



# Insights into the development of crystallinity in liquid urea-formaldehyde resins



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## ABSTRACT

Differently from most thermoset materials, urea-formaldehyde (UF) resins display the appearance of crystalline domains. In the effort of understanding the mechanism of formation of such crystals, wide angle X-ray diffraction (WAXD), infrared spectroscopy and transmission electron microscopy (TEM) were applied. Liquid UF resins with two different F/U mole ratios (i.e. 1.6 and 1.0) were investigated as a function of hardener level and curing times at room temperature. The WAXD results showed that the liquid UF resin with a low F/U mole ratio had a greater crystallinity than the one with a high F/U mole ratio. An advance in crystal formation in the low F/U mole UF resins was visible, especially in the first phases of curing. However, there were no significant differences in the degree of crystallinity as a function of hardener level. IR spectroscopy highlighted the important role of methylolated species in the formation of crystals. TEM results also confirmed the presence of crystals in all the considered liquid UF resins. The concentration of the hardener and the curing time were critical in shaping morphology and particle dispersion. As a function of the curing conditions, the globular structures present in the samples can aggregate into different morphologies, which can be fibrillar and also lamellar. The obtained results stress the importance of controlling the subtle interplay between crosslinking and formulation for the obtainment and control of the size, quantity and morphology of crystals in UF resins, and therefore for an effective tuning of their properties.

## 1. Introduction

Urea-formaldehyde (UF) resin is one of the most widely used thermosetting adhesives in the manufacture of wood-based composite panels such as plywood, particleboard, and medium-density fiberboard because it possesses several features that are desirable for industrial applications [25,30]. For example, UF resin has high reactivity and low press time for full curing, clear glue line, and relatively low price. Unfortunately, there are also some limitations that must be overcome for continuing industrial use of these adhesives, such as low moisture resistance and the tendency of the cured adhesive to emit formaldehyde [12] during manufacturing and service life, which causes a condition commonly referred to as “sick building syndrome” [13]. Fortunately, considerable research efforts are being devoted to overcoming these problems and to the engineering of UF resins for other quality improvements.

Information available to date suggests that the reversibility of the aminomethylene link in UF resins over time is a main reason for long term formaldehyde emission and also for the lower moisture resistance

of wood-based composite panels [4]. In general, the most widely used approaches for reducing formaldehyde emission of UF resin bonded products are either lowering the formaldehyde to urea (F/U) molar ratio or modifying UF resins in either changing the synthesis parameters or adding scavengers following synthesis. However the curing rate of a UF resin with low free formaldehyde content is usually slower and the bond strength of the UF resin bonded product is also lower, which are the main challenges involved in the industrial scale use of low formaldehyde UF resins. Therefore, understanding the hydrolysis process of UF adhesives is important for engineering the resins, in order to minimize formaldehyde emissions. In this regard, it is essential to understand the physical and chemical characteristics of UF resins.

Interestingly, and unexpectedly for a thermosetting polymeric material, the presence of a crystal structure in a UF resin has been occasionally reported [29,12,27,16,23,24,14,5]. Stuligross and Koutsky [29] reported the colloidal character and crystallinity of UF resin when the F/U mole ratio was decreased to 1.0 and also showed that the resin formulation did not change the crystal structure but only the degree of

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crystallinity. In a comparison between a protein and a UF resin, Dunker et al. [3] also reported that a UF resin contained colloidal regions of a semicrystalline nature, and ascribed the origin of the crystal structure to a high degree of order due to hydrogen bonding between colloidal particles. They also mentioned another possibility, i.e. that the crystalline regions could have arisen from the crystallization of some minority components of the UF resin, such as urons or other compounds containing other types of ring structure. John and Dunker (1986) also reported that a physical association in the UF resin solution was related to the crystalline region in solid form. The crystallinity of the cured UF resins depended on the F/U mole ratio and  $\text{NH}_4\text{Cl}$  hardener content, and the crystalline regions of the UF resin corresponded to the mixtures of minimum energy conformations in its molecular forms [14]. Pratt et al. [27] extensively investigated the colloidal particles of a UF resin, which were believed to be related to its crystalline region. They also postulated that the colloidal particles were covered by double layers of formaldehyde. The crystallinity of a melamine-formaldehyde (MF) resin solution was also extensively studied [10,11,15,9]. In addition, in these materials, supramolecular aggregation was observed, due to cooperative secondary intermolecular interactions between monomeric and oligomeric species [10,9]. Colloidal particle formation followed by their clustering has been shown to be the normal way of ageing of aminoplastic resins [31]. Depres and Pizzi [2] also showed that filament-like colloidal aggregates were initially formed in a UF resin, which eventually changed to super-clusters by coalescence during aging. Recently, it was reported that cured UF resins of low F/U mole ratio possessed a greater amount of closely packed spherical structures than those of high F/U mole ratio [20], and that spherical structures were present also in high F/U mole ratio (1.6) UF resins even if they were sparsely observed [20]. Recently, Park and Causin [22] reported that particles are larger in size and more abundant in low mole UF resins, which also exhibit crystallinity. They also reported that, as the F/U ratio decreased, the spatial arrangement of crystalline domains was more regular and the distance between the crystalline domains of UF resins decreased.

