Preparation of Phenol–Urea–Formaldehyde Copolymer Adhesives under Heterogeneous Catalysis

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ABSTRACT: A new synthetic strategy for PUF copolymers based on three steps was developed. In the first step, two precondensates of phenol with formaldehyde and urea with formaldehyde, respectively, were produced. In the second step, the two precondensates were mixed and condensed using a heterogeneous catalyst in a tube reactor at 90°C. The last step is a vacuum distillation to reach the final copolymer compositions. With regard to the properties, the products can be used as adhesive. The copolymers were analysed by gel permeation chromatography (GPC), ^{13}C-NMR-spectroscopy, and MALDI-TOF mass spectrometry. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2946–2952, 2006

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INTRODUCTION

Phenol–formaldehyde (PF) resins have been widely used as adhesives in various applications for more than 50 years.[1] A well-known method to modify PF adhesives is the addition of urea (U) during or after the resin preparation. In most adhesives the amount of urea is less than 10% by weight because higher concentrations will cause lower hydrolytic stability and higher formaldehyde emissions. The addition of urea changes also the characteristic properties of the adhesive. It was clearly shown that the amount of free formaldehyde is decreased.[2] The viscosity is also decreased and the system can be condensed to a higher degree. The urea can be added for instance at a temperature of about 60°C at the end of the condensation step. The amount of urea reacts with free formaldehyde to methylolated ureas and does not react further under alkaline conditions.[3] According to the investigations of Scopelitis and Pizzi,[4] PUF copolymers are formed during curing at higher temperatures.

Kim[5] investigated particle boards produced by the use of PF adhesives with different amounts of urea and found a decrease in the properties with higher concentration of urea. Öldorp and Marutzky[6] found an improvement of internal bond and thickness swelling of PF-bonded particle boards within the narrow limits of urea. More interesting is the fact that the urea could be extracted from the boards afterwards. Obviously, no co-condensation occurred between urea and the PF adhesive by the hardening during board production.

The attempt to combine phenol, urea, and formaldehyde in a real co-condensation was conducted by some groups using different ways of synthesis. Tomita et al.[7–9] started the synthesis with a UF precondensate, added phenol and condensed under acid conditions, followed by a further condensation step under alkaline conditions. Pizzi et al.[10,11] started the condensation of phenol and formaldehyde under alkaline conditions, added urea, and condensed further. Du Guaben et al.[12] used only alkaline conditions to condense urea, phenol, and formaldehyde in one batch.

In the present work we present a new synthetic route to co-condensate phenol, urea, and formaldehyde. It involves a three-step procedure where PF and UF precondensates are first prepared and then, in the following steps, co-condensed in a tube reactor by the use of a ion-exchange resin as heterogeneous catalyst.

Ion exchangers are working satisfactorily as catalysts in many technical processes. Important applications, for example, are etherification (production of methyl-tert-butylether or tert-amylmethylether), esterification (acrylates, fatty acid esters) or the hydrogenation (alcohols from olefins). They can also be used for condensation processes. Technically relevant examples are the production of bisphenol A from phenol and acetone or the cleaning of phenol by condensation of the by-products and following separation. Depending upon the application purpose, basic or acid ion exchangers are used.[13]

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In the present work two different ion-exchange resins were used: Amberlyst IRC-50 and IRA-67. Other technical and scientific applications of IRC-50 are the removal of co-inhibitors before the polymerisation of unsaturated carboxylic acids,[14] the synthesis of peptides and 1,4-benzodiazepines after esterification of the resin,[15] or the preparation of N-vinyl-formamide which can be used as monomer for the production of polyvinylamines.[16] IRA-67 can, for instance, be used to recover fluorinated acids during the production of fluoropolymers[17] or to adsorb organic acids like citric acid during biosynthesis.[18]

MATERIALS AND METHODS

Chemicals

The chemicals used were urea (Norsk Hydro, Brunsbuettel, Germany), phenol, DMSO-d_6 (Sigma-Aldrich, Steinheim, Germany), DMF (Mallinckrodt Baker, Griesheim, Germany), formaldehyde (Leuna, Germany) (37% aqueous solution, technical grade, Arkema).

