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Factor Affecting Gel Time/Process-Ability of Urea Formaldehyde Resin Based Wood Adhesives

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Abstract

Urea-formaldehyde (UF) resin presents the most utilized adhesive system in the manufacture of plywood, particleboard and fiberboard. At the temperatures above 100˚C in the presence of hardener, this resin undergoes cross-linking reaction and the formation of three dimensional cross linked structures takes place and bonding of wood particles in a hot press [1]. UF powder resins show high reactivity and good performance in the production and by their low price; however they lack in water resistance of the hardened resin [2]. Urea-formaldehyde (UF) resins are the most important type of adhesive resins for the production of wood based panels but process-ability and curing behavior of urea formaldehyde resin depended on various factors related to resin properties, types of wood and their properties, amount & type of catalyst, types and amount of polymers addition and environmental conditions [3]. This factor decides the process-ability of UF resin based composite during manufacturing of plywood, particle board and fiberboard. In this review paper, various factors affecting gel time and process-ability of UF resin based wood composite are reviewed.

Keywords

Urea Formaldehyde Resins, Catalysts, Gel Time, Wood, pH, Polyvinyl Acetate, Composite

1. Introduction

Urea-formaldehyde (UF) resin is one of the most important thermosetting adhesive systems of interior class with the largest tonnage consumption (approximately 1 million metric tons/annum) in wood processing industry and particularly in wood-based panel (WBP) production [4]. The resin is used in the pro-

duction of an adhesive for bonding particleboard (61%), medium density fiberboard (27%), hardwood plywood (5%) and a laminating adhesive for bonding (7%) for example, furniture case goods, overlays to panels and interior flush doors [2].

It's relatively low costing and excellent processing features enable the production of panels with required performance and competitive price. UF resin has the main disadvantage of poor resistance to moisture and water, especially at higher temperatures thus it is not recommended to use of UF resins for exterior applications [5] [6].

Ammonium chloride (NH_4Cl) is a common and effective hardener used for accelerating UF-resin curing. In this case, a higher molar ratio (1:1.6 - 1:2) of the UF resin plays a role in supplying enough free formaldehyde to the system to react with NH_4Cl and release HCl. However, the UF resins currently used in the wood product industry are all lower molar ratio resins (normally 1:1.05 to 1:1.1). The limited free formaldehyde in the system limits the release of HCl by reacting with added NH_4Cl [7] [8] [9] [10] [11]. In presence of acid catalyst, urea formaldehyde powder resin undergoes following reactions is shown in **Figure 1**.

-Methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules.

-Methylene ether linkages by the reaction of two methylol groups.

-Methylene linkages from methylene ether linkages by the splitting out of formaldehyde.

-Methylene linkages by the reaction of methylol groups splitting out water and formaldehyde in the process.

In Wood based composite production influence of wood component is also important in the process of manufacturing. Change in fiber source, may have detrimental effects on the mechanical and physical properties of the panel and

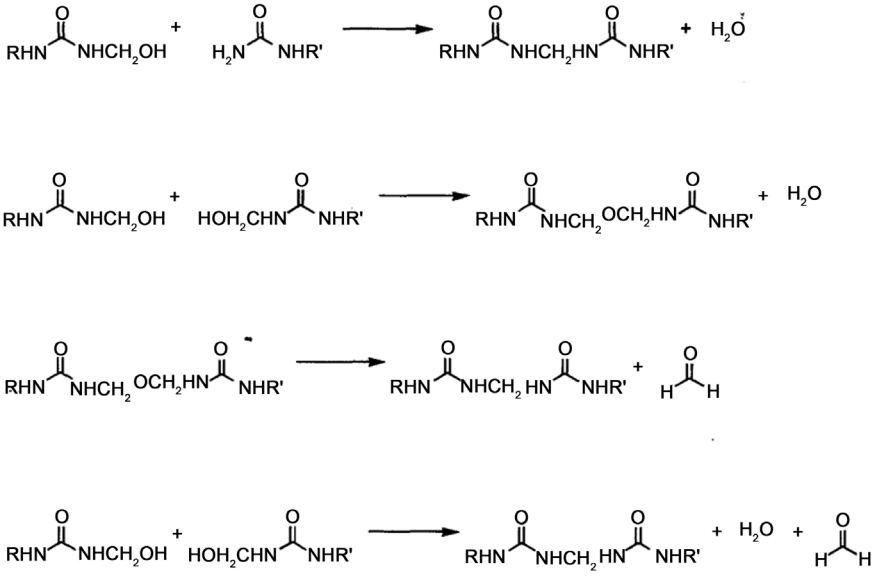

Figure 1. Condensation reactions.

requires changes in the processing conditions, including the resin system used. The acidity of wood and the acid catalyst mixed in the adhesive play a very important role in providing (or generating) the optimum combined pH environment at the inter-phase during UF resin curing. To obtain optimum bond strength, the press time and temperature must be adjusted for the pH environment. If this correction is not precise, the glue line will be uncured or over-cured and will result in poor bond strength [12] [13] [14] [15] [16]. Gel time is a parameter which can correlate with process-ability of manufacturing of wood-based composite panels.

