tester (S.C. Dey Co., Kolkata) according to the ASTM D-2863 method. The sample was placed vertically in the sample holder of the LOI apparatus. The ratio of nitrogen and oxygen at which the sample continues to burn for at least  $30 \text{ s}$  was recorded.

$$\begin{aligned} \text{Limiting oxygen index (LOI)} \\ = \text{volume of } \text{O}_2 / \text{volume of } (\text{O}_2 + \text{N}_2) \end{aligned} \quad (1)$$

**Scanning Electron Microscopy (SEM).** Morphological features of the WSC were studied by using scanning electron

microscope (JEOL JSM – 6390LV) at an accelerated voltage of  $5\text{--}10 \text{ kV}$ . The fractured surface of the sample, deposited on a brass holder and sputtered with platinum, was used for this study.

**Water Vapor Uptake and Dimensional Stability Test.** The WSC samples were cut into pieces of  $2.5 \text{ cm} \times 0.5 \text{ cm} \times 2.5 \text{ cm}$  for the measurement of water vapor uptake and dimensional stability test. The samples were oven-dried and conditioned at room temperature ( $30^\circ\text{C}$ ) and 30% relative humidity before the test, and dimensions and weights of the oven-dried samples were measured. The test was carried out by placing the samples at 65% relative humidity and maintaining a temperature of  $30^\circ\text{C}$ . Weights and volumes of the samples were measured after 12, 24, 36, 48, 60, and 72 h. Water uptake is expressed as a percentage of moisture absorbed based on oven dry weight.

$$\text{Water vapor uptake (\%)} = (W_t - W_o) / W_o \times 100 \quad (2)$$

where  $W_t$  is the weight of the specimen after water absorption, and  $W_o$  is the weight of oven-dried specimen.

Swelling was considered as a change in volume and is expressed as the percentage of volume increase compared to oven-dried samples

$$\% \text{ Swelling} = (V_f - V_o) / V_o \times 100 \quad (3)$$

where  $V_f$  is the volume of the specimen after water absorption, and  $V_o$  is the volume of the oven-dried specimen.

## RESULTS AND DISCUSSION

**Characterizations of DMDHEU, NMA, and MMA-g-Starch. NMR Study.** NMR studies were used to confirm the formation of cross-linkers and grafting of MMA onto starch. In DMDHEU (Figure 1a), a series of peaks appeared at 62.82, 80.63, and 158.5 ppm and were assigned to  $-\text{NHCH}_2\text{OH}$ ,  $-\text{CHOH}$ , and carbonyl and carbon.<sup>27–29</sup> Figure 1b shows the NMR spectrum of NMA. The peaks appearing at 128.86, 127.66, and 63.12 ppm were due to  $\text{CH}_2=\text{CH}-$  and  $\text{NHCH}_2\text{OH}$ . The carbonyl carbon peak was observed at 168.85 ppm. In the  $^{13}\text{C}$  NMR spectrum, the presence of the characteristic peaks of chito-oligosaccharide containing NMA as a side chain was reported.<sup>30</sup> Because the grafting percentage is expected to be less than 10% by using  $0.1 \text{ mL}$  MMA per gram

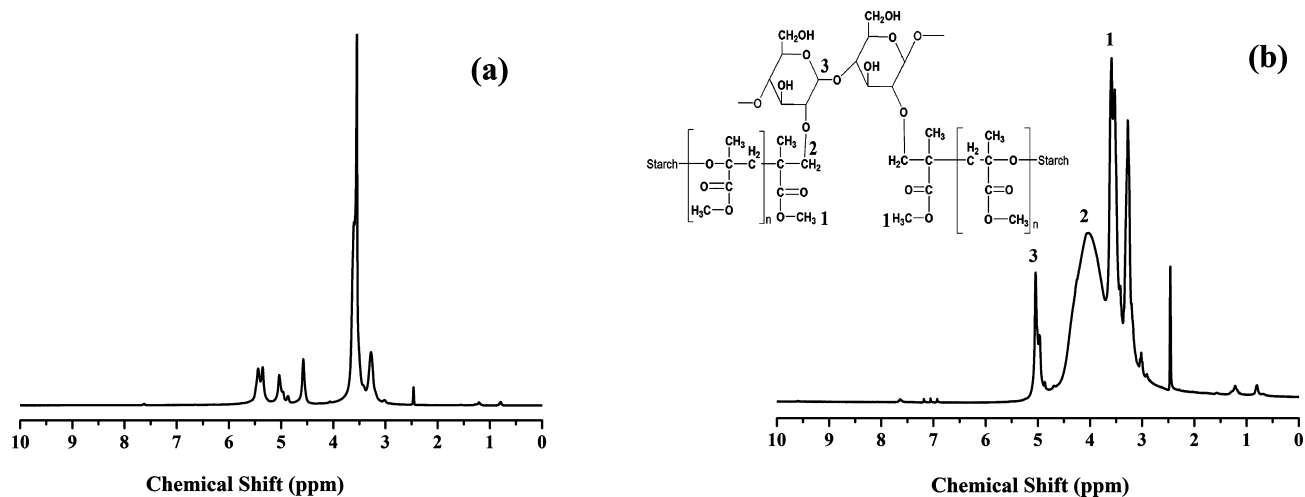


Figure 2.  $^1\text{H}$  NMR spectra of starch and MMA-g-Starch.

starch and considering the low isotopic abundance of  $^{13}\text{C}$ , no distinct changes in the  $^{13}\text{C}$  NMR pattern could be observed for starch and MMA-g-starch samples.