Preparation of PUF copolymers under heterogeneous catalysis

It is well known that UF polymers are mostly condensed under acidic conditions, while PF polymers can be produced under alkaline (resol) or acidic conditions (novolak). But under acid conditions, phenol–formaldehyde polymers are mostly linear. To form a duroplastic network from urea, phenol, and formaldehyde, the optimum pH value must be chosen very carefully so as to get copolymerisation and not homopolymerisation with free urea or free phenol at the end of the condensation step, respectively. Therefore, a new approach was used to condense the monomers under neutral conditions by means of a heterogeneous catalyst.

First step

Phenol–formaldehyde precondensate: 2 mol of phenol (188.0 g) were mixed with 5 mol of formaldehyde solution (405.8 mL) and the pH was adjusted to 8.0 with about 15.8 mL of a solution of NaOH (0.1 mol/L). The mixture was then heated up to 90°C and maintained at this temperature for 20 min.

Urea–formaldehyde precondensate: 4 mol of formaldehyde solution (324.6 mL), which contain some amounts of formic acid, were adjusted to a pH of 3.0 by adding a solution of NaOH (0.1 mol/L). After the addition of 2 mol of urea (121.2 g), the pH automatically had a value of 6.8. The solution was held at room temperature for 15 min by gentle heating.

Second step

After mixing the two precondensates (PF and UF), a pH of 8.2 was measured. The pH was then adjusted to a pH of 7.0 by addition of a solution of HCl (0.1 mol/L). The mixture was passed 13 times through the ion-exchange resins inside a double-walled tube reactor (Fig. 1), which is heated up to 90°C by means of a thermostat. On the top and bottom of the reactor the catalyst was captured by glass wool. A drip funnel was installed on the top of the reactor for easier dosage. The catalyst package is composed of a mixture of 20 g Amberlyst IRA 67 and 10 g Amberlyst IRC 50 (both from Rohm & Haas, Frankfurt, Germany). The properties of both catalysts are shown in Table I. Both catalysts were dispersed in water and mixed manually before filling into the reactor. This composition was used to form a catalytic environment with alkaline and acidic centres. The solution of the reaction product was caught in a flask which is heated up to a temperature between 60°C and 70°C. The reaction was stopped by cooling when a viscosity of 50 mPa·s was reached.

Third step

The amounts of water and free formaldehyde in the solution were reduced via vacuum distillation and by this the desired viscosity was also adjusted. To stabilise the reaction product and achieve a longer storage stability, about 2% NaOH (w/w) was added as solution.
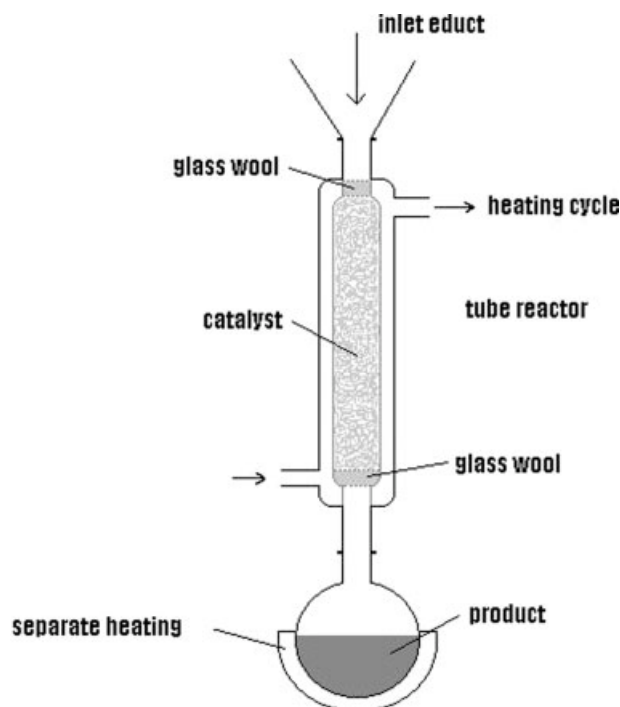

Figure 1 Diagram of the tube reactor.

