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# 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 $NH_4Cl$ 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 superclusters 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 $-CH_2-$ 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 inhomogenously 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, homogenously 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 ($NH_4Cl$) 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.

**Table 1**
Properties of liquid UF resins with low and high F/U mole ratio.

| F/U mole ratio | Solids content (%) | Viscosity (mPa·s) | Gel time (s) |
|---|---|---|---|
| 1.6 | 60.1 | 718 | 66 |
| 1.0 | 61.8 | 585 | 204 |

### 2.3. Liquid UF resin sample preparation for WAXD and TEM

About 10 g of each liquid UF resin with low and high F/U mole ratio was mixed with liquid $NH_4Cl$ solution as hardener at different addition levels such as 0 wt%, 0.1 wt%, 3 wt%, and 5 wt% based on the non-volatile solid content of the liquid resin.

For the WAXD sample preparation, each of these liquid UF resins were diluted in dimethyl sulfoxide (DMSO) to 5 wt% concentration based on the non-volatile solid content. About 10 g of the diluted liquid UF resin was poured onto an X-ray thin film of polyimide (Kapton 9430, PANalytical, Netherlands) that was insensitive to X-rays, and then was exposed to X-ray radiation.

### 2.4. Wide-angle X-ray diffraction

The WAXD patterns were recorded in the diffraction angle (2θ) range from 10 to 50° with a step of 0.05° by a X-ray Diffractometer (Empyrean, PANalytical, Netherlands) (located at Korea Basic Science Institute, Daegu, Korea), working in a transmission geometry on the diffracted beam. Cu-$K_\alpha$ (1.540 Å) radiation was used for the diffractometer.

### 2.5. Infrared spectroscopy

IR absorption spectra were acquired on a Nexus FTIR spectrometer (Thermo Nicolet). A layer of resin was deposited between two NaCl pellets. The spectral region spanned was from 4000 to 450 $cm^{-1}$, with a resolution of 4 $cm^{-1}$. Two hundred and fifty-six acquisitions were gathered.

### 2.6. Transmission electron microscopy

For TEM sample preparation, drops of each diluted liquid UF resin in DMSO with different hardener levels were applied dropwise onto parafilm. Then, a carbon-coated 100-mesh copper grid was placed on the liquid UF resin drop. After 10 seconds, the grid was removed using fine forceps and excess liquid UF resin was removed from the edge of the grid with filter paper. The grids were then kept in a convection oven at 50 °C for 24 h. After that, the grids were kept in a petri dish prior to stain. The specimens were then negatively stained with 2% uranyl acetate. The procedure is as follows: a small drop of 2% uranyl acetate aqueous solution was applied dropwise onto parafilm using a glass pipet. The specimen was then placed thereon for 10 s and immediately removed using forceps for washing with filtered water (purified water was filtered using a disposable syringe, with pore size 0.45 µm prior to use) twice. The specimens were viewed with a H-7100 Hitachi TEM operating at 75 kV (located at Korea Basic Science Institute, Daegu, South Korea).

## 3. Results and discussion

### 3.1. Properties of UF resins

The properties of the UF resins studied in this work are shown in Table 1. As the F/U mole ratio decreased, a slight increase in the non-volatile solids content was recorded. This can be ascribed to the adjustment of the final F/U mole ratio by addition of the second urea. The viscosity and the gelation time of the resin adhesive decreased as the F/U mole ratio decreased. In other words, a lower F/U mole ratio is associated with a reduction in the reactivity of the resin adhesive. A lower viscosity is related to the degree of polymerization and improves adhesion, but, as a consequence, it is associated with a lower cohesion strength. This could be due to a decrease in the amount of free formaldehyde in the UF resin adhesive, which makes the curing conditions less acidic. It is already known that free formaldehyde in a UF resin decreases with a decrease in the F/U mole ratio [18].

