

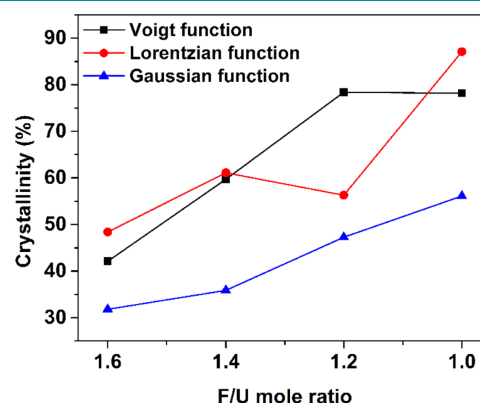
Determination of Crystallinity of Thermosetting Urea-Formaldehyde Resins Using Deconvolution Method

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Abstract: Current low formaldehyde/urea (F/U) molar ratio urea-formaldehyde (UF) resins are quite different from high molar ratio UF resins used 20 years ago in terms of their crystallinity. For the first time, this paper reports a method of determining the crystallinity of thermosetting urea-formaldehyde (UF) resins of different molar ratios with the deconvolution method, using Voigt, Lorentzian, and Gaussian function. The Gaussian deconvolution of X-ray diffraction (XRD) patterns was the most suitable and reliable curve-fitting method, which gave the crystallinity value from 31.8% to 56.1% as the molar ratio decreased from 1.6 to 1.0. These results also indicated that low-molar-ratio (1.2 and 1.0) UF resins were semi-crystalline, whereas high molar-ratio (1.6 and 1.4) resins were amorphous. The Gaussian function was also employed to determine the crystallinity of the low-molar-ratio (1.0) UF resins cured at different curing and hardener conditions. Hardener level had greater influence on the crystallinity than hardener type even though the curing temperature and time affected the crystallinity.



Keywords: thermoset, urea-formaldehyde resins, crystallinity, deconvolution, curing, hardener.

1. Introduction

Urea-formaldehyde (UF) resins, *i.e.*, thermosetting polymers synthesized with urea and formaldehyde *via* an addition and condensation reaction, are the most widely used adhesive for the manufacturing of wood-based composites. Conventional UF resins have high formaldehyde/urea (F/U) molar ratio (> 4.0), and are especially attractive due to their low cost, good performance, and colorlessness.^{1,2} However, formaldehyde emission (FE) from wood-based panels employing these resins is harmful to human health. This has forced resin producers to lower the molar ratio in order to satisfy the FE regulations of various countries worldwide.³⁻⁵ Current low-molar-ratio (≤ 1.0) UF resins generate low amounts of FE, but this limited FE is realized at the expense of the adhesion. Thus, current low-molar-ratio UF resins are quite different from those resins used in 20 years ago in terms of their crystallinity. In other words, the low-molar-ratio UF resins have crystalline structures, which lead to poor adhesion, unlike their high-molar-ratio counterparts that have amorphous structures.⁶⁻⁸ In previous studies, the relationship between the crystallinity and the performance of low-molar-ratio UF resins has been investigated by determining the degree of crystallinity in these resins.^{9,10} In recent years, the degree of crystallinity as a way of characterizing some materials was determined *via* various techniques including X-ray diffraction (XRD), ¹³C nuclear magnetic resonance (NMR), or Fourier

transform infrared (FTIR) spectroscopy.¹¹⁻¹⁴ The crystallinity of UF resins is most commonly determined by means of XRD methods.^{9,15,16} In general, the peak height method, peak deconvolution method, and amorphous subtraction method are three common methods of calculating the crystallinity from XRD spectra.¹⁴ However, the peak height method is less commonly used than the other two methods¹⁴ as the simple height comparison employed neglects peak-width variations, thereby leading to inaccurate crystallinity calculation. Furthermore, the calculations consider only the highest peak and, hence, the contributions of other crystalline peaks are excluded. The other two methods yield better results than the peak height method. However, finding an appropriate amorphous standard that is similar to the amorphous component of the sample represents a major challenge of the amorphous subtraction method. Applying this method to UF resins is difficult as the amorphous-component contribution to the low-molar-ratio resins remains unknown. The peak deconvolution method uses a curve-fitting process (based on assumptions of the shape, number of peaks, and position of deconvoluted peaks)¹⁴ to separate the amorphous and crystalline peak. The deconvolution of XRD spectra is commonly performed using the Gaussian,¹⁷⁻¹⁹ Lorentzian,²⁰ and Voigt²¹ functions. Thus, these peak deconvolution methods could be employed as the calculation method of determining the crystallinity of low-molar-ratio UF resins.

However, to the authors' knowledge, we, for the first time, employed these three functions to calculate the crystallinity of UF resins. Thus, herein, we focused on identifying the appropriate function for estimating the crystallinity of UF resins at different molar ratios. The dependence of this crystallinity on curing

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conditions (temperature and time) and hardener conditions (type and level) was also evaluated.

2. Experimental

2.1. Materials and methods

Technical grade urea and formalin (37%) were used for the synthesis of UF resins. Aqueous solutions of formic acid (20%) and sodium hydroxide (20%) were used to adjust the pH level during the synthesis. Aqueous solutions (20%) of ammonium chloride (NH_4Cl), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) were used as hardeners. Different levels of each hardener were added to the synthesized UF resin based on the non-volatile resin solids.

The UF resins considered in this study were all prepared by means of a traditional alkaline-acid two-step reaction performed in the laboratory. For the reaction, the formalin was placed in the reactor, adjusted to pH 7.8 with aqueous NaOH, and then heated to 40 °C. Subsequently, a certain amount of urea was added to the reactor. The mixture was then heated to 90 °C under reflux for 1 h to allow for methylation reactions. The resulting methylolureas underwent condensation in the second stage of the UF-resin synthesis. During this process, formic acid (20 wt% solution) was added to the reactor, to realize a pH of ~4.6. The condensation reactions were allowed to run until a target viscosity of 'J-K' was reached, as determined *via* bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA) measurements. Different final F/U mole ratios of the UF resins were obtained by adding different amounts of the second urea to the resin. Afterward, the resins were cooled to room temperature and the pH was then adjusted to 8.0.

2.2. Characterization and analysis

An X-ray diffractometer (D/Max-2500 Rigaku, Tokyo, Japan) was used to obtain XRD patterns for calculating the crystallinity of the cured UF resins. Low-molar-ratio UF resins with a F/U molar ratio of 1.0 were used for four levels (1, 3, 5, and 10%) of three hardener types (NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, and $\text{Al}_2(\text{SO}_4)_3$). The resins were then cured at 120 °C for 60 min. In addition, 3% NH_4Cl as a hardener was employed for different curing temperatures (80 °C, 120 °C, 150 °C, and 180 °C) and times (1 h, 2 h, and 4 h) of the resins. The samples without hardener (0% content) were solidified overnight at 120 °C to remove water from the resins. The milled and powdered samples were analyzed at ambient temperature *via* XRD with a $\text{CuK}\alpha$ -1 X-ray source (wavelength (λ): 0.15406 nm). The angle of incidence was varied from 10° to 60° (step: 0.02°/min) during the measurements.