TABLE I
Characteristic Properties of the Used Catalysts (Ion-Exchange Resins)

Property/system	IRA-67	IRC-50
Behaviour	Weak anionic	Weak cationic
Matrix	Microporous polystyrene	Macroporous polyacrylate
Bead size	16–50 mesh	
Ionic form	Free base	H^+
Moisture content	60%	48%
Total exchange capacity	5.6 meq/g	10 meq/g
pH range	7–9	5–14

GPC

The GPC system (Thermo Separation Products) was equipped with a SCM 400 membrane degasser, a Spectra Physics SP 8800 pump, an AS 3000 auto sampler (including a column oven), a Shodex RI detector (Showa Denko, Japan) and a Spectra Physics UV detector. The data were collected using WinGPC software (HS-GmbH, Germany). No calibration was done because the retention times of phenol and methylolated phenols are much different from urea–formaldehyde oligomers.

The columns for separation were two 300×8 mm i.d., 5 µm, MZ gel SD plus (10^3 and 50Å) and a precolumn (MZ Analysentechnik, Germany). Oven and tray temperatures were kept at 80°C and 30°C, respectively. The flow rate was 1.0 mL/min and a sample injection volume of 20 µL was used.

The samples were filtered through a 0.45 µm filter (Polypropylene, PTFE, Roth, Germany). The concentration of the samples and the standards were 20 mg/mL. The samples were dissolved in N,N'-dimethylformamide by gentle warming and shaking.

NMR

The ^{13}C-NMR measurements have been carried out on a Bruker AM-400 spectrometer. The pulse sequence was recorded with NOE, a pulse angle of 30° and 11,000 scans were accumulated. DMSO-d_6 (Aldrich) has been used as solvent. The signal given by DMSO-d_6 has been taken as internal reference. The signals were assigned according to the literature.[7–11]

MALDI-TOF

The samples were analysed on a Kratos Maldi Compact 4 instrument, which was equipped with a nitrogen laser (337 nm, 3-ns pulse width) and a time-of-flight analyser (TOF). The mass spectra were received in positive reflection mode using an acceleration voltage of 20 kV. One hundred scans were added to obtain a full spectrum. The mass peaks were assigned according to the literature.[19]

The samples were dissolved in a mixture of acetone and acetic acid (4 mg/mL). 2,5-dihydroxybenzoic acid (DHB) was used as matrix. A solution of the matrix in tetrahydrofurane (THF) in a concentration of 10 mg/mL was prepared. A 50 : 50 (w/w) mixture of both solutions was prepared and 2 µL of this mixture were pipetted on the sample plate. The sample was dried in air such that the sample molecules were uniformly embedded in the matrix.
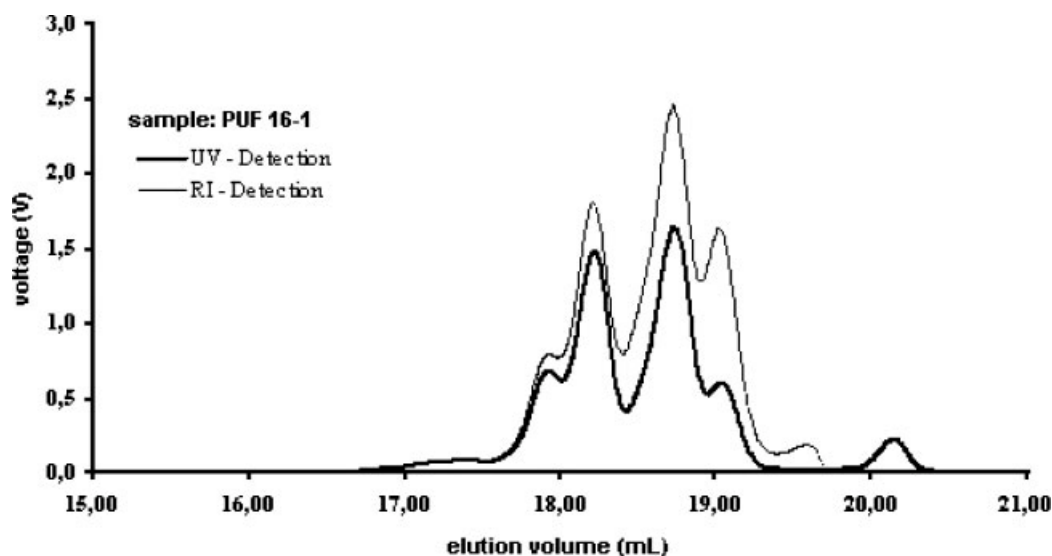

