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PHYSICO-MECHANICAL AND THERMAL PROPERTIES OF THERMOPLASTIC POLY(VINYL ALCOHOL) MODIFIED THERMOSETTING UREA FORMALDEHYDE RESIN

ABSTRACT

Urea formaldehyde (UF) resins are brittle and to improve their tensile properties poly(vinyl alcohol) (PVA) has been used to modify the UF resin. An easy improved procedure was developed to make PVA modified UF resin on the basis of conventional synthesis of UF resin. Prepolymer of UF was mixed with different weight percentages of PVA (1-5%) to synthesize modified UF resin which can be used to make adhesive for forest products. Both UF and modified UF resins were characterized by FTIR, physico-mechanical and thermal properties analyses. Modified UF resin containing 2 wt. % PVA exhibited better results than the UF.

Keywords: *Modified urea formaldehyde resin; polyvinyl alcohol; thermal and tensile properties*

INTRODUCTION

Urea formaldehyde (UF) resins are thermosetting polymers which are widely used in particleboard, medium density fiber board, interior plywood manufacturing, finishes and molded objects etc [1-4]. These are amino plastic resins which have a countless variety of condensed structures under various reaction conditions even though they are a chemical product from the reaction of two simple monomers: urea and formaldehyde [1]. They have many advantages, such as high reactivity, colorless glue line, good performance, easy processing and low cost raw materials [2-4]. UF resins are important as adhesive for wood industry during the past century due to their attractive properties at reasonable price, accounting for approximately 60% of the wood adhesive market [3]. However, they have drawback such as formaldehyde emissions and the brittleness of cured UF resin during the use of UF-bonded panels. These disadvantages of unmodified resins prevented them from achieving very wide usage which can be reduced by modification of UF resins [3-4]. Bio-oil modified UF resin showed improved performance by reducing formaldehyde emissions and improving thermal stability [3]. Polydimethylsiloxanes with different functional groups were

successfully encapsulated in UF microcapsules for self-healing applications [5]. Bio-based dialdehyde starch (DAS) was chemically introduced into the melamine-urea-formaldehyde (MUF) resin by in situ polymerization between the aldehyde group in the DAS and the amino group and hydroxymethyl group in the resin to improve the strength of MUF resin [6]. Polyamine modified UF resins offers promise for improving the durability and stability of UF bonded wood products by decreasing the internal stress developed during resin cure and by improving the ability of the cured resin to withstand cyclic stresses [7]. Use of the modified starch as an alternative biobased binder for formaldehyde based resins has shown increased particleboard performance [8]. A multitude of pathways have been explored for the improvement of UF resins behavior relating either to their synthesis procedure or application parameters during panel manufacture that manifest the advantageous properties and improved bonding ability of the innovative UF resin [9]. Thermoset epoxy resins can be toughened successfully by blending a small amount (about 10-15% by weight and having size 0.1 to 5 mm) of liquid rubber or by incorporating the preformed rubbery particles directly [10]. There are many different chemical reactions have been published for the modification of thermoset resin. Many research works have been done to reduce formaldehyde emissions and to reduce brittleness of thermoset resins by the incorporation of different types of modifiers in the cured thermoset resin matrix. Low molar ratio (LMR) UF resins showed poor adhesion in wood-based composite panels due to the presence of inherent crystalline domains, modified cellulose nanomaterials (CNMs) such as TEMPO-oxidized cellulose nanofibrils (TEMPO-CNFs) can prevent the formation of crystalline domains in LMR UF resins [11]. Oxidized starch (OS) modified UF resin adhesives using blocked pMDI as a cross-linker has been prepared and characterized for plywood and improved performance showed by the modified UF resin with 10% OS [12]. UF resins were modified with different amounts of almond shells and the results indicated that the optimal addition of almond shells is 3 wt % which can significantly reduce the formaldehyde emission and increase wet shear strength and thermal stability of the urea formaldehyde resin adhesive [13]. The effects of CaCO_3 on the physical and chemical properties of the UF resin has been investigated and reported that UF resin modified with 2% of CaCO_3 showed the improved properties than neat UF resin [14]. UF resins were successfully modified using nanocellulose with an additive concentration of 3% and the results showed that nanocellulose addition enhanced the resin properties, such as shorter gelation time, faster curing rates at low activation energy, higher tensile shear strength (TSS), and lower formaldehyde emission (FE), compared to those of neat resins [15]. The loading of pristine nanoclay (PNC) and modified nanoclay (MNC) into UF resins improved the adhesion and reduced the formaldehyde emission of UF resins in plywood [16]. UF resin was modified with wood-derived pyrolytic oil (PyO) to form various blending of pyrolytic oil-urea formaldehyde (PyOUF) adhesive and applied to make particleboard with higher property values [17]. The modification of UF resins with 5% octadecylamine (ODA)-modified bentonite (ODA-BNT) nanoclay showed better adhesion strength and lower free formaldehyde compared with neat UF resins [18]. The effect of sodium carboxymethyl cellulose (Na-CMC) added to UF resin on particleboard production has been investigated and the physico-mechanical properties of particleboard showed the best internal bond (IB) strength in the panels with the 20% Na-CMC admixture [19]. Finely ground birch (*Betula verrucosa* Ehrh.) bark (BB) can be effectively utilized as an eco-friendly additive in UF adhesives to reduce harmful formaldehyde emission up to 14% for the plywood sample produced with 15% BB [20]. UF resin (3%) and ammonium lignosulfonate (ALS) content varying from 6% to 10% (based on the dry fibers) was applied to bond high-density dry fiberboard (HDF) panels which exhibited very satisfactory physical and mechanical properties with extremely low formaldehyde content [21]. Phenol-urea-formaldehyde (PUF) resin