Deconvolution of the XRD patterns was performed using OriginPro 9.0 software (OriginLab Corporation, Northampton, MA, USA). Individual crystalline and amorphous peaks were extracted by means of a curve-fitting process associated with Voigt, Lorentzian, and Gaussian functions applied to the diffractograms. The assumption was that the sharp peaks corresponded to crystalline domains and the broad peaks corresponded to the amorphous contribution. In addition, the number of fitting

peaks for XRD patterns was fixed for high and low molar ratio UF resins. Two fitting peaks (one crystalline and one amorphous) and five fitting peaks (four crystalline and one amorphous) were selected for high molar ratio UF resins (F/U = 1.6 and 1.4) and low molar ratio resins (F/U = 1.2 and 1.0), respectively. Iterations were repeated until the maximum F number was obtained. The crystallinity of each sample was calculated as follows:

$$\text{Crystallinity (\%)} = \frac{S_c}{S_t} \times 100 \quad (1)$$

where, S_c and S_t represent the area of the crystalline domain and the area of the complete domain (crystalline + amorphous), respectively. The crystallite size was also estimated from Scherrer's equation, which is given as follows [9]:

$$R = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where, k is a constant factor ($k = 1$), λ is the wavelength of the X-ray radiation ($\lambda = 0.154 \text{ nm}$), β is the full width at half maximum (FWHM) intensity in radians, and θ is Bragg's angle in radians. The most prominent crystalline peak in the XRD pattern, *i.e.*, the peak at $2\theta = 21.77^\circ$ corresponding to the low-molar-ratio UF resins with 1.0 F/U molar ratio, was chosen for the crystallite size calculation.

3. Results and Discussion

3.1. Different F/U molar ratio UF resins

Figure 1 shows the results of the peak deconvolution performed on XRD spectra collected for UF resins at different molar ratios, using the Voigt-function (*i.e.*, a convolution of the Lorentzian and Gaussian distributions).²² The narrow (sharp) peaks correspond to crystalline regions, whereas the broad peaks are associated with amorphous regions. As the figure shows, the peak width increased with increasing UF-resins mole ratio. This function provided the crystallinity of 42.1% and 78.2% for the UF resins with F/U = 1.6 and 1.0, respectively (see Figure 4), indicate that the crystallinity increased significantly when the molar ratio was reduced to 1.0.

Figure 2 shows the results of the Lorentzian-function peak deconvolution performed on XRD spectra collected for cured UF resins at different molar ratios. As the molar ratio decreased from 1.6 to 1.0, the crystallinity increased from 48.4% and 87.1%, respectively, as shown in Figure 4. The pattern is similar to those obtained from the Voigt function. However, compared with the values generated by the Voigt function, those results from the Lorentzian function are closer to each other at high-molar-ratio (F/U 1.6 and 1.4), but they were significantly different for the low-molar-ratio (F/U 1.2 and 1.0) resins. This may have resulted from the fact that the Lorentzian function is more appropriate for peaks with "Lorentzian wings", where narrow peak tops are accompanied by broad/slightly extended sides.²²

Figure 3 shows results of the Gaussian-function peak deconvolution performed on XRD patterns obtained for the UF resins. The degree of crystallinity revealed by this function increased from 31.8% to 56.1% as the F/U molar ratio decreased from

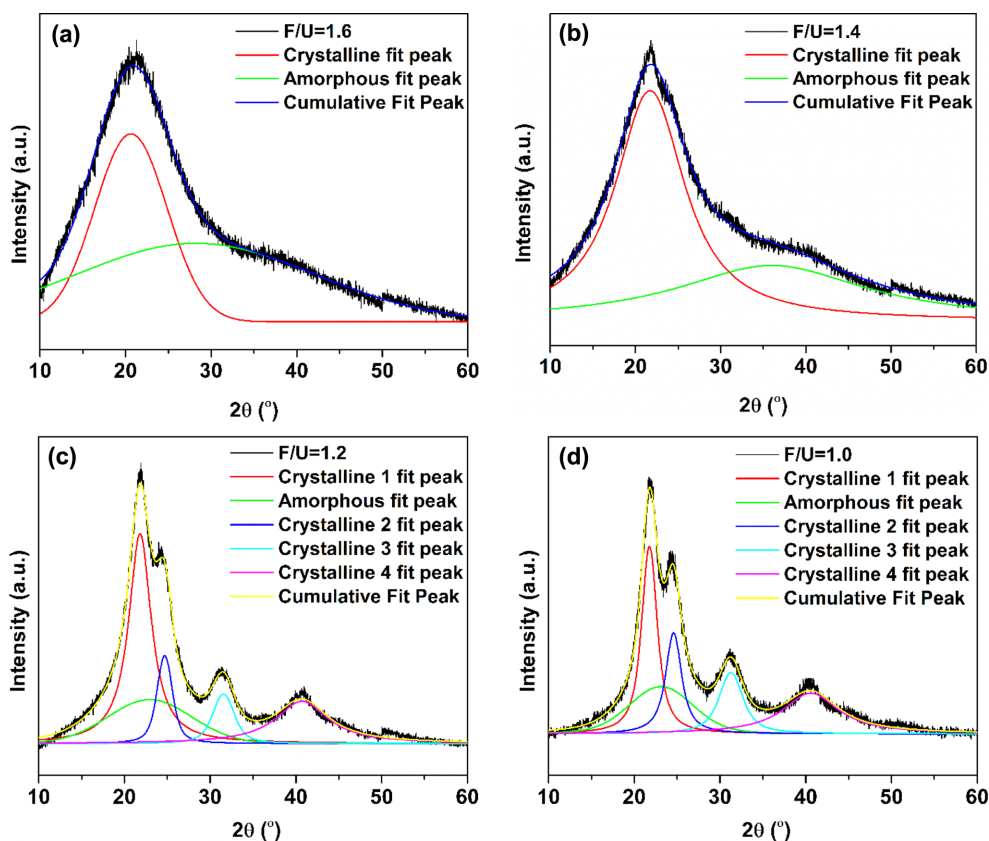


Figure 1. Voigt-function deconvolution of XRD patterns obtained for cured UF resins at molar ratios of (a) 1.6, (b) 1.4, (c) 1.2, and (d) 1.0.

