

# Microcrystallinity and Colloidal Peculiarities of UF/Isocyanate Hybrid Resins

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**ABSTRACT:** Combined mixtures of polymeric diphenylmethane diisocyanates (pMDI) with Urea-formaldehyde-resins (UF) adhesives for wood panels are shown (a) by X-ray diffraction analysis (XRD) of the cured adhesive to present a certain percentage of microcrystallinity, this being due exclusively to the proportion of urea-formaldehyde resin present in the mix and, (b) by polarized light optical microscopy

(PLOM) to present colloidal structures in which oligomers and colloidal structures of one resin have migrated within the colloidal structures of the other resin. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2633–2636, 2007

**Key words:** urea-formaldehyde; isocyanates; resins; colloids; X-ray; crystal structures

## INTRODUCTION

Urea-formaldehyde (UF) resins have been shown to copolymerize in water with pMDI (polymeric diphenylmethane diisocyanate), and the type of linkages and compounds formed have been isolated, analyzed, and clearly determined by several techniques and by several research groups.<sup>1–4</sup> While reaction of the isocyanate group with water to form polyureas networks always occurs to a greater or lesser extent, in water the reaction that, in absence of UF hardeners and at long curing times, predominates is the reaction of the UF methylol group ( $-\text{CH}_2\text{OH}$ ) with the isocyanate group to form urethane bridges,<sup>1,4</sup> other reactions only having been observed in absence of water.<sup>5</sup> The final hardened resin network then presents, in almost equal proportions both urethane bridges, methylene bridges pertaining to a normal UF resin network, as well as polyureas, all covalently linked in the same network.<sup>1,4</sup> This situation occurs at long curing times and when salts normally used as hardeners of the UF resin are not present.

The strength of a joint bonded with UF/pMDI glue-mixes is much improved compared with others, because of the coreaction between isocyanate groups and UF resins methylol groups to form a certain number of urethane crosslinks. This seems to occur in presence of water and also under the predomi-

nantly acid hardening conditions characteristic of aminoplastic resins (thus, in presence of a hardener). The system was tried with encouraging results for moisture resistant plywood,<sup>2</sup> and it is now proposed as being of some interest and as giving encouraging results in the bonding of straw-based particle-board.<sup>6,7</sup>

Recently, colloidal particles formation followed by their clustering have been shown to be the normal way of ageing of all aminoplastic resins,<sup>8–14</sup> including urea-formaldehyde (UF) resins.<sup>8,14</sup> Ageing (or further advancement of the resin by other means such as longer condensation times) causes whitening of the resin. This is a macroscopic indication of both the formation of colloidal particles and of their clustering. Some clustering appears rather early in this process, even when the great majority of the resin does visually appear to be in colloidal state, being transparent. However, it eventually progresses to resins which are mostly in colloidal, clustered state, followed much later on by a supercluster formation starting to involve the whole resin.

This paper then deals with the microcrystallinity and the colloidal state of the hardened products of the UF/pMDI coreaction at an industrial significant curing time, thus at short gel times obtained by addition of a hardener.