Figure 2   GPC elugram of the PF precondensate PUF 16-1.

TABLE II
Characteristic Properties of the PUF Adhesives

Property/system	PUF 15	PUF 16
Solid content	54.5%	48.6%
Viscosity	470 mPa·s	215 mPa·s
Water solubility	1 : 22	1 : 42
Content of alkaline	2.2%	1.9%
Ph value	10.3	10.1
Storage stability (20°C)	4 weeks	4 weeks

RESULTS

In the first step, PF and UF methylolation reactions were carried out and two typical precondensates were formed. These methylolation reactions followed industrial procedures and have been described several times in the literature, for example, in Mueller.[20]

For the methylolation of phenol, a molar ratio of phenol to formaldehyde of 1 : 2.5 was used. This composition was chosen to keep the amount of free phenol in the final product as low as possible. In preliminary tests it was noticed that it is not possible to incorporate residual free phenol into the copolymer in the condensation step. The phenol-formaldehyde precondensate was analysed by GPC, see elugram in Figure 2. The precondensate mainly consists of methylolated phenols, see peaks at elution volumes of 18 to 19 mL, and some dimers, see peaks at elution volumes of 17 to 18 mL. Only a small amount of free phenol remains in the precondensate, that is indicated by the peak at 20.3 mL. As can be seen, both detectors give almost identical signals. However, the UV detector is able to detect even the free phenol, while the RI detector signal is disturbed in this region by the negative refractive index of the solvent. The degree of condensation is rather low at this stage of the reaction (lowest elution volume 17

mL). The methylolation reaction is stopped after 20 min to prevent condensation.

The precondensate of urea and formaldehyde was produced in an analogous manner. This preparation is also often described in the literature, for example, in Horn et al.[21] The molar ratio of urea to formaldehyde was 1 : 2. Under this condition all the urea is reacting with formaldehyde and mono-, di-, and trimethylolureas and some higher oligomers are formed. Condensation of the system was prevented by the reducing temperature (20°C) and the reaction time. The success of the methylolation was checked by GPC (no figure is presented).

The precondensates were merged and the mixture was brought to pH 7.0 so as to have no homogeneous catalyst (H_3O^+ or OH^--Ions) available. The condensation reaction was carried out in the tube reactor. There were two reaction pathways available: the reaction mixture could react with the acidic (Amberlyst IRC 50) or alkaline (Amberlyst IRA 67) sides of the catalytic mixture. The optimum composition of the catalyst mixture was discovered in several trials by checking the maximum increase of viscosity during this reaction step. The reaction was stopped when the mixture reached 50 mPa·s. This was done to prevent the mixture from sticking to the heterogeneous catalyst.