adhesives were modified by adding various ratios of resorcinol to make an easy-cured and high-performance phenol-resorcinol-urea-formaldehyde (PRUF) resin adhesive for wood manufacturing [22]. Better internal bond strengths of particleboards above the requirements of the standard EN 312 were obtained by the incorporation of 10% of hydroxymethylated thick spent sulfite liquor (TSSLH) with UF resin [23]. Highly branched polyurea (HBPU) was synthesized to modify traditional low molar ratio UF resin and with the addition of HBPU, the formaldehyde emission level of the plywood panels was decreased by more than 30% [24]. Thermoset epoxy resins were modified with thermoplastic polyethersulfone for high-performance applications [25]. Incorporation of plasticizers, like thermoplastic or rubbers to increase the toughness of thermosets is the most promising strategy [26]. Thermoplastic PVA is a water soluble hydrophilic synthetic polymer [27]. Thermoset UF resin is also a water-based polymer resin which has a wide range of raw materials [28]. Considering the miscibility and compatibility between water based thermoset UF resin and water based thermoplastic PVA resin, the present research was undertaken to investigate the effect of PVA resin on UF resin.

In this research, PVA modified UF resin has been synthesized in both liquid and solid form which can be used to make adhesive for plywood and wood products. To improve the tensile strength of the UF resin and to reduce the free formaldehyde content of UF resin, PVA was used as a modifier at prepolymer stage during the synthesis process of UF resin. FTIR, physico-mechanical and thermal characterization of the synthesized resins were investigated and reported.

MATERIALS AND METHODS

Materials

Starting material urea was supplied by BDH Laboratories Ltd., England. Formaldehyde (37%), polyvinyl alcohol, sodium hydroxide, lactic acid (90%), methanol, sodium sulphite were collected from Merck, Germany.

Synthesis of urea formaldehyde resin by condensation polymerization method

The first reaction was carried out following conventional method [29]. Then the reaction parameters of this work were selected from the series of reactions carried out by observing reaction parameters variation effect on fixed molar ratio of urea and formaldehyde following viscosity and FTIR spectroscopic analyses. Sodium hydroxide solution (NaOH) (1N) was prepared. Starting material urea and formaldehyde (37%) were taken into a round bottom flask at 1:2 molar ratios. At first step, hydroxymethylation of urea was done under basic conditions by adding NaOH solution (1N) to make pH of 7.5-8. The reaction flask was fitted with a condenser and stirred for one hour at room temperature. In the second step, lactic acid solution (1N) was prepared. The reaction mixture in the flask was heated at around 98-100°C. After 20 minutes, it was made acidic pH 5.5-6.5 by the addition of lactic acid (1N) and the condensation reaction was carried out for 4-5 hours. After completion of the reaction the reaction mixture was cooled and neutralized by adding sodium hydroxide (1N). Water was removed by vacuum distillation and then the solution was casted onto the glass petridish. It was dried in air first and then oven at 60°C. The dried sheets were taken for further investigation.