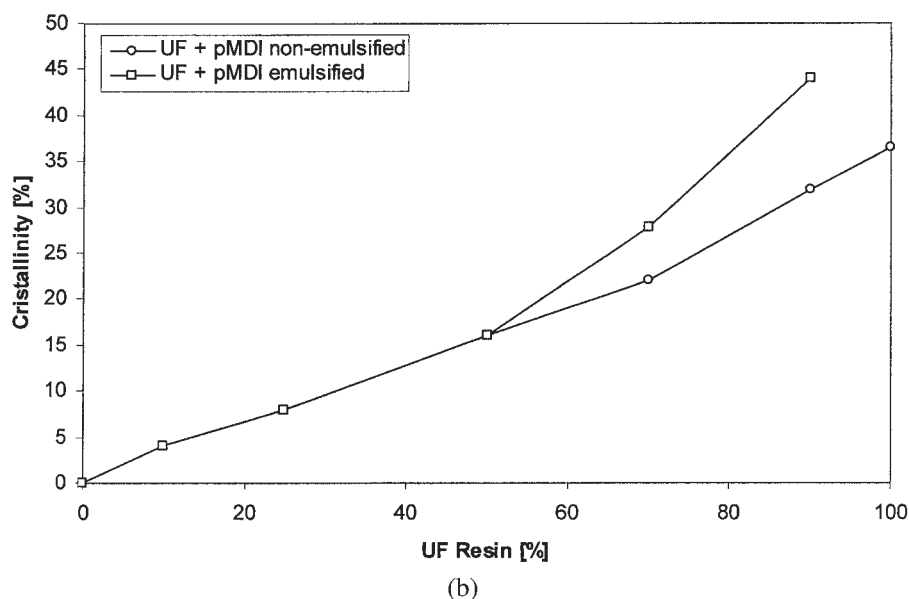
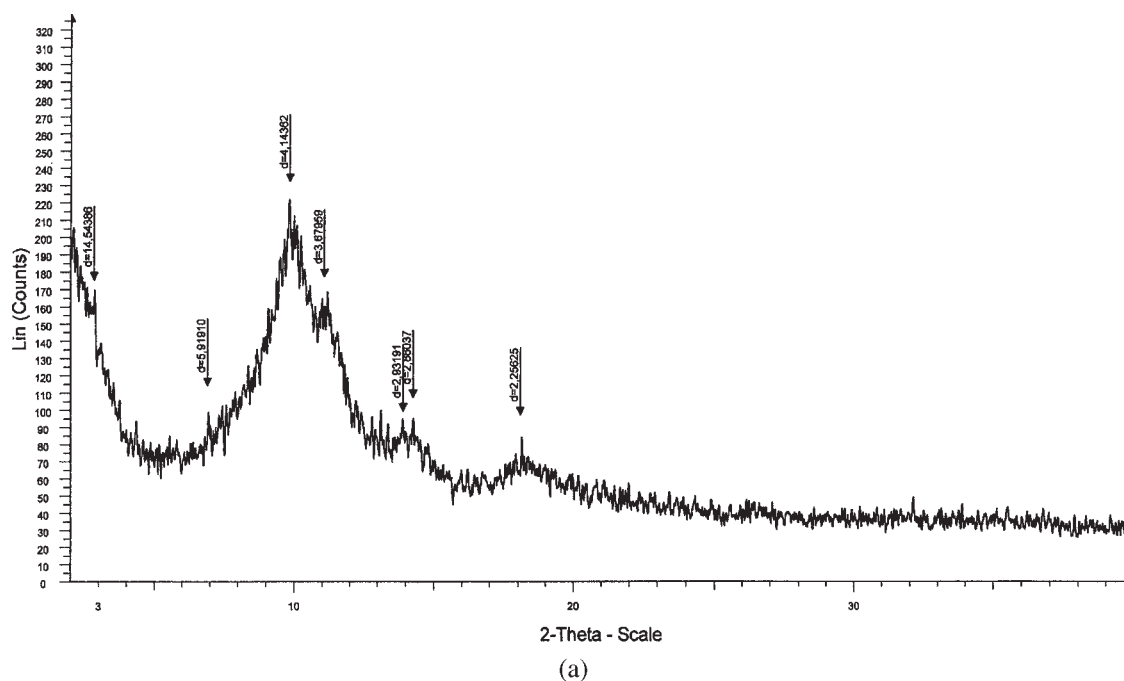
## EXPERIMENTAL

In the first phase the research work was mainly focused on the analysis of the colloidal state of UF/pMDI glue-mixes. Therefore, a commercial UF resin of F/U molar ratio of 1.1, of 68% solids content in

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water was mixed with one of two commercial polymeric isocyanates for wood bonding, of which one is an emulsifiable isocyanate (Woodcure-300, WC-300 and WB-300, ex Nippon Polyurethane Industry). The ratios for the studies were (based by weight on a resin solids/resin solids ratio) UF/pMDI = 0/100, 10/90, 25/75, 50/50, 70/30, 90/10, and 100/0. To these mixes 1% by weight on resin solids of a 10% solution of ammonium sulfate was added as hardener. First, the colloidal state of the hybrids was analyzed starting directly after mixing, monitoring the

changes until the cured stage of the hybrids, by means of polarized light optical microscopy (PLOM). In a second study, gel times of new mixed hybrids were determined at 100°C according to the standard FESYP (Federation Des Syndicats des Producteurs de Panneaux) test. These were at around 3 min under the conditions used. The gelled/hardened resins obtained by the gel test were air-dried at ambient temperature and then ground for X-ray diffraction (XRD) analysis and solid state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy.