### 3.2. Development of crystallinity in UF resin adhesives

It has been already noted by some of us [20] and by other authors [29,27,3]; Despres and Pizzi, 2006) that the development of crystalline regions within UF resins could be detrimental for some properties, viz. adhesive strength, but at the same time it can decrease formaldehyde emissions. The main reason why crystalline domains have a negative effect on bond strength lies in the fact that at low F/U ratios crosslinking is less efficient, and that the molecules arranged in the crystal lattice cannot participate in the formation of the crosslinked structure of the resin, whereas they are kept together just by comparatively weak intermolecular interactions [5]. The kinetics of crystal formation was therefore studied in this work through time-dependent wide-angle X-ray diffraction measurements. Fig. 1 compares the WAXD patterns as a function of time obtained from a UF resin with an F/U ratio of 1.0 and with varying hardener contents.

On the basis of what was reported earlier [22], the peaks marked by an asterisk in Fig. 1a are indicative of the presence of a crystalline phase, superposed to an amorphous halo, which is also shown in Fig. 1a. The WAXD traces recorded in this work are similar to those observed by Park and Jeong [21]. The nature of the crystalline phase can be attributed to a mixture, mainly of dimethylol urea, with minor contributions from urea and monomethylol urea [21]. A distinct crystallinity is evident in all the samples with a low F/U ratio, i.e. F/U=1.0, confirming the literature [7,26]. However, it is notable that crystalline domains are present in the material right after mixing, at t=0 of the experiments and that crystallinity is rather independent of hardener content. Fig. 2 shows the development of the degree of crystallinity as a function of time in the studied samples.

The degree of crystallinity tends to gradually increase in the first 400 minutes, eventually reaching a plateau. Both the initial and the final degrees of crystallinity are the same, within experimental error, for all samples sharing the same F/U ratio, irrespective of hardener content. The rate of development of crystallinity, indicated by the slope of the diagrams in Fig. 2, does not depend much on the F/U ratio. In other words, the F/U ratio influences only the quantity of crystalline domains, which however develop in about the same amount of time. A similar behavior was observed on the sample series with the larger F/U ratio of 1.6 (Fig. 3).

The most notable difference was that the degree of crystallinity was much lower in this case: the crystalline peaks, which in Fig. 1 were sharp and intense, are much broader and weaker in Fig. 3, reflecting a smaller quantity and size of crystalline domains.

However, also in this case, crystalline peaks appear in the XRD pattern since the beginning of the experiment and without any hardener added (Fig. 3a). This is a clear indication that the crystallinity in UF resins is not associated with the curing step, but develops with the formation of methylolurea species. This is confirmed by the similarity of the XRD patterns of the UF resins with that of dimethylolurea crystals [21]. IR spectroscopy further corroborated the critical role played by methylolated species in the crystallization of UF resins. Fig. 4 compares the IR spectra of the resins with different F/U mole ratios.

The FTIR spectra of liquid UF resins with F/U mole ratios of 1.0 and 1.6 are quite similar to each other, but there are some differences in absorbance bands relating to specific chemical groups. These differences were used to compare the chemical features of two different