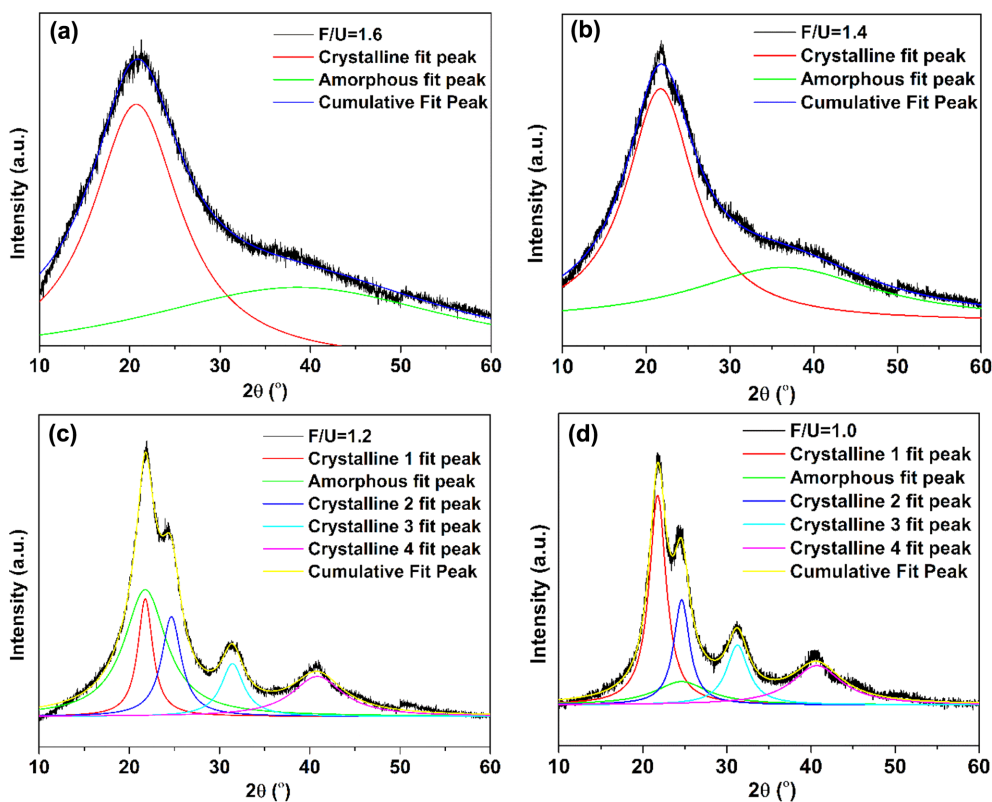


Figure 2. Lorentzian-function deconvolution of XRD patterns obtained for UF resins cured at molar ratios of (a) 1.6, (b) 1.4, (c) 1.2, and (d) 1.0.

1.6 to 1.0 (Figure 4). The fitting curves of the amorphous peak corresponding to the low-molar-ratio (1.0 and 1.2 F/U) resins were broader than the other two functions and closer to the

actual XRD patterns. In other words, this function provided better fitting, despite the similarity among the regression coefficients (Table 1). The crystallinity values obtained for the UF resins are

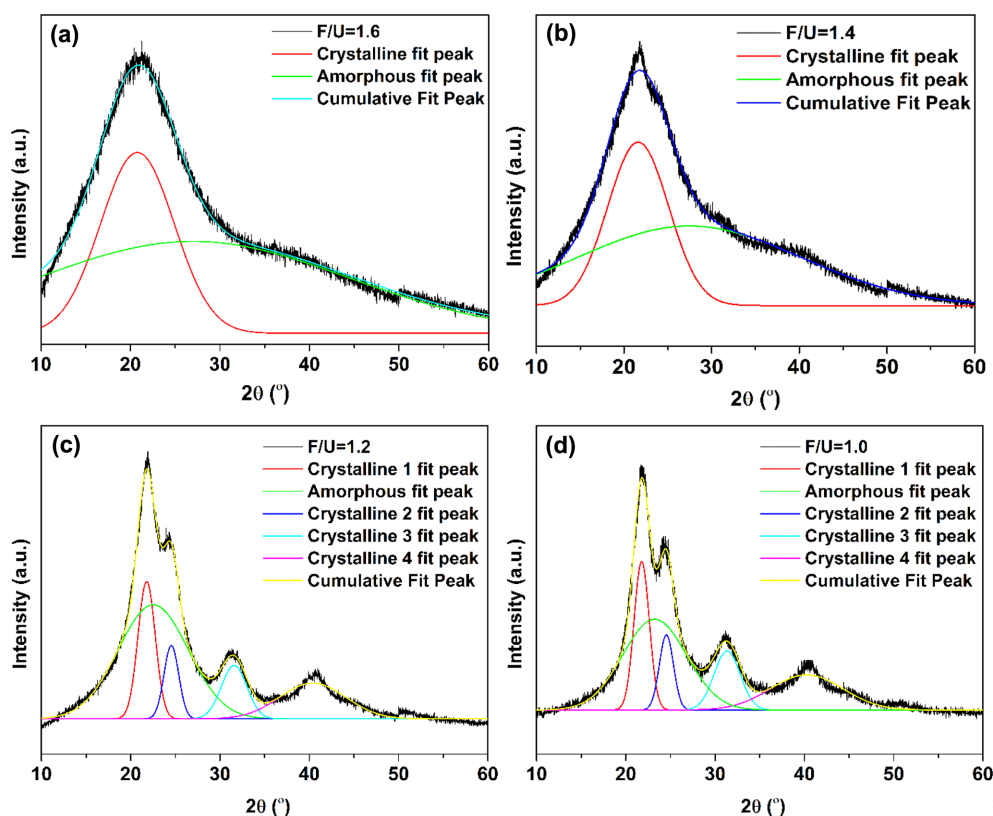


Figure 3. Gaussian-function deconvolution of XRD patterns obtained for cured UF resins at molar ratios of (a) 1.6, (b) 1.4, (c) 1.2, and (d) 1.0.

also consistent with the reported results.^{9,23} According to previous studies, the Gaussian profile is most applicable to solid samples, powders, gels or resins, whereas the Lorentzian profile is best suited to gases and some liquids. Liquids are, in general, best treated by the combined Gaussian-Lorentzian (G-L) function or the Voigt profile.²⁴ Correspondingly, compared with the other two functions, the Gaussian function yielded more accurate results for the calculation of UF-resin crystallinity. Therefore, in the present study, this function was employed for the crystallinity determination of low-molar-ratio UF resins subjected to different curing and hardener conditions.

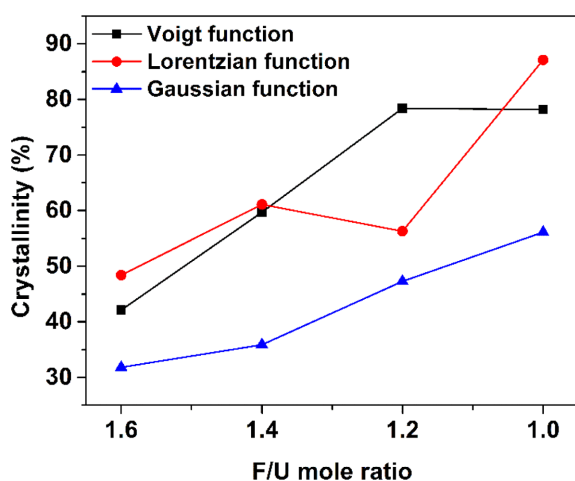


Figure 4. Crystallinity values determined by applying three types of curve-fitting functions to the XRD patterns of the cured UF resins at different molar ratios.

