Highly flexible glycol-urea-formaldehyde resins

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ABSTRACT

Urea-formaldehyde resins are successfully used in many contexts, but their tightly crosslinked thermoset structure impairs some applications, due to stiff and brittle behavior. In this work we show that copolymerization of urea and formaldehyde with glycols introduces linear flexible segments in the polymer structure, thus increasing the resilience and flexibility of the resin after curing. Glycols with different molecular weights (106, 200 and 400 g/mol) were incorporated in the synthesis in different amounts. The chemical and physical-mechanical properties of the resulting products were investigated in detail, namely using FTIR, ^{13}C RMN, GPC/SEC analysis, dynamic mechanical analysis, adhesive bond strength, and tensile-strain testing. Use of poly-ethyleneglycol with molecular weight 200 g/mol yielded the most promising glycol-urea-formaldehyde resin, with remarkable resilience and good adhesion properties. When used for paper impregnation, the modified resins yielded flexible and tough papers, in comparison with a conventional urea-formaldehyde resin, which produced brittle papers that fractured easily upon bending.

1. Introduction

Urea-formaldehyde (UF) resins are a type of so-called amino resins. They are currently used on a wide range of products: abrasives, foams, impregnated paper laminates, textiles, molded compounds, and adhesives [1]. After thermal curing they display very good adhesion on many substrates, particularly lignocellulosic, showing high tensile strength and excellent solvent and heat resistance. Their high crosslink density results in high stiffness and brittleness [1], which is a limitation for applications where a final product with flexibility and resilience is desired. One example is resin-impregnated paper, used as finishing foil for wood based panels by the furniture industry [2]. After curing, the UF-impregnated paper becomes extremely brittle, which forbids post-forming over curved surfaces. The same occurs with fabric substrates [1,3], which cannot be post-formed, and become prone to wrinkling when impregnated with UF resins. In the context of adhesives, it has been argued that improving the flexibility of the crosslinked structure of UF resins would improve the bond quality, since it would allow decreasing internal stresses at the glued joint [4–6]. Also foams based on amino-formaldehyde resins would benefit from being less brittle for some applications [7–9].

A number of studies can be found in the literature focused on decreasing the brittleness of urea and/or melamine-formaldehyde resins [8,10–20]. All strategies are based in the same principle: decreasing the high crosslink density that characterizes these resins. One approach found in some patents from the 70s and 80s, with limited details, is copolymerization with glycols for production of post-formable laminates based on resin-impregnated paper [13–15]. The feasibility of reacting glycols with urea-formaldehyde polymer has been demonstrated before. The hydroxymethyl groups present in an UF resin can be etherified with alcohols in acidic medium [1]. Gresham et al. [21] claimed in 1944 the preparation of glycol formals, obtained by reacting ethylene glycol with formaldehyde in the presence of sulfuric acid. Hodgins and co-workers described an urea-formaldehyde-ethylene glycol resin appropriate for coatings, discussing the flexibility of the final product as a function of the carbon length of the acetal formed [22,23].

In the present work we describe the copolymerization of linear glycols with urea and formaldehyde as a strategy to dramatically increase the flexibility of the cured resins. Being incorporated in the polymer structure, the glycols introduce flexible soft segments and act as spacers between crosslinking sites, therefore decreasing crosslink density. Glycols with different molecular weights are tested, and their effect on different chemical and physical properties of the final product

is discussed. The applicability of the resulting resins in paper impregnation and as adhesive systems is demonstrated. To the best of our knowledge, this is the first time that a detailed study of the glycol-urea-formaldehyde reactive system is presented in the literature.
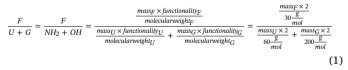
2. Materials and methods

2.1. Materials

Urea (U), formaldehyde (F) solution at 55 wt%, sulfuric acid (H_2SO_4) solution at 98 wt%, sodium hydroxide solution at 50 wt% (NaOH), ammonium sulfate ((NH_4)$_2SO_4$) solution at 30%, diethylene glycol (DEG) and polyethylene glycol with number average molecular weight 200 g/mol (PEG200) were provided by EuroResinas – Indústrias Químicas S. A. (Sines, Portugal). Polyethylene glycol with number average molecular weight 400 g/mol (PEG400) and hexamethylene-diamine ($C_6H_{16}N_2$) were purchased from Sigma-Aldrich, USA. The overlay paper used for resin impregnation was supplied by Euroresinas – Indústrias Químicas, S.A. (Sines – Portugal).

2.2. Synthesis of glycol-urea-formaldehyde resins

The glycol-urea-formaldehyde (GUF) resins were prepared in a three-necked 2500 ml glass flask under atmospheric pressure, adapting the so-called strongly acid process [24,25]. Formaldehyde 55% solution was charged into the reactor and the pH value was adjusted with a strongly acid. Urea and glycol (molar ratio F/U = 2 and equivalent molar ratios F/(U + G) = 1.41, 1.26 or 0.93) were added in equal parts over a time span of 120 min. The reaction was carried out at 80 °C. After 60 min of reaction, the pH was adjusted to > 9.0 with sodium hydroxide solution at 50% and the solution was cooled to room temperature. Solid content of all resins was adjusted to 50%. The hypothetical chemical reaction scheme is depicted in Fig. 1.