Synthesis of PVA modified urea formaldehyde resin by condensation polymerization method

At first stage, hydroxymethylation of urea was done according to the same method mentioned above for UF resin synthesis. Aqueous solutions of PVA (1, 2, 3, 4 and 5 wt. %) on the weight of urea and formaldehyde were prepared separately. At the second stage, after 2 hours of condensation reaction PVA solution was added into the reaction mixture and the condensation reaction was carried out for 2-3 hours at 98-100 °C. After completion of the reaction, the reaction mixture was cooled, neutralized and water was removed by vacuum distillation. The solution was casted onto the glass petridish and dried in air first and then oven at 60 °C. The resulted sheets were taken for further investigation. PVA modified UF resins were synthesized at different additions of PVA (1-5 wt. %) by following the same procedure described above. Flow chart of manufacturing process of UF and PVA modified UF is presented in Figure 1.

Fig. 1. Manufacturing process of UF resin and PVA modified UF resin

Determination of free formaldehyde content

Free formaldehyde content of synthesized resins was measured by sodium sulphite method [30]. Sodium sulphite solution was prepared and thymolphthalin indicator was added into it and then neutralized by 1 N HCL. Synthesized resins sample was added into the sodium sulphite solution and titrated with 1 N HCL until complete decolourization was obtained. The free formaldehyde (%) content was calculated from the formula given below:

$$\text{Free formaldehyde (\%)} = V \cdot c \cdot E / 10 \cdot \alpha$$

Where V is the volume of HCL (ml), c is the concentration of HCL (mol/dm³), E is the equivalent weight of formaldehyde, and α is the weight of samples (gm).

Determination of physical properties

The densities and pH of the synthesized liquid polymers were measured at 24°C using Density and Refractometer (DMA 5000, Anton Paar, Austria) and Jenway pH & conductivity meter, (model-3540, UK) respectively. Miscibility of synthesized liquid polymers in water

were observed and presented in result and discussion section. Melting points of the synthesized dried solid polymers were determined using dried solid particles of polymer using Gallenkamp melting point apparatus, made in England. The viscosities of liquid polymers were determined using Rotational Viscometer (Anton Paar, Austria) at 24°C and presented in result and discussion section.

FTIR spectroscopic characterization of the UF and modified UF resin

The infrared spectra of the UF, PVA and modified UF were recorded on a FT-IR/NIR Spectrometer (Frontier, Perkin Elmer, USA). The sample pellets for FTIR spectroscopy were prepared by dried powdered samples mixing with dried powdered potassium bromide (KBr) in a small agate mortar pestle. The mixture was taken in a die and pellet was made by applying vacuum pressure. FTIR spectra were obtained by printed form and presented in the result and discussion section.

Mechanical properties of the UF and modified UF resin

Mechanical properties of the dried sheet of UF and modified UF were performed by universal testing machine (model-Titan 5, James Heal, UK) for all specimens. Tests were performed according to ASTM D 882-02, (Standard Test Method for Tensile Properties of Thin Plastic Sheeting). The speed was 10 mm/min. The load vs elongation curves were obtained from the instrument and the tensile strength (σ_{UT}) is calculated from the formula below:

$$\text{Tensile strength, } \sigma_{UT} = W / A_T$$

Where W is breaking load and A_T is the cross sectional area.

Thermal properties of the UF and modified UF resin

Simultaneous thermal analysis (STA) of the dried UF and modified UF containing 2 wt% PVA were carried out using STA machine (model no-F₃ Jupiter, NETZSCH, Germany). The temperature range was 30-600°C, at a heating rate of 10°C/ min under a constant nitrogen flow rate of 80 ml/min.

RESULTS AND DISCUSSION

Synthesis of urea formaldehyde resin

In this work, UF resin was synthesized to make modification on it. The molar ratio of U/F was 0.5 and hydroxymethylation of urea occurred at the first stage. The first stage of condensation polymerization was to prepare monomethylol urea and dimethylol urea by hydroxymethylation of urea as illustrated below. The condensation reaction of monomethylol urea and dimethylol urea was carried out to prepare urea formaldehyde resin at 98-100 °C for 4-5 hours as illustrated below. Reaction parameters time, temperature and pH were selected by observing the results of these parameters variation effect on fixed molar ratio of urea and formaldehyde.