Table 1. Coefficient correlation values (R^2) obtained when applying three types of curve-fitting functions to the XRD patterns of the cured UF resins at different molar ratios

F/U molar ratio	Coefficient correlation (R^2)		
	Voigt function	Lorentzian function	Gaussian function
1.6	0.99423	0.99371	0.99347
1.4	0.99400	0.99401	0.99256
1.2	0.99586	0.99556	0.99493
1.0	0.99378	0.99330	0.99218

Figure 4 shows the crystallinity values determined by applying different deconvolution functions to XRD patterns of cured UF resins at different molar ratios. Similar R^2 values are obtained irrespective of the fitting function (Table 1). However, the crystallinity values obtained by the Voigt and Lorentzian functions varied more than those corresponding to the Gaussian function. For example, the crystallinity value of UF resins with F/U = 1.0 associated with Voigt function was lower than UF resins with F/U = 1.2. As shown in Figure 4, a similar inconsistency was also found in the crystallinity value from Lorentzian function. Cured UF resins with F/U = 1.4 had higher value than UF resins with F/U = 1.2. Therefore, when the fact that the solid form of the resins samples, the consistency of the degree of crystallinity, and the aforementioned R^2 values were taken into consideration, the Gaussian function was identified as the most appropriate and reliable among the three functions used to fit the XRD patterns of the resins. In addition, the curve fittings of the patterns and the obtained crystallinity degree of the resins

revealed that the low-molar-ratio (*i.e.*, 1.2 and 1.0) UF resins are crystalline, whereas the high-molar-ratio (*i.e.*, 1.6 and 1.4) resins are amorphous.

3.2. Different curing conditions for low-molar-ratio UF resins

To assess the influence of curing conditions (*e.g.*, curing temperature and time) on the crystallinity of the cured UF resins, we used a Gaussian function to determine the degree of crystallinity (see Figures 5-7). Figure 5 shows the peak deconvolution (performed with the function) of XRD patterns obtained for resins cured at temperatures ranging from 80 to 180 °C. As shown in Figure 7(a), over this temperature range, the crystallinity increased from 52.75% to a maximum of 56.13% and then

decreased continuously thereafter. This may be attributed to the occurrence of hydrogen bonding and cross-linking during the curing process. In other words, the low-molar-ratio UF resins (1.0) contained linear molecules that formed crystalline domains through h-bonds.^{7,8} The occurrence of the maximum crystallinity at 120 °C may have resulted from the optimum condition that yields the most ordered structure. However, owing to cross-linking, the crystallinity decreased when the curing temperature was further increased.

The Gaussian-function deconvolution results obtained for XRD patterns associated with curing time ranging from 1 h to 4 h are shown in Figure 6. As shown in Figure 7(b), the crystallinity decreased from 56.13% to ~ 54.97% during this curing period. This decrease may have resulted from an increase in the occur-

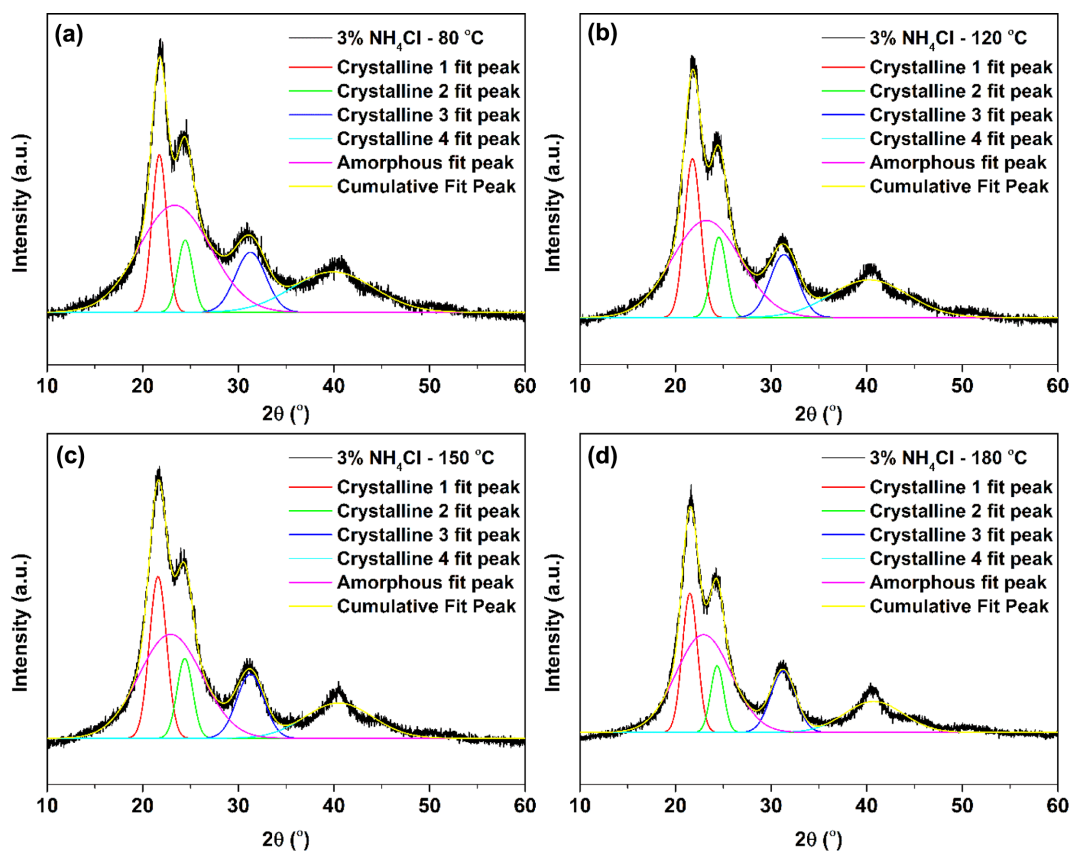


Figure 5. Gaussian deconvolution of XRD patterns obtained for the low-molar-ratio (1.0) UF resins cured at temperatures of (a) 80 °C, (b) 120 °C, (c) 150 °C, and (d) 180 °C.