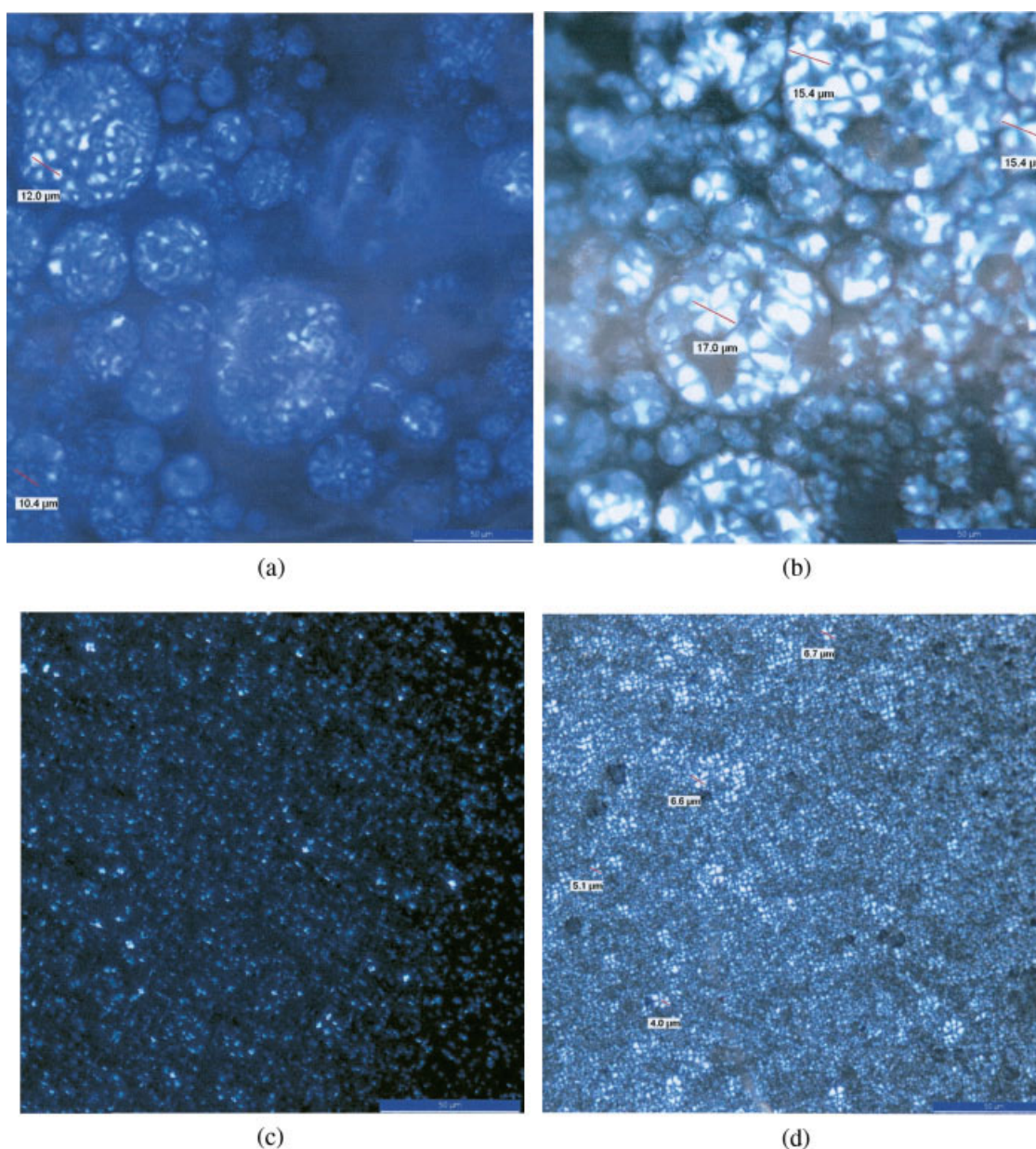
**Figure 1** X-ray diffraction of hardened UF/pMDI resin system, (a) X-ray diffractogram of reflections as a function of angle  $2\theta$  for the resin 70 : 30 UF : pMDI. (b) Variation of percentage crystallinity as a function of the percentage proportion of UF resin solids in the UF/pMDI system when using emulsified and nonemulsified pMDI.