The  $^1\text{H}$  NMR spectra of starch and MMA-g-starch are shown in Figure 2. The signals of proton species of starch at  $\delta = 3.25$ , 3.5, 4.5, 5.03, and 5.35 were found to be in accordance with the literature.<sup>31,32</sup> However, in the MMA-g-starch, the appearance of a sharp new signal at  $\delta = 5.08$  (3), 4.0 (2) ppm and the increased intensity of the peak at 3.63 (1,  $-\text{OCHH}_3$ ) supports the successful incorporation of MMA onto starch surface.

**FTIR Study of Cross-Linker.** The results obtained from NMR spectroscopy support the results of FTIR. A FTIR study is used to confirm the grafting of MMA onto starch and the formation of DMDHEU and NMA. The FTIR spectra of starch, MMA-g-starch, NMA, and DMDHEU are shown in Figure 3. Curve 3a

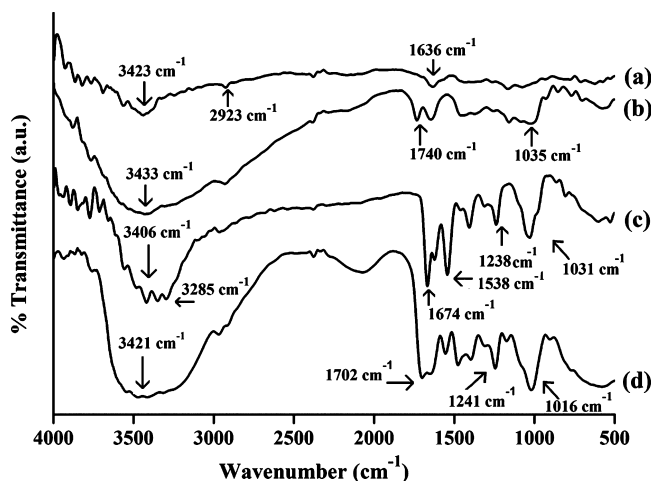


Figure 3. FTIR spectra of (a) starch, (b) MMA-g-starch, (c) NMA, and (d) DMDHEU.

assigned for starch showed the presence of a band at  $3423\text{ cm}^{-1}$  for  $-\text{OH}$  stretching,  $2923\text{ cm}^{-1}$  for  $-\text{CH}$  stretching, and  $1636\text{ cm}^{-1}$  for  $-\text{OH}$  bending vibration. Curve 3b shows the spectrum of MMA-g-starch. The appearance of the characteristic band of the  $\text{C}=\text{O}$  group around  $1740\text{ cm}^{-1}$  confirmed the incorporation of PMMA into the starch polymer.<sup>10</sup> The absorption band found in the range of  $1030\text{--}1035\text{ cm}^{-1}$  was due to the vibration of the ester group of PMMA.<sup>8</sup> In the

spectrum of NMA (curve 3c), the absorption bands appeared in the range of  $3450\text{--}3250\text{ cm}^{-1}$  ( $-\text{OH}$  and  $-\text{NH}_2$  stretching),  $1674\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching),  $1538\text{ cm}^{-1}$  ( $\text{CO}\text{--}\text{NH}$  stretching),  $1238\text{ cm}^{-1}$  ( $\text{NH}\text{--}\text{CH}_2$  stretching), and  $1031\text{ cm}^{-1}$  ( $-\text{CH}$  asymmetric stretching).<sup>33</sup> The spectrum of DMDHEU (curve 3d) showed an absorption band at  $3421\text{ cm}^{-1}$  for  $-\text{OH}$  stretching,  $1702\text{ cm}^{-1}$  for  $\text{C}=\text{O}$  stretching,  $1241\text{ cm}^{-1}$  for  $-\text{CHOH}$  stretching, and  $1016\text{ cm}^{-1}$  for  $-\text{CH}_2\text{OH}$  stretching.<sup>34</sup>

**FTIR Study of the Composites.** FTIR studies of the composites confirm the changes in chemical structure of wood resulting from the use of cross-linkers with MMA-g-starch. Figure 4 shows the FTIR spectra of wood and WSC

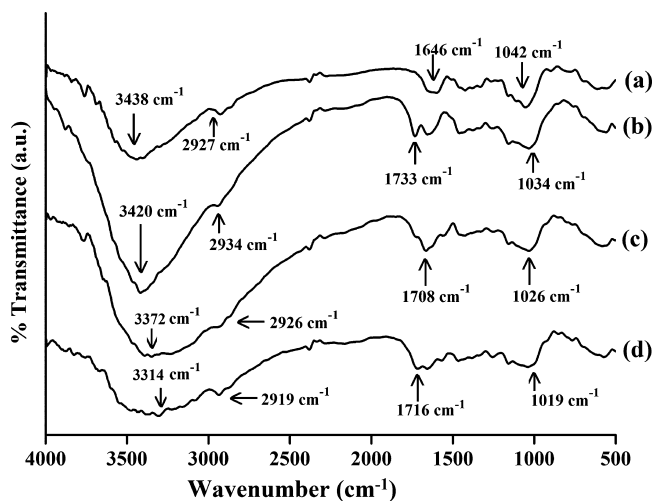
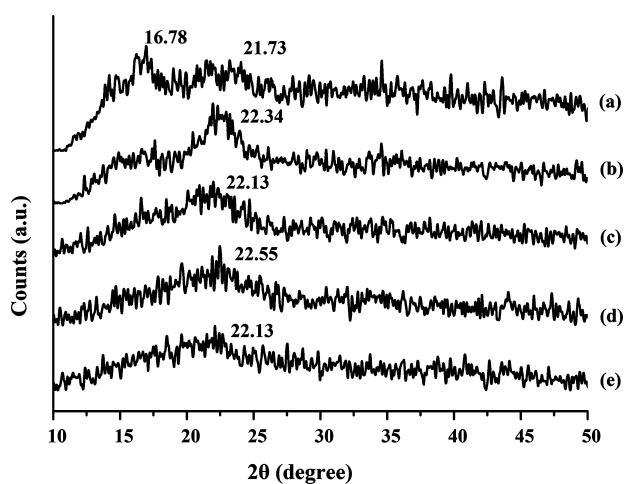