As pointed out earlier, the lower formaldehyde emission associated with low F/U mole ratio resins happens at the expense of performance, especially of adhesion strength. This latter property is in turn determined by the ability of adhesive evenly wetting the surfaces to be connected. The reason for the lower adhesion strength with low F/U mole ratio resins has been investigated in the past. In particular, Pizzi showed, by comparing molecular mechanics simulations and experimental evidence, that the species mainly responsible for adhesion to cellulose are methylolated oligomers (Pizzi, 1999). A lower F/U ratio inevitably decreases the availability of methylolated species and therefore has a detrimental effect on bond strength. Ferg et al. [5] investigated the existence of a correlation between crystallinity and adhesion strength of the hardened resin. They argued that, analogously to other semicrystalline polymers, the crystalline regions are not physically separated from the amorphous domains. Rather, the same molecules can participate with different portions of their chains to the crystalline or amorphous regions of the semicrystalline framework. The consequence of this behaviour is that, in the crystalline domains, crosslinking by  $-\text{CH}_2-$  bridges does not occur. Since just secondary intermolecular forces keep the molecules in the crystalline state, the result is a weaker adhesion strength. Such a decrease in performance is therefore not related to the presence *per se* of the crystals in the resin, but on a lower entity of crosslinking which can be attained, given the lower F/U molar ratio. The role of crystallinity on decreasing bond strength is ultimately linked to the fact that crystalline or orderly packed UF resin molecules are not contributing to the formation of tridimensional network structure in the bond-line [5].

Another important aspect to consider is that the crystallinity of a UF resin may change when in contact with wood. Levendis et al. [14] maintained that a UF resin lost crystallinity when in contact with wood. Consequently, it was not considered of much importance to understand

more about crystals in UF resins, if they disappeared under applicative conditions. However, recent results of our group showed that a UF resin cured in the presence of wood still contained polycrystals with various morphologies in tracheid lumen [28]. Moreover, in previous work [22,20], has shown that crystals, when present in UF resins, are quite inhomogeneously dispersed, thereby probably contributing to the inefficiency in the adhesion of UF resins with a low F/U ratio as pointed out by Pizzi [23].

The motivation of this study is therefore to shed some more light on the mode and on the kinetics of formation of crystallinity in UF resins. Understanding this issue in more detail, in fact, offers the possibility to devise pathways to avoid or hinder the formation of crystals, thereby exploiting all the functionalities present in the system for creating a widely crosslinked framework rather than “wasting” some of them creating crystals. Another possible consequence of the understanding of crystallisation can be that of being able to control, spatially and temporally, the formation of crystals, homogeneously distributing them in the whole material. Crystal formation could also turn out to be advantageous for certain aspects of the performance of glues, namely for their mechanical properties. In analogy to natural rubber [1], in fact, crystalline domains, if grown in a controlled and homogenous way, could indeed act as fillers, achieving a self-reinforced all-polymeric nanocomposite with improved mechanical properties than the neat, non-crystalline resin.

Even though a previous study by one of the authors showed that crystalline regions may form in cured UF resins and that such domains are not significantly influenced by curing time, temperature, or hardener levels [20], however, there is a lack of evidence on the crystallinity and on the domains of these crystallites in liquid UF resins. This is especially relevant because it allows us to detect at which stage the crystals start to appear and how their formation changes with curing time, which impacts the building of a three dimensional network and subsequently the performance of the resin when used as an adhesive. Therefore, this study was initiated to examine the crystallinity and micro-morphological features of liquid UF resins using wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM), with the expectation that the information obtained would be helpful in understanding why low F/U mole ratio UF resins, in general, provided a poor adhesion at the expense of a low formaldehyde emission from wood-based composite panels bonded with them. In order to achieve this, we investigated the degree of crystallinity and the micromorphological features of liquid UF resins with low and high F/U mole ratios as a function of curing time and hardener levels at ambient temperature.

## 2. Experimental

### 2.1. Materials

Both urea and formalin (37%) used for the synthesis of UF resins were technical grade. Aqueous solutions of both formic acid (20 wt%) and sodium hydroxide (20 wt%) were used to adjust the pH during the UF resin synthesis process. An aqueous solution (20 wt%) of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) was used as hardener.

### 2.2. Preparation and characterization of UF resins

Two types of UF resin with low and high F/U mole ratios (i.e., 1.0 and 1.6) were prepared at a laboratory scale following a conventional alkaline-acid two-step reaction (pH 7.8 for addition and 4.6 for condensation) by adding the second urea. Details of liquid UF resin synthesis and measurements of the resin properties as shown in Table 1 are described in a previous work [19]. After urea had dissolved, the UF resin was cooled to room temperature, and the pH adjusted to 8.0.

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