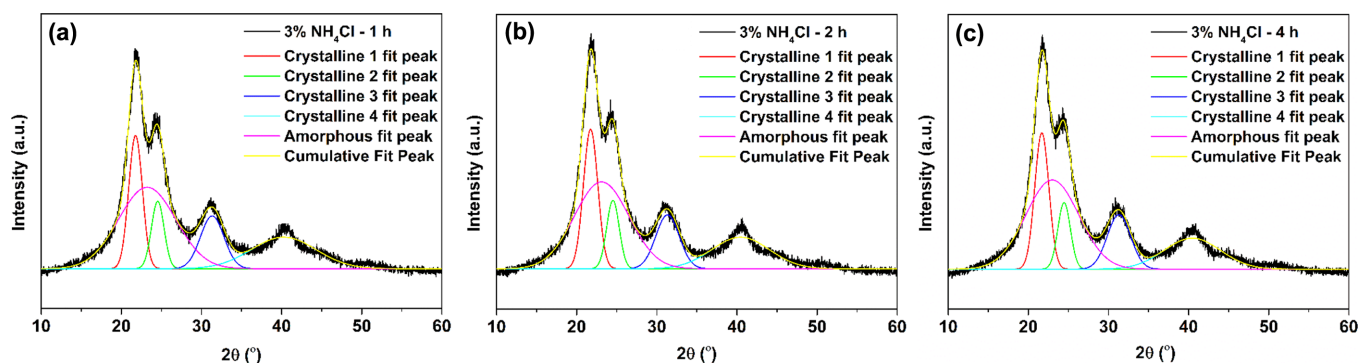


Figure 6. Gaussian XRD peak deconvolution of 1.0 F/U mole-ratio UF resins cured for (a) 1 h, (b) 2 h, and (c) 4 h at 120 °C with 3% NH_4Cl hardener.

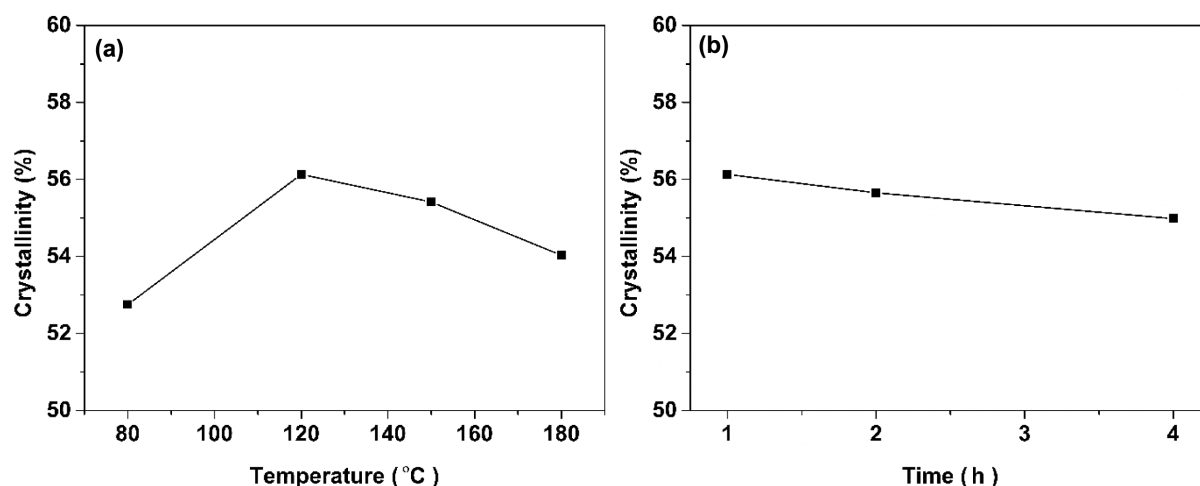
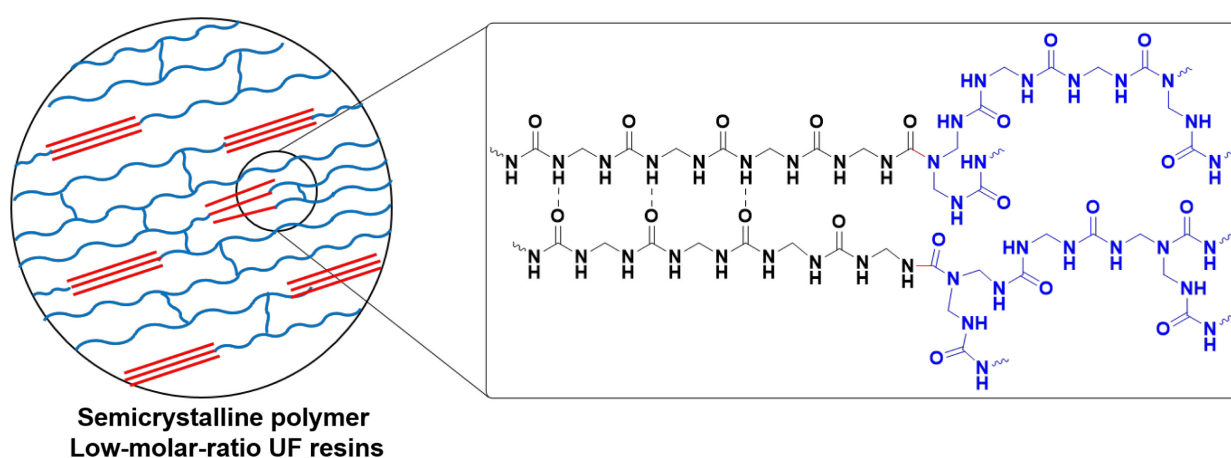


Figure 7. Variation in the crystallinity of cured low-molar-ratio UF resins with (a) curing temperature and (b) curing time.



Scheme 1. Schematic showing the deformation of crystalline regions with increasing temperature and time.

rence of cross-linking with increasing curing time. These results suggest that the crystallinity of the cured low-molar-ratio UF resins increased to reach an optimum condition (in this case, 120 °C and 1 h), and then decreased with increasing curing temperature and time.

As shown in Scheme 1, it could be explained by the possibility that UF resins oligomers were further underwent to form more cross-linking network as the curing temperature and time increased. An increase in the cross-linking formation will obviously reduce the hydrogen bonds that were responsible for the crystallization, which consequently decreased the crystallinity.

3.3. Different hardener types and levels for low-molar-ratio UF resins

In addition to the curing conditions, the influence of hardener type and level on the crystallinity of low-molar-ratio UF resins was also investigated (see Figures 8-11 for the corresponding results). Figure 8 shows the Gaussian deconvolution of the XRD patterns obtained for UF resins cured at NH_4Cl levels ranging from 1% to 10%. The amorphous peaks became narrow with increasing hardener level, giving greater contribution to crystalline peaks, in turn, an increase on the crystallinity. In fact, the crystallinity of the resins increased from 52.48% to 58.01%

when the NH_4Cl level increased from 1% to 10% (Figure 11).

This may have resulted from the catalyzing effect of the NH_4Cl hardener. That is, (compared with lower content) higher NH_4Cl content leads to more rapid formation of longer linear chains of low-molar-ratio, such as $F/U = 1.0$ UF resins. Previous studies have reported that, due to hydrogen bonding, the ordered packing structure of linear molecules comprising the UF resin oligomers contributes to the formation of crystalline regions in low-molar-ratio UF resins.^{7,25} Thus, it is reasonable that the crystallinity degree of these resins will increase with increasing hardener content, as illustrated in the Scheme 2.