Figure 4. FTIR spectra of (a) wood, (b) W/MMA-g-starch/GA, (c) W/MMA-g-starch/N, and (d) W/MMA-g-starch/D.

cross-linked with GA, NMA, and DMDHEU. Wood (curve 4a) showed the presence of bands at  $3438\text{ cm}^{-1}$  ( $-\text{OH}$  stretching),  $2927\text{ cm}^{-1}$  ( $-\text{CH}$  stretching),  $1646\text{ cm}^{-1}$  ( $-\text{OH}$  bending),  $1042\text{ cm}^{-1}$  ( $-\text{CO}$  stretching), and  $1000\text{--}650\text{ cm}^{-1}$  ( $-\text{CH}$  bending, out of plane). Curves 4b–4d represent the spectra of WSC cross-linked with GA, NMA, and DMDHEU, respectively. The band corresponding to  $-\text{OH}$  stretching appeared in the range of  $3314\text{--}3420\text{ cm}^{-1}$ . It was observed that the intensity of the hydroxyl peak decreased and shifted to  $3420$

$\text{cm}^{-1}$  (curve 4b),  $3372 \text{ cm}^{-1}$  (curve 4c), and  $3314 \text{ cm}^{-1}$  (curve 4d) from  $3438 \text{ cm}^{-1}$  (curve 4a) of virgin wood. The decrease in intensity and shifting of the  $-\text{OH}$  stretching peak were the maximum for WSC cross-linked with DMDHEU followed by WSC cross-linked with NMA and GA. The decrease in peak intensity and shifting to a lower wavenumber in the composite might be due to the enhancement of interaction between hydroxyl groups of wood with starch and cross-linker. A similar decrease in hydroxyl group peak intensity and shifting to a lower wavenumber was reported by Deka et al. while studying the FTIR analysis of wood polymer composites.<sup>35</sup> The shifting of the hydroxyl peak to a lower wavenumber was also cited in the literature.<sup>36–39</sup>

**XRD Results.** XRD studies were done to study the effect of chemical modification on crystallinity due to incorporation of different cross-linkers in WSC. The X-ray diffractograms of WSC cross-linked with different cross-linkers, namely, GA, NMA, and DMDHEU are shown in Figure 5. Curve 5a



**Figure 5.** X-ray diffraction of (a) starch, (b) wood, (c) W/MMA-g-starch/GA, (d) W/MMA-g-starch/N, and (e) W/MMA-g-starch/D.

representing the diffractogram of starch shows a little broader peak at  $2\theta = 21.73^\circ$  and a comparatively sharper peak at  $2\theta = 16.78^\circ$ . A comparatively sharper peak due to the diffraction of a (002) plane of wood cellulose was found to appear at  $2\theta = 22.34^\circ$  (curve 5b). In all the curves of WSC, the characteristics peak of cellulose was observed (curves 5c–5e). There was no significant shifting of peak corresponding to the 002 plane of cellulose. However, the peak intensity of wood cellulose gradually decreased when different cross-linkers were used with the wood. The peak intensity of WSC cross-linked with DMDHEU (curve 5e) was found to be less compared to those of WSC cross-linked with either GA (curve 5c) or NMA (curve 5d). The reduction in peak intensity suggested a decrease in crystallinity in the composites.<sup>35</sup>

**Table 1. Mechanical Properties of WSC**

sample	flexural properties		tensile strength (MPa)	hardness (shore D)
	strength (MPa)	modulus (MPa)		
W/MMA-g-starch/GA	30.8	2152	13.6	64.1 ( $\pm 1$ )
W/MMA-g-starch/N	42.7	4369	14.8	66.3 ( $\pm 0.5$ )
W/MMA-g-starch/D	44.7	5011	15.6	72.0 ( $\pm 1$ )

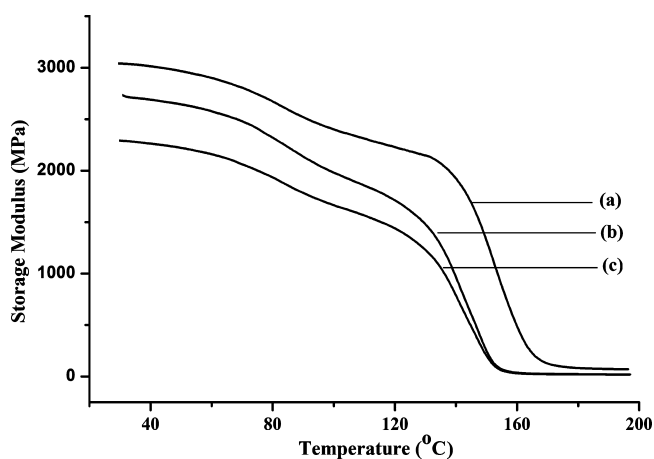
**Mechanical Properties and Hardness Study.** The flexural, tensile, and hardness values of the composites cross-linked with different cross-linkers are shown in Table 1. DMDHEU cross-linked composites showed higher flexural as well as tensile values compared to composites cross-linked with either NMA or GA. Both the flexural and tensile properties of the cross-linked composites followed the order of DMDHEU treated > NMA treated > GA treated.