To reach a higher viscosity (necessary for an adhesive) in order to reduce the amount of free formaldehyde, a vacuum distillation was carried out. The excess of formaldehyde was caused by the high starting molar ratios and could be easily detected by nose. The main goal was to obtain a copolymer which contains almost no free monomers (urea, phenol, and formaldehyde) and where 50% of the phenol was substituted by urea. To check the reproducibility of the procedure the optimised synthesis was
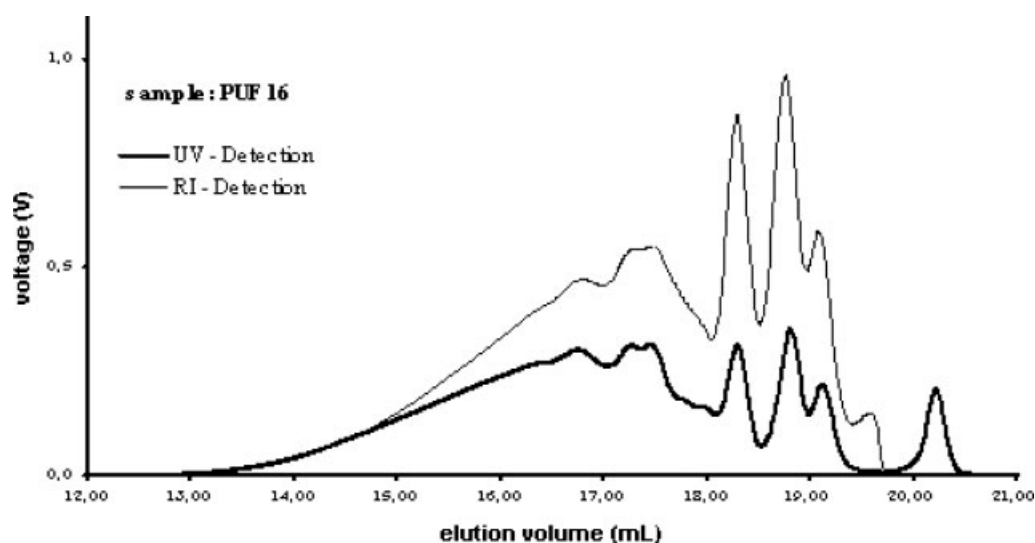

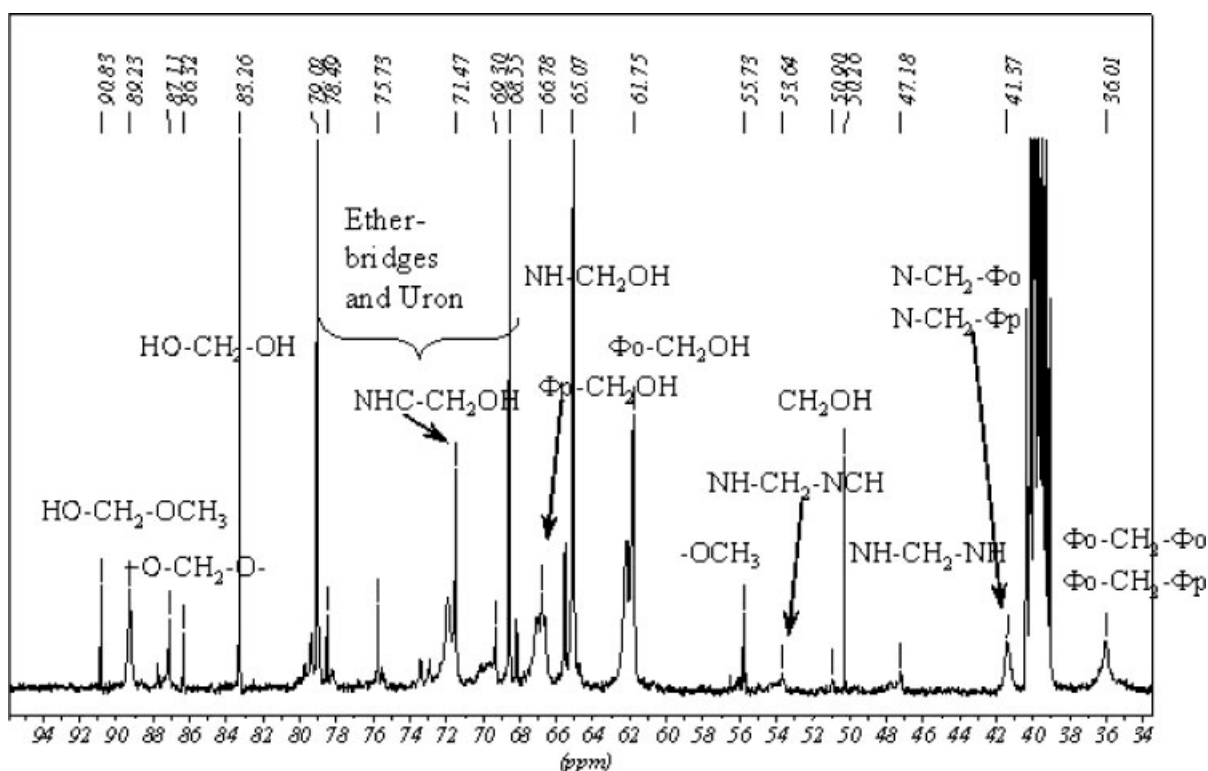Figure 3 GPC-elugram of PUF copolymer PUF 16 after 10 cycles in the tube reactor.