GUF resins were synthesised with different glycols (DEG, PEG200 and PEG400) and different molar ratios. F/(U + G) refers to the equivalent molar ratio, defined as the number of reactive groups present in formaldehyde over the number of reactive groups present in urea and glycol. It is considered that formaldehyde has one carbonyl group that allows two reactive sites, urea has two NH_2 groups and glycol has two hydroxyl groups available for reaction. One example if PEG200 is used:

$$\frac{F}{U+G} = \frac{F}{NH_2 + OH} = \frac{\frac{mass_F \times functionality_F}{molecular\,weight_F}}{\frac{mass_U \times functionality_U}{molecular\,weight_U} + \frac{mass_G \times functionality_G}{molecular\,weight_G}} = \frac{\frac{mass_F \times 2}{30\frac{g}{mol}}}{\frac{mass_U \times 2}{60\frac{g}{mol}} + \frac{mass_G \times 2}{200\frac{g}{mol}}}$$

(1)

Samples were named according to the type of glycol used in the synthesis and the F/(U + G) ratio. For example, "PEG200_1.26" means: GUF resin synthesized with PEG with molecular weight of 200 g/mol and a F/(U + G) ratio of 1.26.

In contrast with the conventional alkaline-acid process, in the strongly acid process it is difficult to control the condensation step at molar ratio F/U < 2, because resin gelification often occurs inside the reactor [25]. For this reason, the corresponding reference UF resins without glycol with F/U = 1.41, 1.26 or 0.93 were not synthesized.

2.3. Generic characterization of UF resins

The solid content (%) was determined by evaporation of volatiles in two grams of resin for three hours at 120 °C in an oven. The experimental solid content was determined by the mass ratio of the sample after and before drying.

The kinematic viscosity was determined by Ford Cup n° 4 method. The measurements were performed at 25 ± 1 °C.

The pH was measured using a combined glass electrode.

The density (kg/m^3) was measured using a hydrometer.

Gel time is the time needed for the resin gelification under hot and/or catalysed conditions. It was measured using a laboratory test tube immersed in boiling water or oil at three conditions: neat resin at 120 °C, resin with 3% of ammonium sulfate at 100 °C, and resin with 3% of hexamethylenediamine at 100 °C. The purpose was to evaluate the reactivity of the polymer under acid and alkaline conditions.

Free standing GUF films were prepared by casting-evaporation. 25 g of solution of GUF resin was poured into a PTFE-coated mould. This was then kept at room temperature for 48 h, then 4 h at 80 °C, 2 h at 100 °C, and finally 3 h at 120 °C. The films obtained were about 1 mm thick and 100 mm in diameter. The rigidity/flexibility of the films was firstly evaluated by manual testing. This qualitative evaluation was considered pertinent for the purpose of the discussion presented here.

The storage stability was evaluated comparing the pH and viscosity of the resins after 0, 60 and 240 days of shelf time. pH and viscosity were measured as described above.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR measurements were performed with a Bruker Vertex 70 spectrophotometer. The samples were scanned using a Platinum-ATR single reflection diamond ATR module. Spectra were recorded in the wavenumber range 4000–500 cm^{-1} by signal averaging of 64 scans at a resolution of 4 cm^{-1}. The samples were resin films prepared as described above.

2.5. Liquid ^{13}C NMR experiments

About 40 mg of liquid sample was directly mixed with 0.75 ml deuterated water and the mixture was placed in an NMR tube. The high concentration of the samples allowed very good signal/noise ratios. The spectra were obtained on Bruker Avance III (75.47 MHz for 13C) using a repetition delay of 1.5 s, 536 scans and about 30 min for accumulate. Chemical shifts are expressed as parts per million.

2.6. GPC/SEC analysis

GPC/SEC equipped with a Knauer RI detector 2300 and a Knauer injector with a 20 µl was used. The columns were PSS GRAM with a pore size 30 Å and a particle size of 100 µm, conditioned at 60 °C using an external oven. The flow rate was 1 ml min^{-1} and dimethylformamide was used as the mobile phase. Samples for analysis were prepared by dissolving a small amount of resin (100 mg) in dimethylsulfoxide (3 ml), followed by vigorous stirring during 1 min. Subsequently, the sample was left to rest (10 min), filtered through a 0.45 µm nylon filter and then the sample was injected [26].

2.7. Film flexibility

Free standing films were prepared by the casting-evaporation process. Approximately 20 g of resin was prepared and poured into a PTFE coated mold. This was then kept at 60 °C for 12 h, until water evaporated and film was formed. To cure the resins, temperature was increased to 80 °C for 4 h, 120 °C for another 4 h and 1 h at 150 °C to ensure complete cure. The films obtained were about 1 mm thick and 100 mm in diameter. The flexibility of the films was subjectively evaluated by bending manually and checking for the occurrence of fracture or fissures.

2.8. Mechanical properties of resins supported in overlay paper

The mechanical properties of the resins were quantitatively evaluated after curing on a substrate, since it was not possible to produce defect-free films. The substrate chosen was overlay paper (grammage 20 g/m^2). Sheets of this paper (dimensions 21 × 30 cm^2) were