## RESULTS AND DISCUSSION

The XRD analysis of UF/pMDI mixes displayed a characteristic amorphous material pattern; characteristic of UF resins,<sup>15</sup> to which is superimposed a less evident microcrystalline pattern. An example of the variation of the intensity of diffraction peaks as a function of the  $2\theta$  angle is shown in Figure 1(a). The percentage crystallinity obtained by the XRD analysis of the series of different UF/pMDI combinations is shown in Figure 1(b). Figure 1(b) shows that the percentage proportion of UF resin and the relative crystallinity of the system present an almost linear rela-

tionship. For UF resin solids percentages over 70%, the relative crystallinity of both emulsified and non-emulsified pMDI/UF mixes seems to increase at a slightly faster rate.

For a pure UF resin at 100% urea, the level of crystallinity obtained was of 37%, which approximately corresponds to a resin of a molar ratio U : F of around 1 : 1.1, as confirmed by the results of other authors. At lower UF ratios (< 50%) there appears to be a slightly higher reaction between UF and MDI. The mix with emulsified pMDI has a higher degree of crystallinity. This means that there is less interaction between UF and emulsified MDI than between



**Figure 2** Polarized light optical microscopy of died hardened resins (a) UF/pMDI 70/30, (b) UF/pMDI 50/50, (c) UF/pMDI 100/0, UF alone control, (d) UF/pMDI 0/100, pMDI alone control. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



UF and nonemulsified MDI, hence there appears to be an easier possibility of coreaction between nonemulsified MDI and UF.

The patterns of the colloidal particles and clusters which can be seen in the PLOM micrographs shown in Figure 2 seem not to be crystalline ones. If they are, this exclusively depends on the percentage of UF present in the mix. What is interesting to see in Figure 2(a, b) is the existence of round particles, within which exist other different and clearly colloidal particle aggregates in the hardened state of the system. Thus, one of the resins of this mixed system form the big colloidal particles, within which are contained the colloidal particles of the second resin. As the images in Figure 2(a, b) refer to the hardened resin, it is of interest to see that the particles within particles hardened configuration is conserved even in the hardened state of the mixed resin. As regards, which resin is within and which resin is the one forming the enveloping particles, the indications are that the enveloping resin is the isocyanate and the aggregates inside are the UF resin, as Figure 2(c, d) clearly show when the isocyanate is absent. This is an interesting observation if one considers that water is not present in this resin system, the resins in Figure 2 being in their hardened state. It allows to think that higher molecular weight UF oligomers migrate away from the water starting from when they reach a certain colloidal size or molecular weight to migrate within the isocyanate droplets. The reaction of hardening then occurs UF to UF within the droplet of isocyanate, and UF-to the containing MDI also within the isocyanate droplet.

Already presented  $^{13}\text{C}$ -NMR spectra of the hardened UF/pMDI resin systems have shown that urethane bridges derived by the reaction of the isocyanate group with the hydroxymethyl group of urea do form, even at fast curing times.<sup>1,4</sup>

## CONCLUSIONS

The research work presented is focused on the characterization and understanding of the UF/pMDI hybrid adhesives-panel properties interactions for wood based panels, specifically for particle boards, MDF, and HDF. This initial study showed interesting results regarding the crosslinking behavior of the hybrid adhesive systems and the interactions between UF with emulsified and nonemulsified pMDI, in particular the existence of colloidal particles of a resin having migrated within the particles of the second resin of the mixed hybrid system.

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