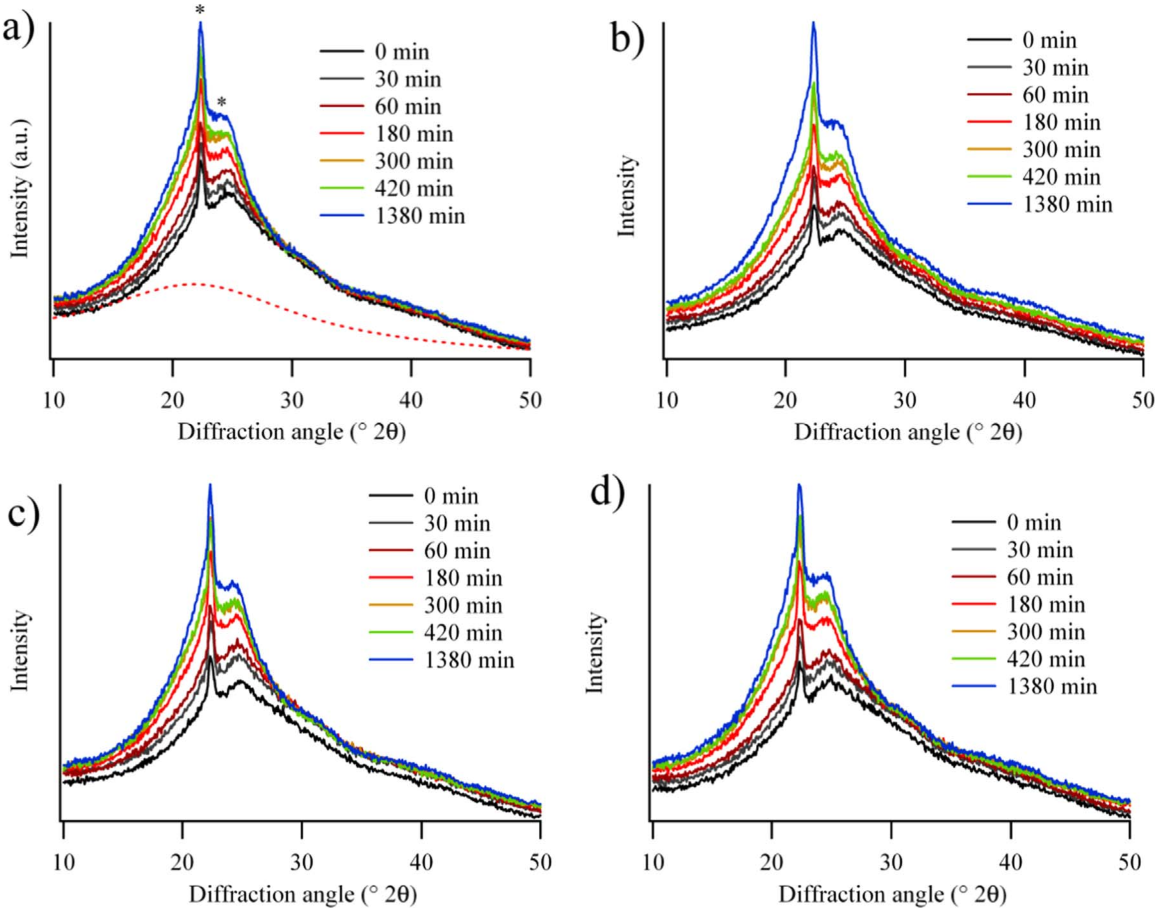

**Fig. 1.** WAXD patterns of UF resins with F/U ratio = 1.0 with varying hardener ($NH_4Cl$ solution, 20% w/w) content, taken at different times. a) 0% hardener, b) 0.1% hardener, c) 3% hardener, and d) 5% hardener. The dotted line in part a) is the amorphous halo used in the fitting of the experimental traces.

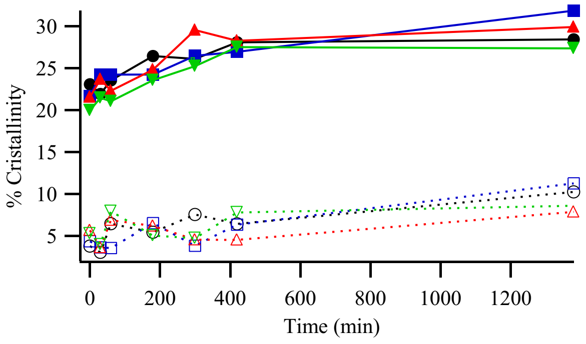

**Fig. 2.** Degree of crystallinity as a function of time in the studied samples. Filled symbols and solid lines represent the resin with F/U ratio = 1.0, open symbols and dotted lines represent the resin with F/U ratio = 1.6. •,○ 0% hardener, ■,□: 0.1% hardener, ▲,Δ: 3% hardener, ▼,∇: 5% hardener. The lines are added just to guide the eye.

UF resins. The spectra for a F/U mole ratio resin of 1.0 showed more absorbance bands (arrow heads) compared to those of a resin with a F/U mole ratio of 1.6 (arrows).

Additional bands, namely at 1440, 1351, and 1033 $cm^{-1}$ (arrow heads) appeared for the UF resin with a 1.0 F/U mole ratio. Two absorptions at 1440 and 1351 $cm^{-1}$, that are assigned to CH and amide (NH) stretching, indicate the presence of monomethylolurea, as confirmed by the bands at 1033 $cm^{-1}$ and at 1135 $cm^{-1}$ that are related to C-O-C from monomethylolurea [17,8].