Figure 9 shows the Gaussian deconvolution of the XRD patterns obtained for the UF resins cured at different $(\text{NH}_4)_2\text{SO}_4$ levels. As shown in the figure, the intensity of the crystalline peaks increased with increasing hardener level, indicative of an increase in the crystallinity, as presented in Figure 11. The crystallinity increased from 50.80% to 55.65% as the $(\text{NH}_4)_2\text{SO}_4$ level increased from 1% to 10%. The increase in crystallinity was slightly lower than that of the NH_4Cl level. The crystallinity at 10% NH_4Cl level was higher than that of 10% $(\text{NH}_4)_2\text{SO}_4$, resulting probably from a difference in the number of NH_4^+ ions. For example, for the same level of hardener, $(\text{NH}_4)_2\text{SO}_4$ contained twice as many NH_4^+ ions as NH_4Cl . NH_4^+ ions lead to cure acceleration, as shown in the following reaction:²⁶

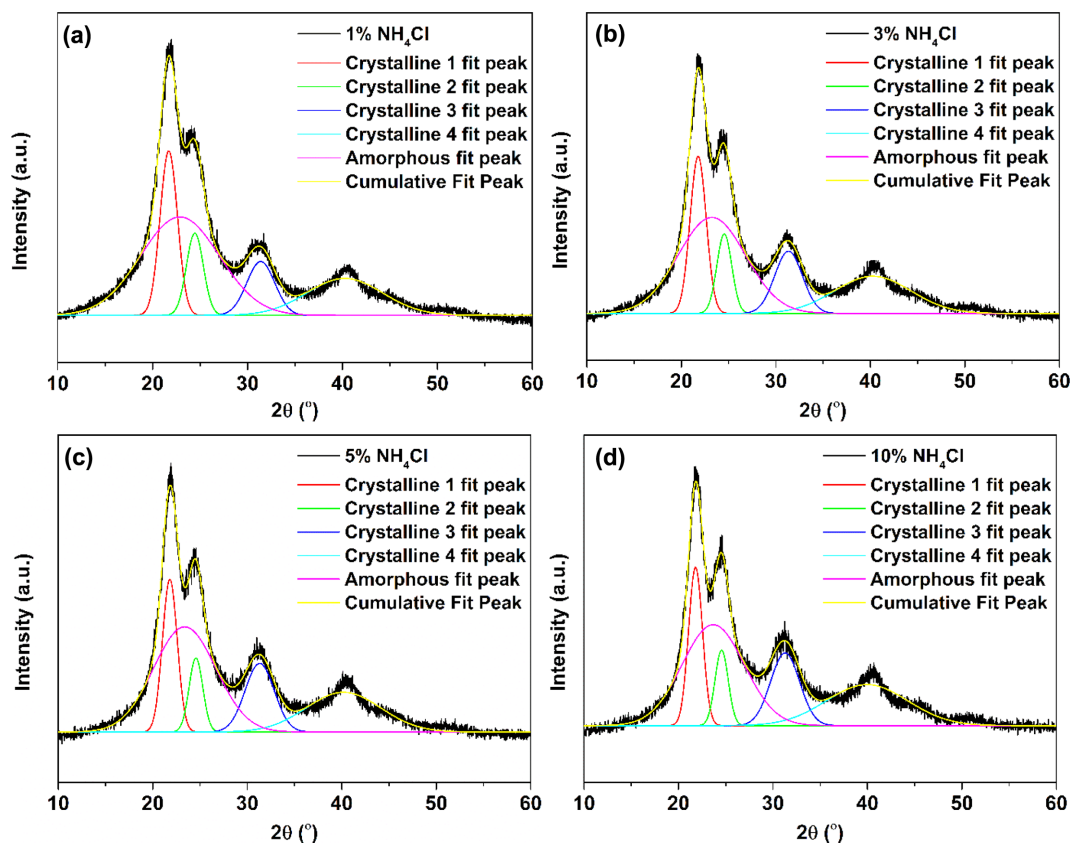


Figure 8. Gaussian deconvolution of XRD patterns obtained for low-molar-ratio UF resins cured at NH_4Cl hardener levels of (a) 1%, (b) 3%, (c) 5%, and (d) 10%.

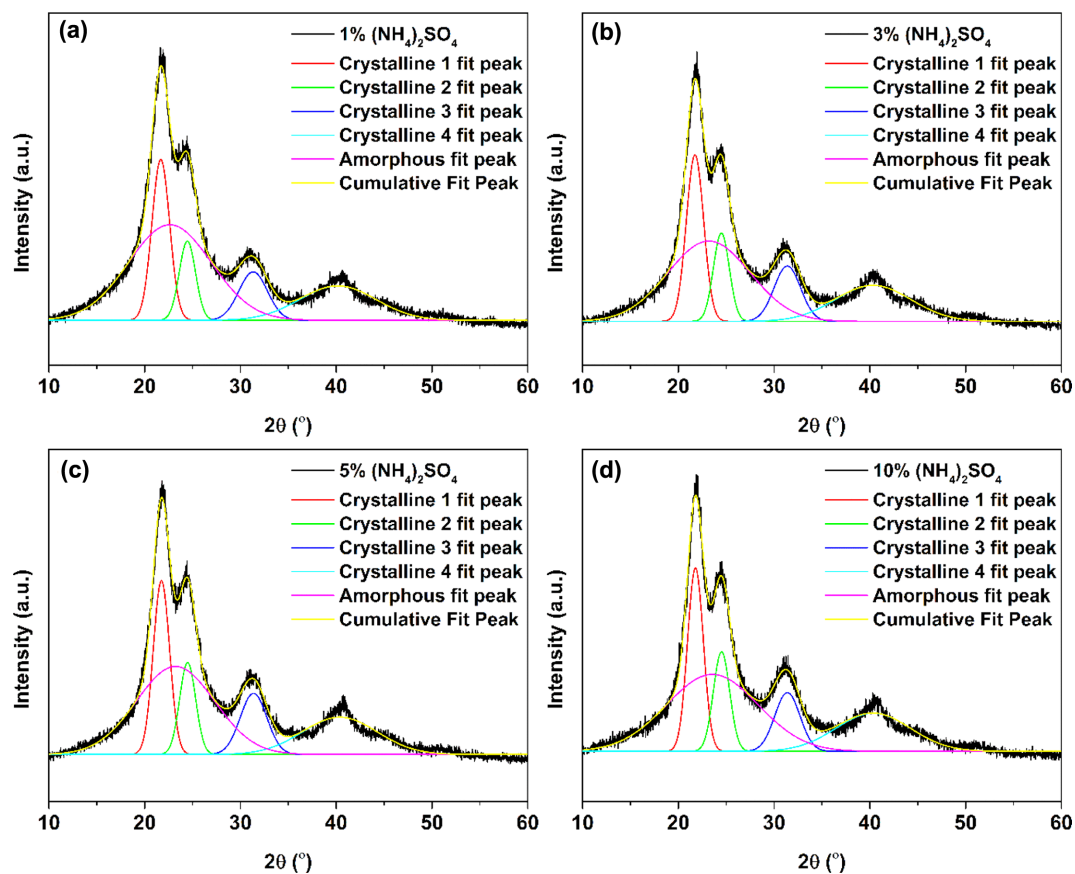
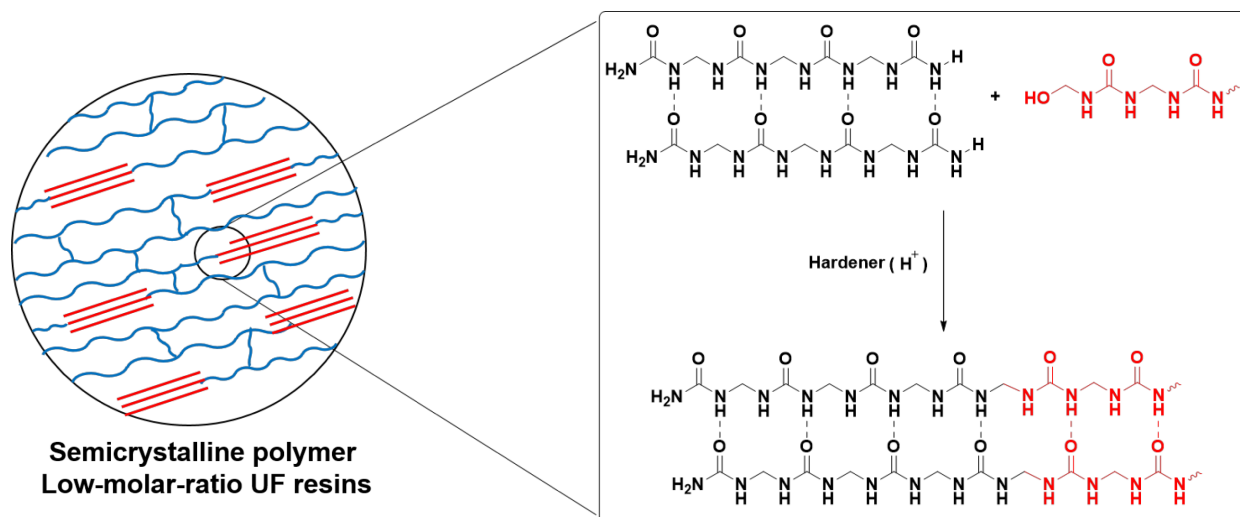