2. Factors Affecting Gel Time of UF Resin

Gel time of UF resin depends majorly on wood substrate, final properties of UF resin and formulation components.

2.1. Wood Related Factors

The four major components of woody biomass are: cellulose, hemicelluloses, lignin, and mineral components.

2.1.1. Wood Extractives

Some earlier studies have shown that the gel-time of UF adhesive is affected by wood extractives (Albriton and Short 1979). Another study revealed that the gel-time of UF adhesive for a defined temperature is strongly dependent on the pH and the buffer capacity of wood extracts (Johns and Naizi 1980). Stefke and Dunky (2006) have noticed only slightly retarding effect of cold water wood extractives on curing of UF adhesive. More detailed information about this problem, especially concerning kinetic analysis of UF adhesive curing, was obtained by the differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods (Mizumachi 1973, Xing *et al.* 2005, Gao *et al.* 2008). Albritton and Short (1979) as well as Slay *et al.* (1980) reported that both ethanol-soluble and water-soluble extractives from pressure-refined fibers had a significant effect on UF resin gel time. Some researchers have shown that wood extractives [12] [17] [18] [19] [20] [21] strongly affect the gel time of UF resins. Barks showed lower pH values and higher acid and alkaline buffering capacities than wood of the same species, which may be due to its plentiful extractives.

2.1.2. Wood pH Values (Fiber Acidity)

Johns and Niazi (1980) and Peng and Li (1983) found that both wood buffering capacity and pH were strongly related to the gel time of UF resin mixed with wood flours. Park *et al.* (2001) revealed that fiber acidity strongly affected the internal bond strength (IB) of MDF panels boned with UF resin. Some researchers have shown that wood pH values, and buffering capacities [17] [18] [19] [20] [21] strongly affect the gel time of UF resins. Park *et al* revealed that the fiber acidity strongly affected the internal bond strength of medium-density fiberboard panels bonded with a UF resin [22]. Xing *et al* also reported that the pH value and buffering capacities of refined fibers affect some properties of me-

dium-density fiberboard panels [23].

Key Points related to wood pH:

- pH and buffering capacity varies depending on the type of raw material..
- The softwood species studied had lower pH values than hardwood species.
- It indicated that with increasing tree age, poplar wood pH value increased, whereas acid buffering capacity decreased.
- It is known that soil is mostly acid, which explains why the pH value of most wood species is about 4 - 5 [12] [13] [14] [15] [16].

Wood pH value:

There are three procedures used, to obtain wood pH measurement.

1. Hot water extraction
2. Cold water extraction
3. Press chips to obtain pressed [17].

Buffering capacity of wood:

The aqueous extract is prepared by refluxing 25 g of dry furnish in 200 g of distilled water for 20 min. Two replicates for each sample are prepared. After refluxing, the mixture is filtered through a filter paper using a vacuum. The aqueous extract is diluted to 500 ml and cooled to room temperature before titration. All pH and buffering capacity measurements are made with a pH meter. Prior to each titration, the pH meter is calibrated with standardized buffer solution to a pH of either 4 or 7, depending on the type of measurement to be done. After calibration, 100 ml of extract solution is pipette into a 200-ml beaker, the initial pH of the solution is recorded, and it is then titrated to a pH of 3 or 8 with nominal 0.025 N H_2SO_4 or 0.025 N NaOH solutions. For each titration, two replicate measurements are done. Thus, the initial pH value for each sample is the average of eight measurements, while each buffering capacity value (mmol l^{y1}) is the mean of four determinations [12] [13] [14] [15] [16].

2.1.3. Wood Particle Size/Fiber Dimensions

Medved and Resniksuggested that reducing the wood particle size/fiber dimensions could reduce the gel time of UF resins [22]. Molecular weight of UF resin is designed by considering wood structural properties.

2.2. Urea-Formaldehyde Resin Related Factors

2.2.1. Formaldehyde to Urea Ratio

Formaldehyde to urea ratio has been dramatically lowered to approximately 1.02 to 1 by addition of urea at the end of synthesis and by other methods. It is also necessary to use more amount of catalyst when working with UF resin of lower Formaldehyde: Urea molar ratio, as the gel time of resin is slower. If there is less amount of free formaldehyde in system it will increase UF gel time and vice versa.

2.2.2. % Solid Content and pH

The gel time of the UF resin is strongly affected by its solid content and pH of UF resin. The gel time of the UF resin decreased with increasing resin solid con-

tent. It is also depended on final pH of UF resin and pH also depended on %solid content. The concentration of the UF resin decreased with decreasing solid content. More water in the system diluted the curing reactions and acted as an energy barrier to resin curing. Therefore, the cure rate decreased, and this resulted in a longer gel time. Thus, it is important to control the moisture content of raw materials in the manufacture of wood-composite products. The effect of the catalyst content on the gel time is more efficient for resins of lower solid contents than those of higher solid contents [24].