Liquid UF resin with a 1.6 F/U mole ratio showed a band at 1016 $cm^{-1}$ (arrow) which is assigned to the C-O of $CH_2OH$ from dimethylolurea [8], indicating that a high F/U mole ratio UF resin contains various methylolated ureas. The availability of several methylolated species is indeed one of the reasons for the better adhesive strength of resins with a high F/U ratio. These results indicate that a high F/U mole ratio UF resin contains more branched polymethylolated moieties, whereas in low F/U mole ratio UF resins monomethylated species predominate with a more extensive formation of linear chains, as evidenced by the strong signal associated with C-O-C linkages. These differences help low F/U mole ratio UF resins form more ordered crystal structures.

Even though the curing step is not necessary for the insurgence of crystals in UF resins, it is expected to have a relevant role in shaping the morphology of the crystals. The development of crystals in a medium, such as the liquid resin without hardener, which does not change its physical state and its viscosity, will be different from that in a system which gradually proceeds from the liquid to the solid state, such as a resin during curing. This was studied using TEM with the results reported in the following section.

### *3.3. Micro-morphological features of UF resin adhesives*

Micro-morphological features in liquid UF resins of two different F/U mole ratios (1.0 and 1.6) were examined by TEM in relation to different hardener levels and curing time periods. Although the effect of different hardeners levels and curing time periods on the curing behavior of UF resins has been examined previously [19], little information exists on the micro-morphological characteristics of liquid UF resins.

#### *3.3.1. Micro-morphology of 1.0 F/U mole ratio UF resin*

Fig. 5 illustrates the micro structural characteristics of the 1.0 mol UF resin without hardener. Discrete globular particles (circles) are