Figure 9. Gaussian deconvolution of the XRD patterns obtained for the low-molar-ratio UF resins cured at $(\text{NH}_4)_2\text{SO}_4$ levels of (a) 1%, (b) 3%, (c) 5%, and (d) 10%.



Scheme 2. Schematic showing the formation of additional crystalline regions with increasing hardener level.

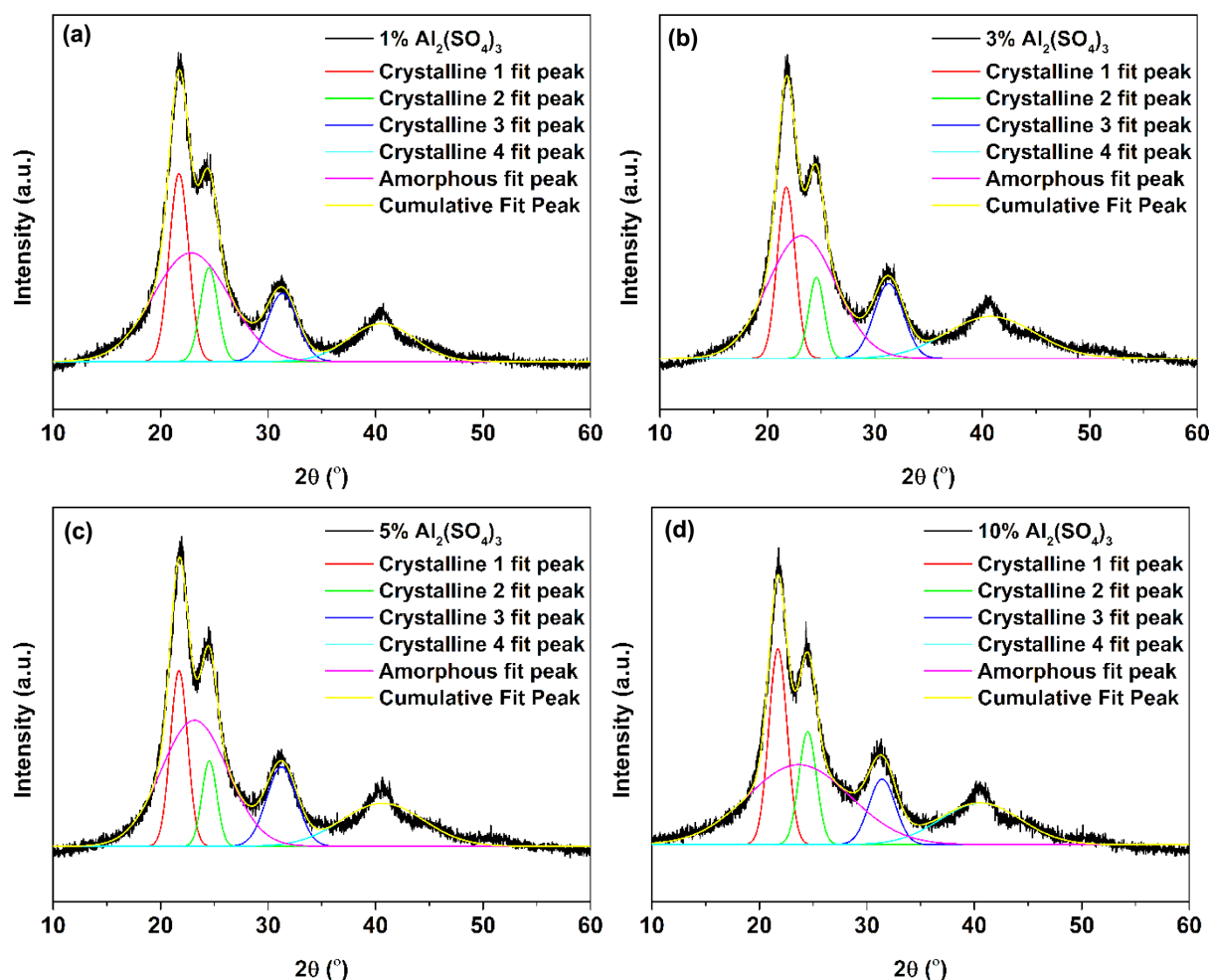
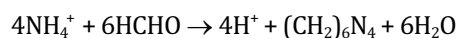


Figure 10. Gaussian deconvolution of the XRD patterns obtained for low-molar-ratio UF resins cured at $Al_2(SO_4)_3$ levels of (a) 1%, (b) 3%, (c) 5%, and (d) 10%.



The number of H^+ ions increased with increasing number of NH_4^+ ions used to react with free formaldehyde. This will contribute to the occurrence of cross-linking, which leads to a decrease in the crystallinity. In addition, an excessively high acid content

followed by decreasing pH levels below 4.0 may lead to degradation of the linear oligomer chains (Scheme 2) comprising the cured UF resins.²⁷ This degradation results in a decrease in the crystallinity of the resins.