FTIR spectroscopic characterization of UF resin

The synthesized UF resin was characterized by infrared spectroscopic analysis. The FTIR spectrum of UF resin is presented in figure 2 (middle part) and described in the table 1. The IR spectrum shows characteristic bands of N-H stretching at the region of 3316.40 cm^{-1} . The characteristic bands at 1631.14 cm^{-1} and 1542.31 cm^{-1} are due to the C=O stretching and N-H bending vibrations. The spectrum is almost similar to the FTIR spectra of the cured UF resin [1, 12, 30].

Table 1. FT-IR spectral data of UF resin

Absorption bands (cm^{-1})	Assignment
3316.40	N-H stretching
1631.14	C=O stretching
1542.31	N-H bending
1383.34	-CH ₂ of methylene bridge
1255.81	C-N stretching
1194.49	C-O stretching
1121.55	N-CH ₂ -N asymmetric stretching
1012.44	C-OH stretching
904.56	C-O-C of ether linkage

Fig. 2. Infrared spectrum of synthesized PVA modified UF Resin (lower part), synthesized UF resin (middle part) and PVA (upper part) respectively

Synthesis of PVA modified UF resin

The modification of UF resin was done during the second stage of UF resin synthesis after 2 hours. PVA was added during the condensation reaction and at this stage prepolymer of UF was reacted with PVA. The condensation reaction between prepolymer of UF and PVA was continued for 2-3 hours to prepare PVA modified UF resin as illustrated below. Modification of UF resins were carried out at different additions of PVA (1-5 wt %) to find out the effect of addition amount of PVA on the properties of resins and the selected addition of PVA was found as 2 wt% by formaldehyde emission and tensile strength. The optimal addition amount of almond shells in UF resin is found as 3 wt% by formaldehyde emission and wet shear strength [13].

FT-IR spectroscopic characterization of modified UF resin

The PVA modified UF resin (containing 2 wt% PVA) was characterized by FTIR spectroscopic analysis. The FTIR spectrum of PVA and PVA modified UF resin are shown in figure 2 (upper and lower part respectively) and described in table 2-3. The FTIR spectrum of PVA modified UF resin (figure 2) shows the characteristic bands of N-H and O-H is overlapped and broadened at the region of 3328.25 cm^{-1} . Other position of bands were shifted

in PVA modified UF resin than UF resin which may be due to changes in the polarity of bonds. These observations indicated that structural changes occurred in modified UF resin and PVA structures were introduced into UF resin during condensation reaction.

Table 2. FT-IR spectral data of polyvinyl alcohol

Absorption bands (cm ⁻¹)	Assignment
3281	O-H stretching
2905	-CH stretching
1420	C=O bending
1323	C=O stretching
1092	-CH ₂ group

Table 3. FTIR spectral data of PVA modified UF resin

Absorption bands (cm ⁻¹)	Assignment
3328.25	N-H and O-H stretching
1637.99	C=O stretching
1554.78	N-H bending
1384.42	-CH ₂ of methylene bridge
1122.50	N-CH ₂ -N asymmetric stretching
1017.20	C-OH stretching

Physical properties of synthesized UF resin and PVA modified UF resin

Some physical properties of synthesized UF resin and PVA modified UF resin were measured and presented in table 4. Free formaldehyde content of PVA modified UF resin decreases with increasing PVA content. Similar observations were reported in biooil modified UF resin and melamine, ethylene urea, hexamethylenetetramine (HMTA) modified UF resin respectively [3, 30].

Table 4. Physical properties of UF resin and PVA modified UF resin

Name of synthesized polymer	Solubility in water at liquid state of polymer	pH at 24°C	Density (g/mL) at 24°C	Viscosity at 24°C (mPa.s)	Free formaldehyde content (%)	Melting Point
UF resin	Soluble	6.11	1.03	85.23	12	Decomposed at 180°C
1 wt. % PVA Modified UF resin	Soluble	6.83	1.05	98.36	6	
2 wt. % PVA Modified UF resin	Soluble	6.79	1.09	109.07	6	
3 wt.% PVA Modified UF resin	Soluble	6.75	1.14	110.33	5	
4 wt. % PVA Modified UF resin	Soluble	6.30	1.20	111.72	5	
5 wt.% PVA Modified UF resin	Soluble	6.15	1.27	115.11	4	