Figure 4 ^{13}C-NMR spectrum of PUF 16 (detail) with the bridge in the ortho-position (Φ_o) and para-position (Φ_p).

repeated once (PUF 15 and PUF 16). The technological properties of the two products are shown in Table II. PUF 15 possessed a higher viscosity and therefore a lower water solubility because the condensation time was slightly longer.

After the adhesive preparation, the products were analysed with regard to molar mass and chemical composition. The molar mass analysis was conducted by gel permeation chromato-graphy (GPC). The results of the GPC analysis of PUF 16 is presented in Figure 3. As was shown previously, a mixture of a PF polymer and a UF polymer can be easily recognised by GPC with two different detector signals.[22] The UV detector is only showing the phenolic part while the RI detector exhibits the total concentration profile of the sample. In the present case, the signals from the RI and UV detectors agree very well. Therefore, it can be assumed that a highly condensed (lowest elution volume 13 mL) PUF copolymer was formed because in this region of the chromatogram both detectors give almost identical signals. Significant differences were only obtained in the regions in which the detectors were selective towards composition. Small amounts of free urea were detected by the RI detector at an elution volume of 19.5 mL and free phenol was detected by the UV detector at an elution volume of 20.3 mL.

The existence of PUF copolymers was also proven by ^{13}C-NMR. If a copolymer is formed, then methyl-ene bridges between phenol and urea must be present in the sample. These linkages between urea and phenol are detected in the region of 40 to 42 ppm, as can be seen in Figure 4. The product also contains certain amounts of free formaldehyde, ethers, urons, and methylol species (see also Fig. 4). A quantitative analysis of all structural elements of PUF 15 and PUF 16 is given in Table III. The copolymers contain mostly methylene bridges between urea and phenol,

TABLE III
Quantitative ^{13}C-NMR Analysis of PUF 15 and PUF 16 in mol % with Methylene Bridges in Ortho-Position (Φ_o) and Para-Position (Φ_p)