Figure 10 shows the Gaussian deconvolution of the XRD patterns obtained for cured UF resins with different levels of $Al_2(SO_4)_3$

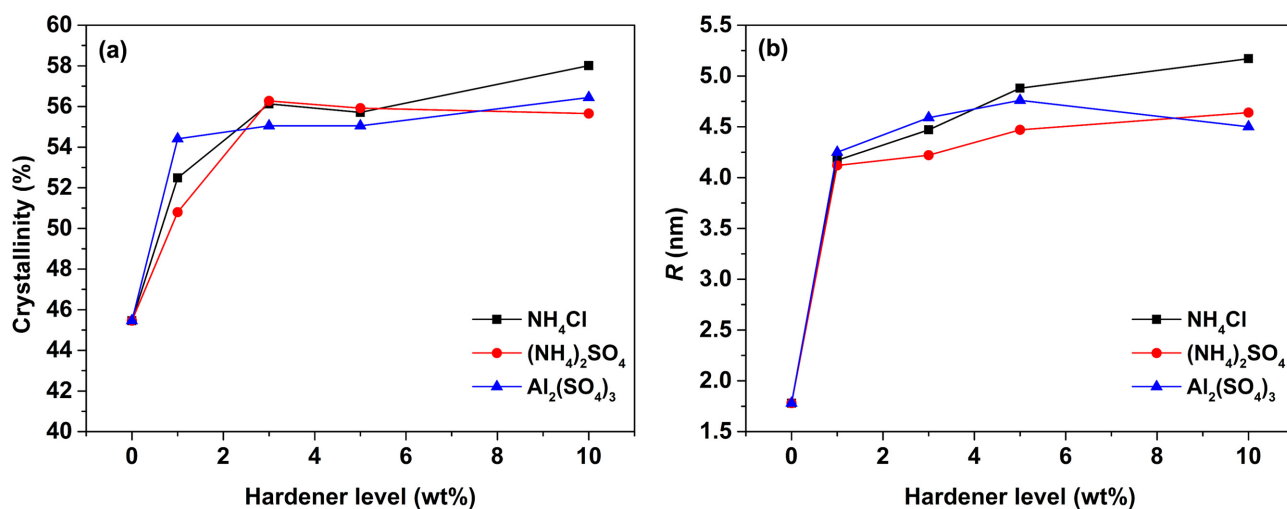


Figure 11. Change in the crystallinity (a) and crystallite size (b) of low-molar-ratio UF resins cured at different hardener levels and with different hardener types.

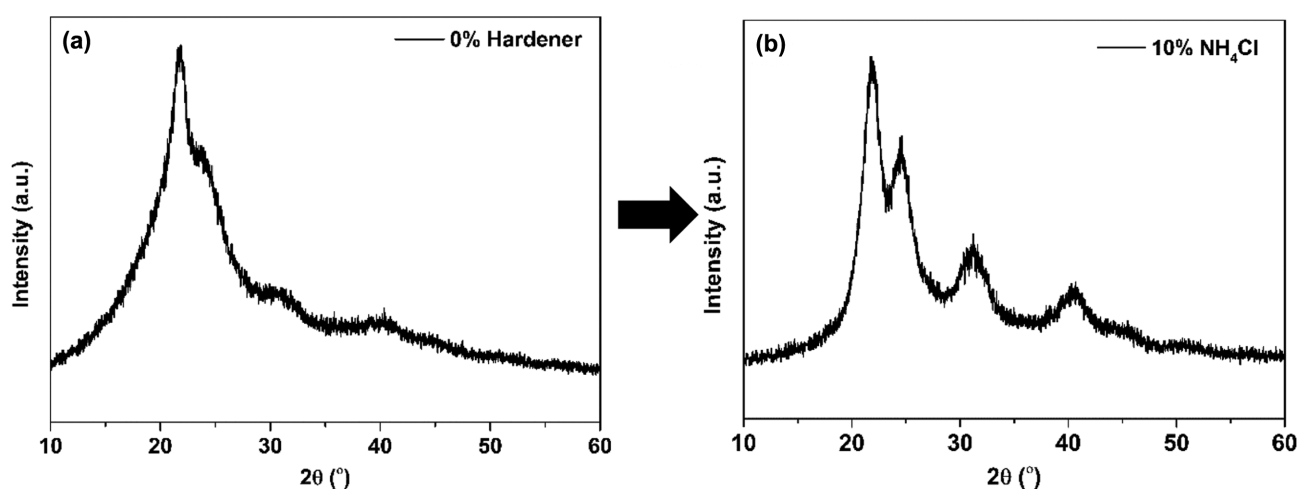


Figure 12. Changes in the XRD patterns of low-molar-ratio UF resins cured with (a) 0% hardener and (b) 10% NH_4Cl .

as a hardener. As the hardener level increased, the intensity of the amorphous peaks decreased, indicating an increase in the crystallinity, as shown in Figure 11. The crystallinity increased from $\sim 54.41\%$ to 56.44% . In general, the increase in crystallinity induced by $\text{Al}_2(\text{SO}_4)_3$ was less than that induced by either NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$. This resulted probably from the fact that the $\text{Al}_2(\text{SO}_4)_3$ contains no NH_4^+ ions, *i.e.*, the main contributor to the curing process in UF resins.

The crystallinity and the crystallite size (calculated from Scherrer's equation) of the low-molar-ratio UF resins increased (in general) with increasing hardener level (see Figure 11). For both parameters, the most significant increase occurred when NH_4Cl is used as the hardener. In this case, the increase in the crystallite size probably resulted from the hardener-induced formation of crystalline regions. This is consistent with previous research where a less cross-linked low-molar-ratio UF resin allowed smoother growth of a crystalline structure, resulting in a larger size than that of the more cross-linked resin.⁹

As shown in Figure 12, the XRD patterns of low-molar-ratio UF resins ($F/U = 1.0$) differed significantly between 0% and 10%

NH_4Cl levels, with the crystallinity increasing from 45.46% to 58.01% within this range of values. These results indicate that, compared with the hardener type, the hardener level had a greater influence on the formation of crystalline domains in the cured-state low-molar-ratio UF resins.

4. Conclusions

The results of this study showed that the Gaussian function was the most appropriate and reliable for the determination of the crystallinity of cured UF resins with different molar ratios. The high-molar-ratio UF resins were amorphous structured, whereas the low-molar-ratio UF resins were crystalline structured. The Gaussian function was successfully used to determine the crystallinity of the low-molar-ratio UF resins subjected to different curing and hardener conditions. An increase in the curing temperature caused the crystallinity of the resins to increase to a maximum, and then decreased, while it slightly decreased with an increase in the curing time. Furthermore, the crystallinity also increased with increasing hardener level. The results also

showed that the hardener level had greater influence on the crystallinity than the hardener type did. The crystallinity of the low-molar-ratio UF resins was maintained, regardless of different curing and hardener conditions.

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