This trend of mechanical properties of the composites by the use of DMDHEU, NMA, and GA was also reported by Hazarika and Maji.<sup>20</sup> The double bond and hydroxyl groups present in NMA are capable of undergoing a self-polymerization and cross-linking reaction with the hydroxyl groups of wood and MMA-g-starch. GA could react through its aldehydic groups. On the other hand, DMDHEU could react through its four hydroxyl groups with wood and MMA-g-starch.<sup>20</sup> As a result, it provided maximum cross-linking and maximum improvements in both the tensile and flexural properties of the composites.

The trend for hardness values was similar to that of the trend for mechanical properties. DMDHEU-treated wood showed the maximum hardness followed by NMA- and GA-treated composites.

**DMA Study.** DMA studies were used to characterize the viscoelastic properties of WSC for determining their stiffness and damping characteristics. DMA was used to characterize the wood products, and it provided the time-dependent deformation behavior (mostly sinusoidal deformation) of the wood composites.

**Storage Modulus ( $E'$ ).** Storage modulus values of WSC that measures the samples elastic behaviors were plotted against temperature. Figure 6 shows the variation of storage modulus

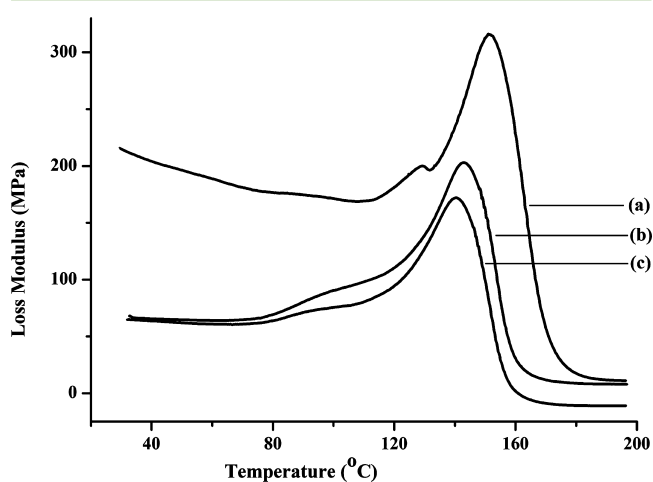


**Figure 6.** Storage modulus of (a) W/MMA-g-starch/D, (b) W/MMA-g-starch/N, (c) W/MMA-g-starch/GA.

of composites cross-linked with DMDHEU (curve 6a), NMA (curve 6b), and GA (curve 6c). Storage modulus values

decreased with an increase in temperature. The storage modulus ( $E'$ ) for the DMDHEU cross-linked composite was larger compared to the NMA and GA cross-linked composites. This was due to higher stiffness caused by the improvement in interaction among the polymer, wood flour, and cross-linker.<sup>40</sup> The cross-linker DMDHEU improved the interaction between wood flour and starch due to the presence of large number of functional groups. The decrease in modulus value for W/MMA-g-starch/N and W/MMA-g-starch/GA was due to less interaction of starch, wood flour, and cross-linker. However, the storage modulus values were found to decrease significantly in the temperature range between 130 and 165 °C as shown by curves 6a–6c because with the increase in temperature, the matrix became softened, which resulted in a lowering of the storage modulus.<sup>41</sup>

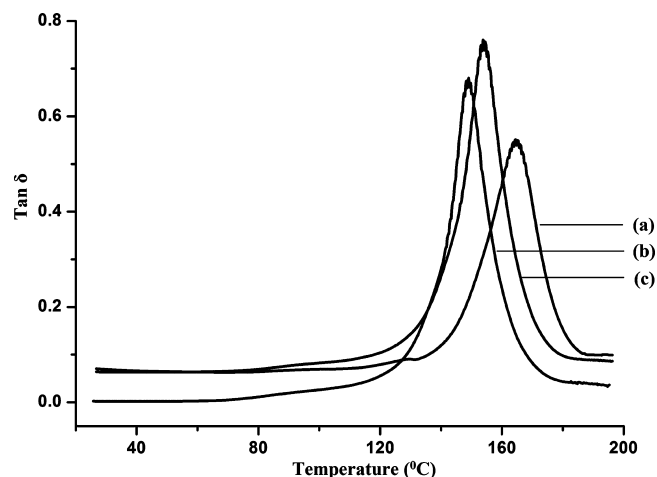
**Loss Modulus.** Figure 7 illustrates the loss moduli of WSC cross-linked with DMDHEU (curve 7a), NMA (curve 7b), and



**Figure 7.** Loss modulus of (a) W/MMA-g-starch/D, (b) W/MMA-g-starch/N, and (c) W/MMA-g-starch/GA.

GA (curve 7c). The DMDHEU cross-linked composites exhibited a higher loss modulus compared to either NMA or GA cross-linked composites. In the DMDHEU cross-linked composites (curve 7a), the value of the maximum peak temperature shifted to a higher temperature range compared to those of NMA and GA cross-linked composites. This suggested an improvement in interaction among polymer, wood flour, and cross-linker.<sup>41</sup>