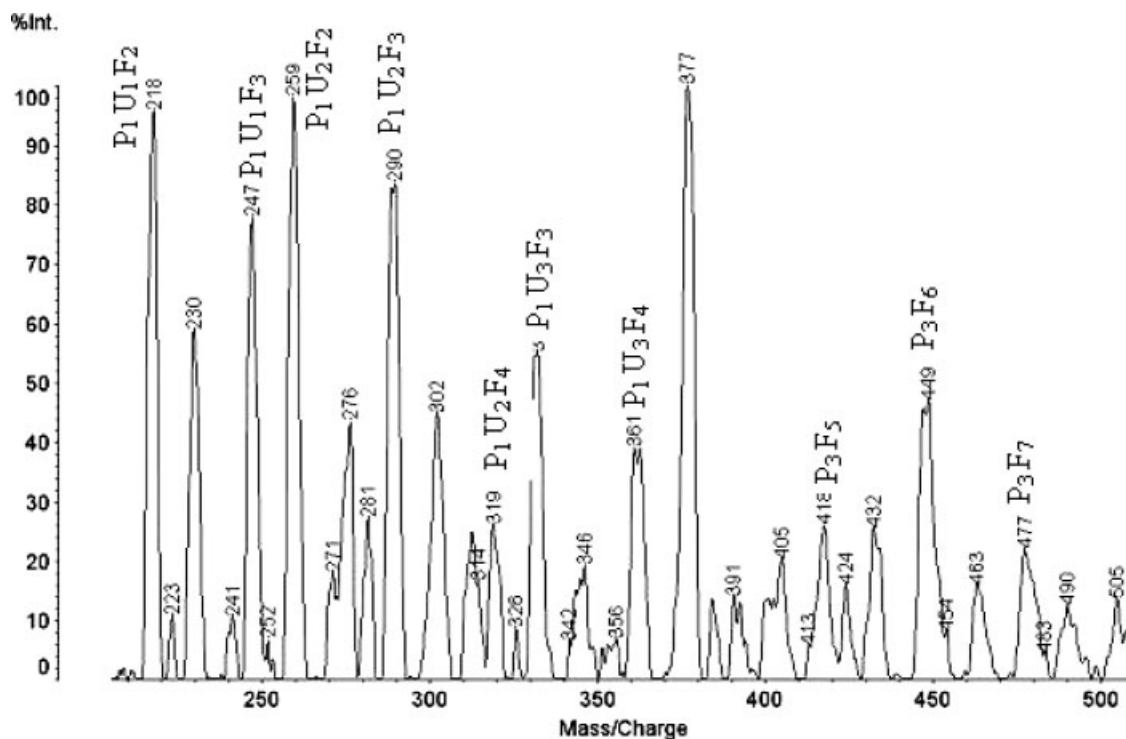| Structural element	PUF 15	PUF 16
$\Phi_o CH_2 \Phi_o$ and $\Phi_o CH_2 \Phi_p$	5.2	4.6
$\Phi_p CH_2 \Phi_p$ + NH—CH_2—Φ_o	4.2	3.6
NH—CH_2—Φ_p + N(C)—CH_2—Φ_o	0.4	0.4
NH—CH_2—NH	1.5	1.6
N(C)—CH_2—Φ_p	0.6	0.7
N(C)—CH_2—NH + N(C)—CH_2—N(C)	1.1	1.4
$\Phi_o CH_2 OH$	18.5	16.1
$\Phi_p CH_2 OH$ and urea methylol	15.2	13.3
Ether bridges	14.7	13.3
Uron—$CH_2 OH$	5.8	6.5
—N(C)—$CH_2 OH$	10.5	9.8
N—$CH_2 OCH_3$	1.9	2.3
Uron rings	12.4	13.5
O—CH_2—O	7.9	12.9
TOTAL	99.9	99.9

Figure 5 MALDI-TOF-MS of PUF 16 copolymer (detail).

but homo-condensation takes also place. Based on all bridges (except ether bridges), the PUF copolymers show around 20% of urea-to-urea bonding, 40% of phenol-to-phenol, and 40% of phenol-to-urea bonding, all via methylene bridges.

This result is confirmed by the MALDI-TOF analysis given in Figure 5 for PUF 16. The following oligomers typical of the PUF copolymer structures are found: $P_1U_1F_2$ (218 g/mol), $P_1U_1F_3$ (247 g/mol), $P_1U_2F_2$ (259 g/mol), $P_1U_2F_3$ (290 g/mol), $P_1U_2F_4$ (319 g/mol), $P_1U_3F_3$ (332 g/mol), $P_1U_3F_4$ (361 g/mol), and $P_3U_1F_7$ (521 g/mol). In addition to these some pure phenolic oligomers were detected: (P_3F_5 to P_3F_7 and P_4F_7).

The adhesives can be used in the wood industry. According to the relative low molecular weight and the low viscosity, they are especially suited for the production of wood-based panels such as particle board, medium-density fibreboard (MDF), or oriented strand board (OSB).

CONCLUSIONS

The use of heterogeneous catalysts for polycondensation has often been described in the literature, but technical applications have been very rare up to now. In this work it was shown that the use of a heterogeneous catalyst in small scale is possible and a true copolymer is formed. Further work will be required to obtain more knowledge about the reactions that take place inside the tube reactor and to reduce the amount of free formaldehyde in the product after condensation. Much more work must be done to optimise the efficiency of the catalyst and to regenerate the catalyst mixture properly, thus allowing production in larger scale.

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