Mechanical properties of UF and PVA modified UF resin

Mechanical properties such as tensile strength and elongation at break (%) of all synthesized polymers were conducted by UTM. The tensile strength of the UF and modified UF resin with 1-5 wt% PVA are presented in figure 3. Tensile strength of 100% UF resin and 100% PVA is 0.13 MPa and 0.17 MPa respectively. It is found that tensile strengths of the UF resin increase with its modification with PVA. It is also found that the tensile strength of the modified UF is higher at 2 wt% PVA loading and then decreases with increasing PVA content. Similar trend of tensile strength was observed in modified melamine formaldehyde resin and modified epoxy resin [31-32]. The addition of PVA improved the tensile strength performance of the PVA modified UF resin due to the form of physical crosslinking between the resin with flexible chain of PVA, so PVA shared part of the stress uniformly when subjected to external forces that increased the tensile strength of modified resin. At higher loading of PVA after 2 wt%, the tensile strength of modified resin decreases with increasing of PVA due to critical content of PVA. This critical loading is mainly because at higher loading the distance between PVA becomes so small that they tend to stack together due to the van der Waals force that leading to non-uniform stress distribution between the resin and PVA [33]. Elongation at break of the UF resin and modified UF resin are presented in figure 4. Elongation at break of 100% UF resin is 271.69% and 100% PVA is 16.92%. It is observed from the figure that elongation at break of 100% UF resin decreases than modified UF resin. It is also observed that elongation at break of modified UF resin increases with increasing PVA content. The toughness or ductility of the modified UF resins decreases than UF resin caused by uncured state of UF. It is also observed that toughness or ductility property of modified UF resin increases with increasing of PVA content. UF resin was significantly toughened by polyurethane (PU) addition and the elongation at break of PU modified UF resin increased with increasing PU content [34].

Fig. 3. Tensile strength vs PVA wt. % of UF resin

Fig. 4. Elongation at break vs PVA wt. % of UF resin

Thermal properties of UF resin and PVA modified UF resin

Thermal analyses of UF resin and modified UF resin having 2 wt. % PVA were conducted by STA and the results are presented in the figure 5-6 and table 5 respectively. The thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) results of UF resin and modified UF resin are expressed in table 5. Temperature of initial mass loss (T_i °C) and temperature of maximum mass loss (T_{max} °C) with percentages of mass loss and percentage of residue with temperature are shown in table 5. From this comparative observation it is clear that modified UF is thermally more stable than UF. Almost similar TGA is found for neat UF resin but modification of UF with calcium carbonate has no significant effect on the thermal stability of UF resins [14].

The main characteristics parameters such as glass transition temperature (T_g) and melting point (T_m) of UF and modified UF is obtained from DSC analysis (figure 5-6). It is found from the figure 5-6 that the first physically change at differential peak temperature (DTp_1) and second physically change at differential peak temperature (DTp_2) are almost same for both UF and modified UF resins (table 5). The glass transition temperature (T_g) and melting point temperature (T_m) of UF may be 172.4°C and 282.4 °C where as for modified UF may be 169.7°C and 279.6°C respectively.

Table 5. STA data of UF resin and PVA modified UF resin

Sample name	T_i °C and mass loss (%)	T_{max} °C and mass loss (%)	Residue (%) at T °C	DTp_1	DTp_2
UF resin	97.7 °C 0.6	355.9 °C 72.55	20.04 at 647.2 °C	172.4 °C	282.4 °C
Modified UF resin having 2 wt.% PVA	99.26 °C 0.74	375.3 °C 76.45	15.76 at 647.1 °C	169.7 °C	279.6 °C

Fig. 5. TGA and DSC curve of UF resin by STA analysis

Fig. 6. TGA and DSC curve of modified UF resin having 2 wt. % PVA

SUMMARY

Synthesis of UF resin and its modification by PVA was successfully carried out. FTIR spectroscopic analyses showed the evidence of the structure of PVA modified UF resin. The amount of free formaldehyde of PVA modified UF resin decreased than neat UF resin and it also decreases with increasing of PVA content in the UF resin. Tensile strength of modified UF resin is higher than that of unmodified UF resin and the highest tensile strength obtained for 2 wt% PVA loaded UF resin. So it can be concluded that addition of PVA can strengthen UF resin by improving its tensile strength and reducing brittleness. Thermo gravimetric analysis also indicated that PVA modified UF is thermally more stable than unmodified UF resin. Therefore, PVA is a potential modifier for UF resin to improve its performance. So, it can be said that PVA modified UF resin will improve the performance of this resin for use as adhesive for plywood and for wood products.

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