**Tan  $\delta$ .** The mechanical loss factor or damping index, which characterized the viscoelastic properties of the composites, is shown in Figure 8. The  $\tan \delta$  value was influenced by the type of matrix, wood flour content, compatibilizer, and processing parameters.<sup>40</sup> DMDHEU cross-linked composites exhibited lower  $\tan \delta$  value followed by NMA and GA cross-linked composites. The decrease in  $\tan \delta$  value might be due to the increased interaction of starch and wood flour with DMDHEU. A similar decrease in  $\tan \delta$  intensity was reported in the literature.<sup>42,43</sup> Moreover, a shifting of the  $\tan \delta$  peak value toward a higher temperature was observed when DMDHEU was added to the composite. The shifting was more in the case of DMDHEU, followed by GA and NMA cross-linked composites. This type of shifting of  $\tan \delta$  peak to a higher temperature due to an increased interaction of the wood and cross-linker was reported by Devi et al.<sup>43</sup> This indicated an



**Figure 8.**  $\tan \delta$  of (a) W/MMA-g-starch/D, (b) W/MMA-g-starch/N, and (c) W/MMA-g-starch/GA.

increase in chemical interaction between wood flour, starch, and cross-linker.

**TGA Analysis.** TGA is performed to analyze the thermal stability of wood, starch, MMA-g-starch, and WSC with different cross-linkers. The initial decomposition temperature ( $T_i$ ), maximum pyrolysis temperature ( $T_m$ ), weight losses (%) at various temperature ( $T_D$ ), and residual weight (RW %) for wood flour, starch, MMA-g-starch, and cross-linked WSC are shown in Table 2. In all the cases, a decrease in weight loss due to removal of moisture was observed below 100 °C.

The thermostability of WSC composites was more than that of wood flour. The  $T_i$  value for starch was the maximum, while that of MMA-g-starch was the minimum. The  $T_i$  value for MMA-g-starch was less than that of pure starch. This might be due to the earlier decomposition of PMMA from MMA-g-starch.  $T_i$  values of the cross-linked composites were in between those of wood flour and starch. DMDHEU cross-linked WSC showed the highest  $T_i$  value. This was followed by NMA and GA cross-linked composites.  $T_m$  values for both stages of decomposition were the maximum for DMDHEU cross-linked composites. In general,  $T_D$  values of cross-linked WSC were larger compared to either wood flour or starch. The highest  $T_D$  values were obtained for DMDHEU-treated WSC. The number of functional groups in DMDHEU was higher compared to either NMA or GA. Hazarika et al. reported that DMDHEU-treated wood/melamine formaldehyde-furfuryl alcohol composites produced maximum improvement in thermal properties.<sup>20</sup> DMDHEU enhanced the interaction between wood and starch through its hydroxyl groups. RW% values of cross-linked composites were higher than those of either wood flour or starch. RW% values were found to be the maximum for DMDHEU cross-linked composites. These results suggested that thermal stability of WSC improved due to cross-linking with DMDHEU, NMA, or GA.

**LOI Test.** LOI studies provided a quantitative measure of flammability of WSC composites. LOI values of the composites are summarized in Table 3. The DMDHEU cross-linked composites exhibited higher LOI values compared to NMA and GA cross-linked composites. The release of oxides of nitrogen on combustion, displacing the oxygen at the surface of the combustible material, appeared to be the mechanism of fire control. DMDHEU provided nitrogen, and hence, an improved flame retardancy property was observed in the DMDHEU

Table 2. Thermal Analysis of Wood Flour, Starch, MMA-g-Starch, and WSC

sample	$T_i$	$T_m^a$	$T_m^b$	temperature of decomposition ( $T_D$ ) in °C at different weight loss (%)				RW% at 600 °C
				20%	40%	60%	80%	
wood flour	168	187	301	236	278	320	484	11.92
starch	244	254	310	276	302	311	397	4.61
MMA-g-starch	127	173	288	144	273	301	503	7.08
W/MMA-g-starch/GA	174	220	336	233	299	360	490	7.79
W/MMA-g-starch/N	183	230	341	244	320	387	526	9.38
W/MMA-g-starch/D	235	240	360	286	338	391	558	9.88

Table 3. Limiting Oxygen Indices (LOI) and Flaming characteristics of WSC

samples	LOI (%)	flame description	smokes and fumes	char
W/MMA-g-starch/GA	44.5	small localized flame	small and black smoke	medium
W/MMA-g-starch/N	50	small localized flame	small and black smoke	medium
W/MMA-g-starch/D	56.5	small localized flame	small and black smoke	medium