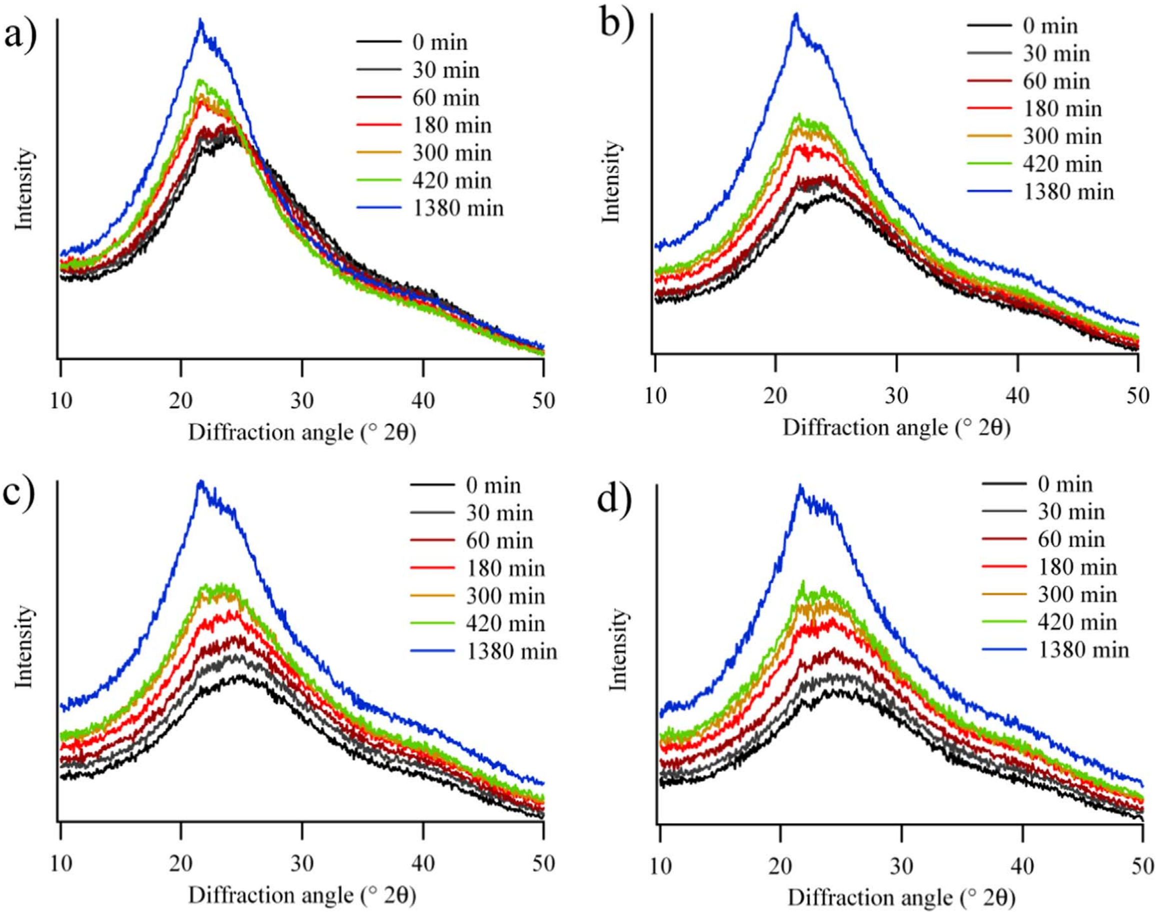

**Fig. 3.** WAXD patterns of UF resins with F/U ratio = 1.6 with varying hardener ($NH_4Cl$ solution, 20% w/w) content, taken at different times. a) 0% hardener, b) 0.1% hardener, c) 3% hardener, d) 5% hardener.

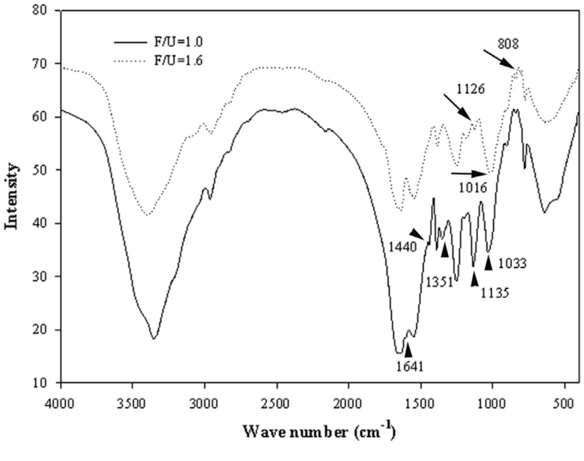

**Fig. 4.** FTIR spectra of liquid UF resins of F/U mole ratio of 1.0 and 1.6.

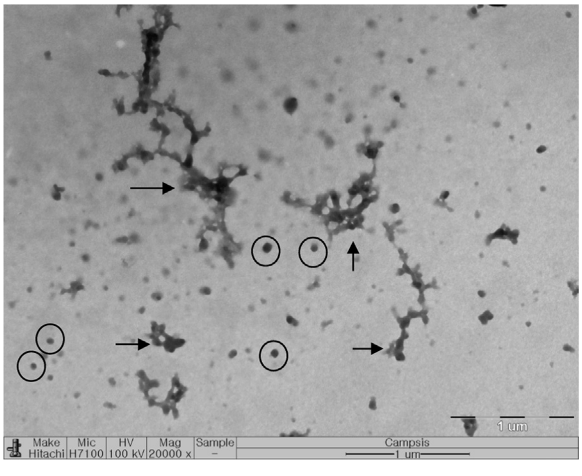

**Fig. 5.** Micro structure of 1.0 mol UF resin without hardener.

present together with nodular filamentous and reticular structures (arrows), which appear to have developed from the coalescence of globular particles, judging by the nodular appearance of such structures. Particles are of variable size, and some particles appear to have stained more intensely than others, which could reflect their mass; larger particles containing a greater amount of resin mass are likely to have stained more intensely than smaller particles. Similarly, nodular regions of the filamentous structures are stained more intensely compared to thinner flattened regions.

Both the hardener level and time of exposure to hardener appear to have an influence on resin architecture. At a 0.1% hardener level, the resin becomes highly coalescent, judging by the absence of single globular particles. As illustrated in Fig. 6, the resin exposed to 0.1% hardener for 3 h displays the presence of beaded (single arrowhead) and nodular (paired arrowhead) filaments with globular particles (arrows) partly coalesced with the filament along the edges. The appearance is suggestive of the formation of interconnected filamentous structures from extensive coalescence of globular particles, as surface protrusions of variable forms on the filaments, from gentle undulations and pointed protrusions to prominent nodular bulges along the filaments, would indicate. The globular nature of the crystalline domains in UF resins had been reported earlier by the use of small angle X-ray Diffraction [22]. At a 3.0% hardener level with 3 h