2.3. Adhesive Formulation Related Factors

2.3.1. Type of Catalysts & Amount of Catalysts

Zanetti and Pizzi (2003) suggested that catalyst buffering action had strong effects on pH, hardening speed, degradation reactions, and the degree of network formed of MUF resins. UO *et al.* (1998) suggested that the gel time of UF resin was directly correlated to pH and acid buffering capacity and inversely correlated to alkaline buffering capacity of six shrub species. The type and content of the catalyst directly affect UF-resin curing and the performances of final products. Poblete and Pinto reported that increasing the level of the catalyst reduces the pH and gel time of UF resins [25]. Myers suggested that the desirability of neutralizing an acidic cure catalyst after wood bonding reduced formaldehyde liberation and increased the durability of bonded products [26]. The results of Elbert show that formaldehyde emissions from UF resins and particleboards are affected by the type and content of the catalyst [27]. However, Lee *et al.* suggested that the amount of the hardener, which in their case varied from 0.8 to 3.2% (based on a resin with 66% solids), had practically no influence on the release of volatile acids from particleboards [28]. Pinto and Poblete showed that increasing the amount of the catalyst caused a reduction in the thickness swelling and water absorption and an improvement in the mechanical properties of particleboards [29]. However, the addition of an acid catalyst could increase the degradation of a cured UF resin in particleboards [30]. Xing *et al.* indicated that an optimal range of catalyst contents exists for the curing of UF resins [31]. Different acids are also used as curing catalyst.

Gel time measurement:

UF adhesive is diluted to 50% solid content and catalyst NH_4Cl is added in range from 0.2% to 2% w/w. The test tube is filled with 2 g of prepared adhesive as above and immersed into boiling water at constant stirring speed throughout the test. The elapsed time until the point when no further stirring is possible is defined as the gel time for a given adhesive sample.

2.3.2. Other Polymer Addition

Extensive study have been conducted to review the use of extenders for UF resin adhesive as several protein and starch based materials were in use. Most of the plywood industries are already using the extenders and also mixture of extender in their products which are cost effective.

Blending of UF resin with starch

UF resin was reactively blended with various concentration of starch [32], esterified starch [33] [34] [35] and oxidized starch [36] as wood and wood composite adhesive. It is found that new system with UF-starch blending has advantages of low brittleness, low formaldehyde emission and water resistance characteristics [32]. In esterified-starch blended UF adhesive strength found to be comparable with synthetic resin adhesive system and content of free formaldehyde was lower than 0.3% [23] [24] [25]. Oxidized starch blended UF resin adhesive has good chemical stability, insulating properties, temperature resistance, aging resistance, oil resistance and mildew resistance and environmentally-friendly starch adhesive has no harm to the human body and can be applied to wood adhesion [37] [38] [39]. UF resin and modified starch mutual react and form a net structure, water resistance of starch glue was improved, and drying time was shortened [40] [41] [42]. So ultimately in above all systems few parts of UF were replaced by starch, because of which formaldehyde emissions were reduced and cost is maintained.

Addition of cross-linker in starch-urea formaldehyde blends system

UF-Starch blended adhesives were modified with different cross-linkers for improvement in performance properties. Starch adhesives were modified by isocyanate as cross-linker [43] [44] [45] [46] [47] [48] as well as starch adhesive with polyvinyl alcohol, borax, and carboxy methyl cellulose (CMC) as system [4] [49] [50] [51] [52] for wood composite can be prepared with isocyante as cross-linker, influence factors on the bonding strength and water resistance of starch adhesive were studied by different solid content, adding isocyanate and additives like PVA, Acrylic emulsion. Bonding strength and water resistance were improved significantly by adding additives and isocyanates to starch. An environmentally friendly wood adhesive was developed by cross-linking cornstarch-UF blend system with hexamethoxymethylmelamine (HMMM). It exhibited excellent mechanical properties comparable to many of the commercially available urea-formaldehyde plywood adhesives used for interior applications [53].

Blending of UF resin with polyvinyl acetate emulsion adhesive

The UF adhesive was modified with poly (vinyl acetate) to increase water resistance.

Modification UF with the use of various natural derived materials like tannin, lignin, cellulose, crude pyrolysis oil of wood, and soy have been carried out [54] [55] [56] [57]. Also combination of UF and MF is used for plywood industries.

3. Conclusions

Process-ability/manufacturing of wood composite like medium density board, particle board, plywood based on UF resin is a difficult task for manufactures because various factors that can interfere with the curing process. From this review paper, we concluded that gel time of urea formaldehyde resin is depended on following factors:

1) Wood extractives

2) Wood pH values (Fiber acidity)

3) Wood particle size/fiber dimensions

4) Formaldehyde: Urea ratio

5) %Solid content of UF resin

6) Type of catalysts & Amount of catalysts

7) Other polymer addition

This factor should be considered during manufacturing of wood composite.

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