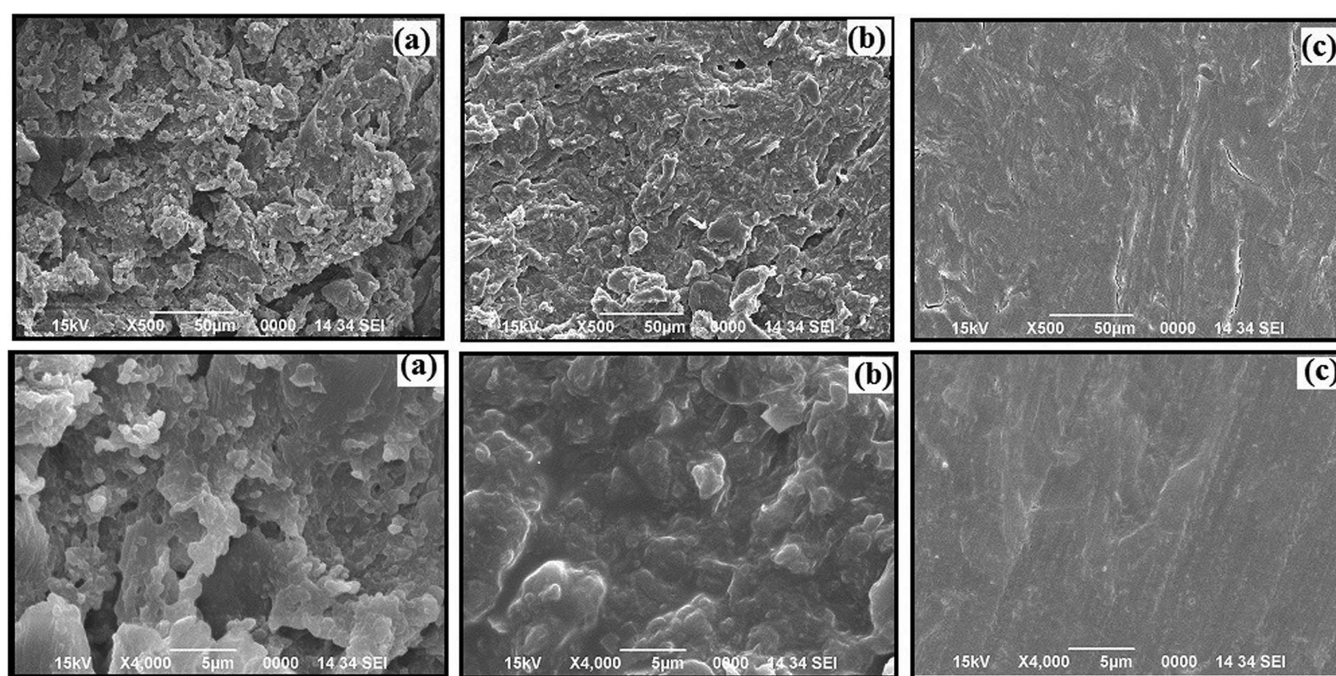


Figure 9. SEM micrograph of (a) W/MMA-g-starch/GA, (b) W/MMA-g-starch/N, and (c) W/MMA-g-starch/D (at high and low resolution).

cross-linked composite.<sup>20</sup> Wu et al. reported that DMDHEU acted as a binder as well as nitrogen provider and thereby enhanced the flame-retarding performance of the composites.<sup>44</sup>

**SEM Study.** The compatibility among wood, MMA-g-starch, and the cross-linkers as well as morphological features of the WSC were studied by SEM. Figure 9 illustrates the SEM micrograph of different cross-linked fractured samples of WSC. The rough surface of GA cross-linked WSC indicated that GA did not interact much with wood and starch polymer in the composites (Figure 9a). The roughness of the fractured surface of WSC decreased when NMA was used as cross-linker (Figure 9b). The use of DMDHEU as a cross-linker further decreased the roughness (Figure 9c). The decrease in surface roughness indicated improvement in interaction as well as compatibility among the polymer, wood flour, and cross-linker.

**Water Uptake and Dimensional Stability Results.** The water uptake results of wood starch composites cross-linked with GA, NMA, and DMDHEU are shown in Figure 10. The composites prepared with starch swelled completely around 6 h

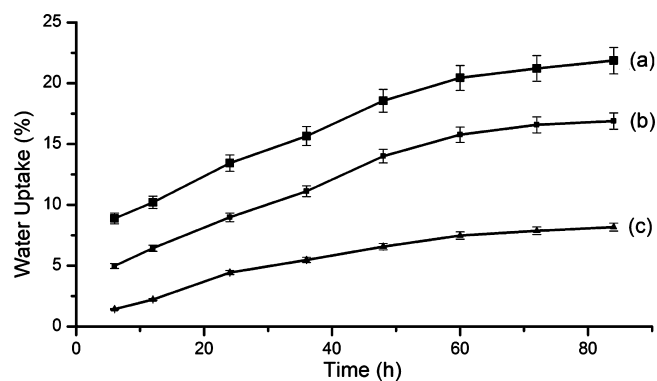


Figure 10. Water absorption of (a) W/MMA-g-starch/GA, (b) W/MMA-g-starch/N, (c) W/MMA-g-starch/D.

(not shown in figure), but the composites prepared with MMA-g-starch significantly decreased the water uptake capacity. With

an increase in time, the water uptake capacity was found to increase for all WSC samples. The increase in water uptake was rapid initially but slowed later. The water uptake capacity was the least with the DMDHEU cross-linked composites. The dimensional stability of the wood starch composites improved possibly due to the interaction of DMDHEU with the functional groups of wood as also reported by Yuan et al.<sup>45</sup>

## CONCLUSIONS

In this study, an eco-friendly method was used successfully to prepare wood starch composites by using MMA-g-starch, wood flour from *I. carnea*, different cross-linkers, and water as a solvent. The use of a greener solvent as well as renewable resources to prepare wood composites provides a new way of reducing the use of hazardous chemicals. FTIR studies indicated that the maximum interaction occurred between DMDHEU, wood, and MMA-g-starch. XRD studies showed a decrease in crystallinity of wood composites due to incorporation of cross-linker and MMA-g-starch. DMDHEU provided the maximum enhancement in mechanical and viscoelastic properties. Considerable improvements in thermal properties and water uptake resistances were obtained due to inclusion of MMA-g-starch and cross-linker in the composites. Cross-linking decreased the surface roughness of the composites as revealed by SEM studies. Flame retardancy of the composites was improved due to cross-linking. The improvement in overall properties was more in DMDHEU-treated wood composites followed by NMA-treated and GA-treated composites.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: tkm@tezu.ernet.in. Tel.: +91 3712 267007, ext 5053. Fax: +91 3712 267005.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The author, Prasanta Baishya, is grateful to the University Grants Commission (UGC), New Delhi, for providing financial assistance (as a fellowship) in carrying out this research.