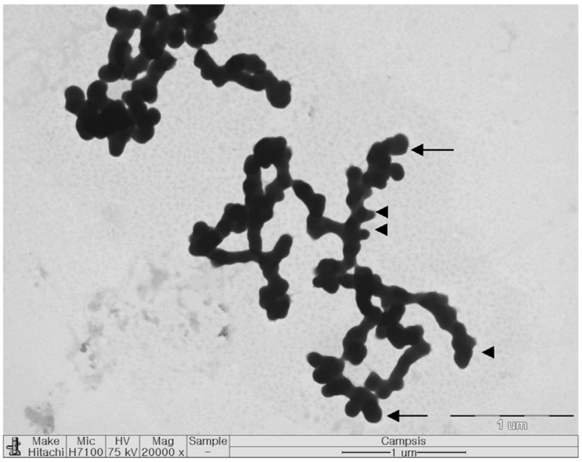

**Fig. 6.** Morphology of liquid UF resin of 1.0 F/U mole ratio after 3 h mixing with 0.1% hardener showed presence of beaded (single arrowhead) and nodular (paired arrowheads) filaments, and still globular particles (arrows) partly coalesced with the filament along the edges. These features are similar to those reported by Ferra et al. [6], who attributed flocculated or agglomerated structures to the influence of aging.

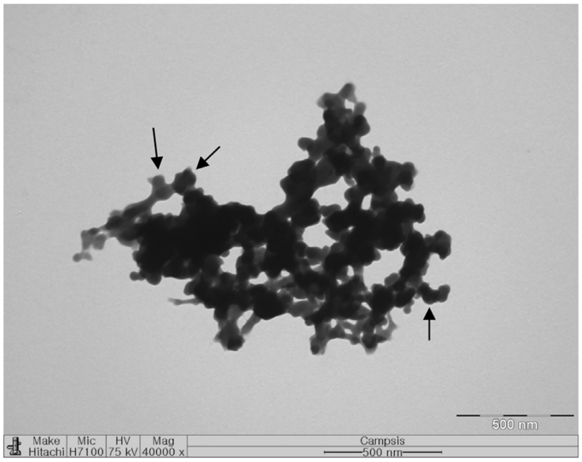

**Fig. 7.** Morphology of liquid UF resin of 1.0 F/U mole ratio after 3 h mixing with 3% hardener displays an architecture suggestive of more advanced network formation, where filaments are highly interconnected, although nodular structures are still identifiable in places along the filaments.

exposure (Fig. 7), the resin displays an architecture suggestive of more advanced network formation, where filaments are highly interconnected, although nodular structures are still identifiable in places along the filaments.

With a 5% hardener level the 1.0 mol UF resin displays a radical change in the morphology of the domains dispersed in the resin, which become more similar to stacks of lamellae, appearing as early as 0.5 h exposure. Such structures were not observed with lower hardener levels, even after prolonged hardening. As illustrated in Figs. 8 and 9, crystals appear to form variable size aggregates. Where identifiable as individual crystals, particularly at the margins of aggregates, crystals have a form of flattened plate with pointed ends (Fig. 9). This gradual development, from the globular particles, which aggregate into filamentous structures and then into platelet-like crystals, along with the anticipation in the appearance of the characteristic morphological features, clearly indicates a role of the hardener, and more generally of the curing step. The cross-linking of the resin drastically decreases the mobility of the prepolymer chains and apparently favors the aggregation of crystallizable domains.