## REFERENCES

- (1) Saheb, D. N.; Jog, J. P. Natural fiber polymer composites: A review. *Adv. Polymer. Technol.* **1999**, *18*, 351–363.
- (2) Ashori, A. Wood plastic composites as promising green composites for automotive industries. *Bioresour. Technol.* **2008**, *99*, 4661–4667.
- (3) Li, M. C.; Lee, J. K.; Cho, U. R. Synthesis, characterization, and enzymatic degradation of starch-grafted poly(methyl methacrylate) copolymer films. *J. Appl. Polym. Sci.* **2012**, *125*, 405–414.
- (4) Liu, H.; Xie, F.; Yu, L.; Chen, L.; Li, L. Thermal processing of starch-based polymers. *Prog. Polym. Sci.* **2009**, *34*, 1348–1368.
- (5) Zullo, R.; Iannace, S. The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure Carbohydrate Polymers. *Carbohydr. Polym.* **2009**, *77*, 376–383.
- (6) Chang, P. R.; Jian, R.; Zheng, P.; Yu, J.; Ma, X. Preparation and properties of glycerol plasticized-starch (GPS)/cellulose nanoparticle (CN) composites. *Carbohydr. Polym.* **2010**, *79*, 301–305.
- (7) Mathew, A. P.; Dufresne, A. Morphological investigation of nanocomposites from sorbitol plasticized starch and Tunicin whiskers. *Biomacromolecules* **2011**, *3*, 609–617.

- (8) Jaymand, M. Exfoliated syndiotactic polystyrene-graft-poly (methyl methacrylate)/ montmorillonite nanocomposite prepared by solvent blending. *Polym. J.* **2011**, *43*, 901–908.

- (9) Kaewtatip, K.; Tanrattanakul, V. Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydr. Polym.* **2008**, *73*, 647–655.

- (10) Ge, X. C.; Xu, Y.; Meng, Y. Z.; Li, R. K. Y. Thermal and mechanical properties of biodegradable composites of poly(propylene carbonate) and starch-poly(methyl acrylate) graft copolymer. *Compos. Sci. Technol.* **2005**, *65*, 2219–2225.

- (11) Iman, M.; Maji, T. K. Effect of crosslinker and nanoclay on starch and jute fabric based green nanocomposites. *Carbohydr. Polym.* **2012**, *89*, 290–297.

- (12) Wu, X. S. Effect of glycerin and starch crosslinking on molecular compatibility of biodegradable poly(lactic acid)-starch composites. *J. Polym. Environ.* **2011**, *19*, 912–917.

- (13) Duanmu, J.; Gamstedt, E. K.; Rosling, A. Synthesis and preparation of crosslinked allylglycidyl ether-modified starch-wood fibre composites. *Starch/Stärke* **2007**, *59*, 523–532.

- (14) Duanmu, J.; Gamstedt, E. K.; Rosling, A. Hygromechanical properties of composites of crosslinked allylglycidyl-ether modified starch reinforced by wood fibres. *Compos. Sci. Technol.* **2007**, *67*, 3090–3097.

- (15) Duanmu, J.; Gamstedt, E. K.; Rosling, A. Bulk composites from microfibrillated cellulose-reinforced thermoset starch made from enzymatically degraded allyl glycidyl ether-modified starch. *J. Compos. Mater.* **2012**, *46*, 3201–3209.

- (16) Duanmu, J.; Gamstedt, E. K.; Pranovich, A.; Rosling, A. Allyloxy-modified starch with low degree of substitution for fiber reinforced thermoset starch composites. *Compos. Sci. Technol.* **2011**, *71*, 520–527.

- (17) Duanmu, J.; Gamstedt, E. K.; Pranovich, A.; Rosling, A. Studies on mechanical properties of wood fiber reinforced cross-linked starch composites made from enzymatically degraded allylglycidyl ether-modified starch. *Compos. part A* **2010**, *41*, 1409–1418.

- (18) Pfeffer, A.; Mai, C.; Militz, H. Weathering characteristics of wood treated with water glass, siloxane or DMDHEU. *Eur. J. Wood. Prod.* **2012**, *70*, 165–176.

- (19) Xie, Y.; Xiao, Z.; Grüneberg, T.; Militz, H.; Hill, C. A. S.; Steuernagel, L.; Mai, C. Effects of chemical modification of wood particles with glutaraldehyde and 1,3-dimethylol-4,5-dihydroxyethyleneurea on properties of the resulting polypropylene composites. *Compos. Sci. Technol.* **2010**, *70*, 2003–2011.

- (20) Hazarika, A.; Maji, T. K. Effect of different crosslinkers on properties of melamine formaldehyde-furfuryl alcohol copolymer/montmorillonite impregnated softwood (*Ficus hispida*). *Polym. Eng. Sci.* **2013**, *53*, 1394–1404.

- (21) Merdas, I.; Thominet, F.; Tcharkhtchi, A.; Verdu, J. Factors governing water absorption by composite matrices. *Compos. Sci. Technol.* **2002**, *62*, 487–492.

- (22) Poathan, L. A.; Thomas, S. Effect of hybridization and chemical modification on the water absorption behavior of banana fiber-reinforced polyester composites. *J. Appl. Polym. Sci.* **2004**, *91*, 3856–3865.