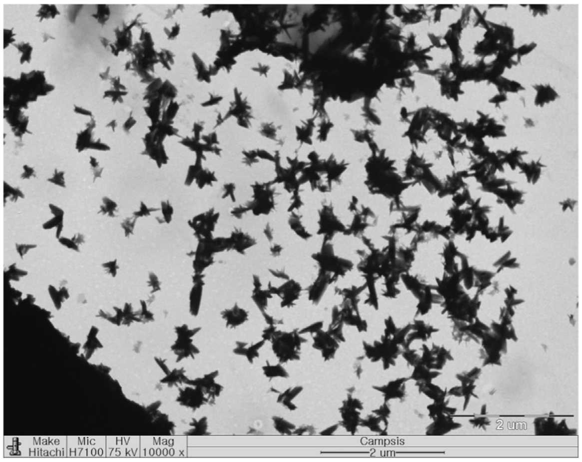

**Fig. 8.** Liquid UF resin of 1.0 F/U mole ratio with 5% $NH_4Cl$, crystals appear to form variable size aggregates.

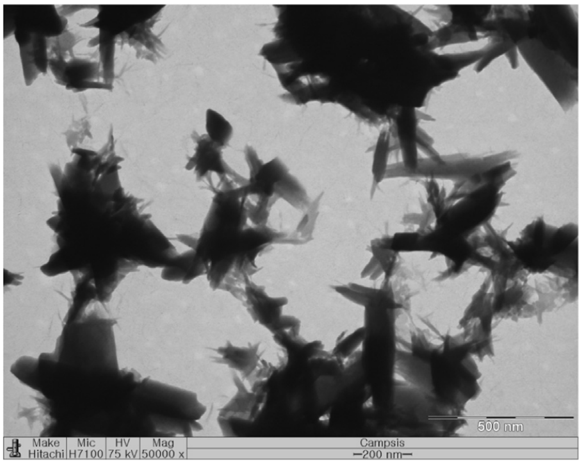

**Fig. 9.** Liquid UF resin of 1.0 F/U mole ratio with 5% $NH_4Cl$. Crystals have a form of flattened plate with pointed ends, where identifiable as individual crystals particularly at the margins of aggregates.

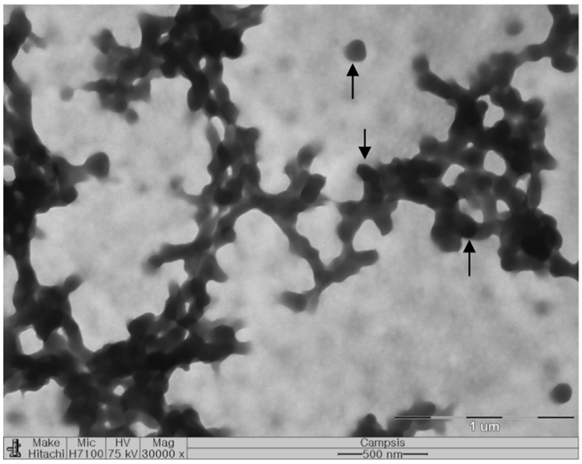

**Fig. 10.** Fusion of globular particles into filamentous networks is also a feature of 1.6 mol resin. This TEM micrograph represents a detail of the resin treated with 0.1% hardener for 3 hours.

### *3.3.2. Micro-morphology of 1.6 F/U mole ratio UF resin*

The fusion of globular particles into filamentous networks is also a feature of the 1.6 mol resin, and in early stages, represented by the 0.1% hardener system for 3 h (Fig. 10) and the 5% hardener system for 0.5 h (Fig. 11). Furthermore, the 1.6 mol resin architecture has considerable micro structural similarity to that of the 1.0 mol resin. In other words, globular particles coalescence results in the formation

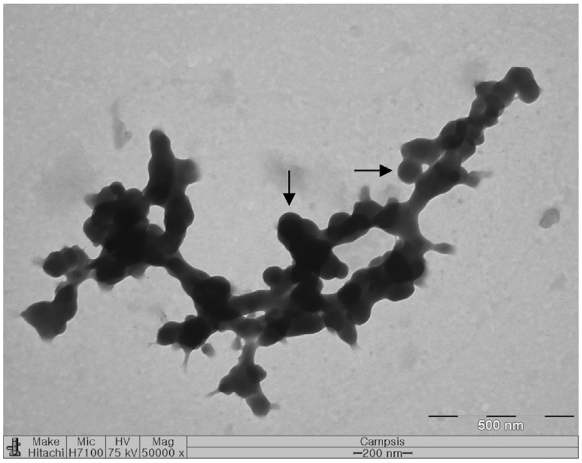

**Fig. 11.** Fusion of globular particles into filamentous networks is also a feature of 1.6 mol resin, and in early stages. This TEM micrograph represents a detail of the resin treated with 5% hardener for 0.5 h.