- (23) Bernard F. North, Treating cellulose textile fabrics with dimethylol dihydroxyethyleneurea-polyol. U.S. Patent 4396391 A, 1983.

- (24) Yao, W.-H.; Chen, J.-C.; Hu, M.-S.; Teng, M.-Y.; Huang, P.-H.; Lin, J.-M.; Chen, C.-C. Crosslinking of cotton cellulose in the presence of serine and glycine. I. Physical properties and reaction kinetics. *J. Appl. Polym. Sci.* **2005**, *97*, 595–603.

- (25) Baltieri, R. C.; Innocenti-Mei, L. H.; Tamashiro, W. M. S. C.; Peres, L.; Bittencourt, E. Synthesis of porous microspheres from amino polymers. *Eur. Polym. J.* **2002**, *38*, 57–62.

- (26) North B. F. Treating cellulose textile fabrics with dimethylol dihydroxyethyleneurea-polyol. U.S. Patent, 4,396, 391, August 2, 1983.

- (27) Angelatos, A. S.; Burgar, M. I.; Dunlop, N.; Separovic, F. NMR structural elucidation of amino resins. *J. Appl. Polym. Sci.* **2004**, *91*, 3504–3512.



- (28) Mercer, A. T.; Pizzi, A. A  $^{13}\text{C}$ -NMR analysis method for MF and MUF resins strength and formaldehyde emission from wood particleboard. I. MUF resins. *J. Appl. Polym. Sci.* **1996**, *61*, 1687–1695.
- (29) Chaung, I.-S.; Maciel, G. E.  $^{13}\text{C}$  NMR study of curing in furfuryl alcohol resins. *Macromolecules* **1984**, *17*, 1087–1090.
- (30) Cho, Y. W.; Han, S. S.; Ko, S. W. PVA containing chito-oligosaccharide side chain. *Polymer* **2000**, *41*, 2033–2039.
- (31) Peng, Q. J.; Perlin, A. S. Observations on N.M.R. spectra of starches in dimethyl sulfoxide, iodine-complexing, and solvation in water-di-methyl sulfoxide. *Carbohydr. Res.* **1987**, *160*, 57–72.
- (32) Gong, Q.; Wang, L. Q.; Tu, K. In situ polymerization of starch with lactic acid in aqueous solution and the microstructure characterization. *Carbohydr. Polym.* **2006**, *64*, 501–509.
- (33) Fang, Y.; Chen, L.; Chen, S. Facile and quick synthesis of poly(N-methylolacrylamide)/ polyhedral oligomeric silsesquioxane graft copolymer hybrids via frontal polymerization. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 1136–1147.
- (34) Jang, T. R.; Sheu, T. C.; Sheu, J. J.; Chen, C. C. Crosslinking of cotton fabrics premercerized with different alkalis part III: crosslinking and physical properties of DMDHEU-treated fabrics. *Text. Res. J.* **1993**, *63*, 679–689.
- (35) Deka, B. K.; Maji, T. K. Effect of coupling agent and nanoclay on properties of HDPE, LDPE, PP, PVC blend and Phargamites karka nanocomposite. *Compos. Sci. Technol.* **2010**, *70*, 1755–1766.
- (36) Awal, A.; Ghosh, S. B.; Sain, M. Thermal properties and spectral characterization of wood pulp reinforced bio-composite fibers. *J. Therm. Anal. Calorim.* **2010**, *99*, 695–701.
- (37) Deka, B. K.; Mandal, M.; Maji, T. K. Effect of nanoparticles on flammability, UV resistance, biodegradability, and chemical resistance of wood polymer nanocomposite. *Ind. Eng. Chem. Res.* **2012**, *51*, 11881–11891.
- (38) Luo, X.; Benson, R. S.; Kit, K. M.; Dever, M. Kudzu fiber-reinforced polypropylene composite. *J. Appl. Polym. Sci.* **2002**, *85*, 1961–1969.
- (39) Hazarika, A.; Maji, T. K. Synergistic effect of nano-TiO<sub>2</sub> and nanoclay on the ultraviolet degradation and physical properties of wood polymer nanocomposites. *Ind. Eng. Chem. Res.* **2013**, *52*, 13536–13546.
- (40) Chui-gen, G.; Yong-ming, S.; Qing-wen, W.; Chang-sheng, S. Dynamic-mechanical analysis and SEM morphology of wood flour/polypropylene composites. *J. For. Res.* **2006**, *17*, 315–318.
- (41) Hristov, V.; Vasileva, S. Dynamic mechanical and thermal properties of modified poly (propylene) wood fiber composites. *Macromol. Mater. Eng.* **2003**, *288*, 798–806.
- (42) Saha, A. K.; Das, S.; Bhatta, D.; Mitra, B. C. Study of jute fiber reinforced polyester composites by dynamic mechanical analysis. *J. Appl. Polym. Sci.* **1999**, *71*, 1505–1513.
- (43) Devi, R. R.; Maji, T. K. Chemical modification of rubber wood with styrene and glycidyl methacrylate. *Polym. Compos* **2008**, *29*, 1258–1262.
- (44) Wu, W.; Yang, C. Q. Statistical analysis of the performance of the flame retardant finishing system consisting of a hydroxy-functional organophosphorus oligomer and the mixture of DMDHEU and melamine–formaldehyde resin. *Polym. Degrad. Stab.* **2004**, *85*, 623–632.
- (45) Yuan, J.; Hu, Y.; Li, L.; Cheng, F. The mechanical strength change of wood modified with DMDHEU. *Bioresources* **2013**, *8*, 1076–1088.