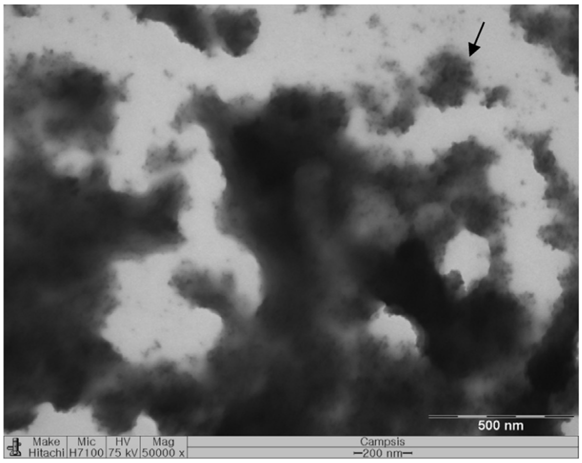

**Fig. 12.** Morphology of liquid UF resin of 1.6 F/U mole ratio with 3% hardener for 23 h.

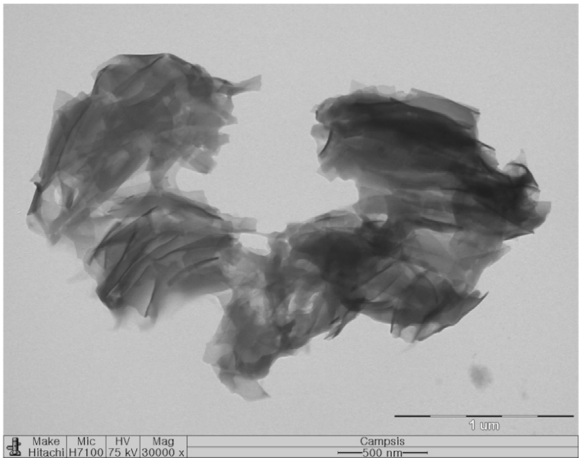

**Fig. 13.** Morphology of liquid UF resin of 1.6 F/U mole with 5% hardener for 23 h.

of interconnected networks of nodular filaments (Figs. 10 and 11).

Overall, the development of morphology with the F/U 1.6 resin confirmed the earlier description of an evolution from globular to filamentous to lamellar structures guided by aggregation and coalescence.

Figs. 12 and 13 show the morphology at more advanced stages during curing, represented by the 3% hardener system for 23 h (Fig. 12) and the 5% hardener system for 23 h (Fig. 13). In these samples, fusion of nodular filaments leads to the formation of a more or less homogenous mass of flattened structures consisting of distinctive and flattened plates, particularly evident in the sample prepared with a higher hardener level of 5% and prolonged exposure of 23 h (Fig. 9).

TEM results confirm that no significant differences exist in the kinetics of development of crystals: since short times globular structures are present in the samples, which however, in dependence of the mobility and the driving force due to the curing process, can aggregate into different morphologies, which can be elongated or plate-like, as a function of time and hardener content.

## 4. Conclusions

This paper confirms the presence of crystalline structures in low F/U mole ratio UF resin, a thermosetting polymer, from a WAXD and TEM investigation. The available samples and the experiments carried out allowed elucidation of the role of several parameters on the development of crystallinity in such resins. The degree of crystallinity was governed mainly by the F/U ratio, with curing time and hardener content having no significant influence. Crystallinity was not associated with the curing process, but is an inherent characteristic of UF resins, which likely appears in the methylolation step of their synthesis. On the one hand the kinetics of crystallization was not dependent on hardener content, but on the other hand the cure kinetics (related to the hardener content) was key in shaping the morphology of the crystalline domains. A faster and more extensive curing favored the coalescence and aggregation of globular crystals, into plate like structures resembling the lamellar stacks of semicrystalline polymers. The presence of crystals is beneficial in decreasing formaldehyde emission, but on the other hand is detrimental for adhesive strength, because it subtracts functionalities which can participate in the crosslinking reactions critical for a successful adhesion process. Therefore, it is desirable to understand and to eventually control crystallinity in UF resins. The results of this work show that in order to do so it is necessary to master the subtle interplay between the inherent tendency towards crystallization and the templating effect of the curing process.

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