

Characterization of Phenol–Urea–Formaldehyde Resin by Inline FTIR Spectroscopy

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ABSTRACT: Phenol–urea–formaldehyde (PUF) resins were synthesized by a two-step polymerization process. The first step was the synthesis of 2,4,6-trimethylolphenol (TMeP) from phenol and formaldehyde, under alkaline conditions. In the second step PUF resins were synthesized by the reaction of TMeP with urea, under acidic and alkaline conditions. The influence of temperature on the synthesis of TMeP was investigated. The molar ratio between TMeP and urea was varied to study the composition effect on the second step of the PUF synthesis and final product proper-

ties. Synthesis of TMeP and PUF resins were monitored by inline FTIR-ATR system. Analytical methods, such as differential scanning calorimetry, nuclear magnetic resonance, thermogravimetric analysis, and infrared spectroscopy were used for characterization of TMeP and PUF resins. Obtained PUF resins were cured and tested on flexural strength. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2016–2028, 2006

Key words: phenol–urea–formaldehyde resin; inline IR spectroscopy; ^{13}C NMR; DSC; TGA

INTRODUCTION

Since their introduction, the highly versatile family of phenolic resins has played a vital role in construction, automotive, rubber, electrical, and appliance industries.¹ One of the main drawbacks of phenol–formaldehyde (PF) resins in the manufacture of wood composites is their lower curing rate than the amino–formaldehyde resins.² The presence of residue free formaldehyde is another disadvantage of this family of resins. Recently, urea has been introduced into PF resins to improve their curing, to lower the content of free formaldehyde, and to reduce the cost of the resin.^{2–19} To develop practical uses of so-called phenol–urea–formaldehyde (PUF) resins, it is necessary to introduce cocondensation between phenol and urea at the time of resin preparation.⁷

One of the most used procedures for PUF synthesis is the two-step polymerization process, by which the trimethylolphenol (TMeP) is formed in the first step. Temperature and pH, conditions under which the reaction between phenols and formaldehyde is carried out, have a profound effect on the characteristics of the resulting product. In the second step of PUF synthesis, urea bonds are formed by the reaction of urea with TMeP. In this step, the molar ratio between TMeP and

urea is of crucial importance. Furthermore, the reaction between TMeP and urea can be carried out under acidic^{2,3,6} or alkaline^{2,8} conditions. It was observed^{2,8} that PUF resins obtained under either alkaline or acidic conditions have enhanced application properties in comparison to the properties of PF resins.

The aims of our work were to study the two-step PUF resin preparation process and to study the properties of different PUF resins. The influence of temperature on the TMeP synthesis and on the composition of the synthesized product (TMeP) was investigated. In the second step, the molar ratio between TMeP and urea as well as the pH of the reaction mixture were varied to study their influence on the structure of PUF resin. Inline FTIR–ATR spectroscopy was found to be a successful and informative analytical tool for determining individual phenol, formaldehyde, and urea conversions as well as intermediate and final product compositions. We detected the formation of different bridges during the reaction of methylolphenol with an excessive amount of urea under acidic and alkaline conditions. According to a review of the literature available to us, the inline FTIR–ATR technique has not been used in the studies of PUF resins synthesis. Analytical methods such as differential scanning calorimetry, nuclear magnetic resonance, thermogravimetric analysis, and infrared spectroscopy were used for TMeP and PUF resins characterization. Since particularly resol-type resins can be considered for practical applications (such as resol wood adhesive), an important part of our research work was focused on the synthesis of PUF resin under alkaline conditions. Ob-

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tained PUF resins were cured and tested for flexural strength.

EXPERIMENTAL

Materials

Phenol (>99%), 37% formaldehyde aqueous solution, sodium hydroxide (98%), solid urea (98%), and sulfuric acid (98%) were used. All the chemicals were supplied by Aldrich.

TMeP synthesis

TMeP was synthesized in a 500-mL semibatch reactor fitted with a reflux condenser, a mechanical stirrer, a digital thermometer, and an IR probe.

First, 1 mol of phenol in aqueous solution (90%) and 40 g of NaOH dissolved in 100 mL of water were charged into a reactor vessel. The sodium hydroxide solution was added to obtain reactive sodium methylolphenate and to adjust the pH to 12. The content was stirred and cooled to 5°C. Formaldehyde (2.5 mol) in aqueous solution was added dropwise into the reactor. After adding the formaldehyde solution, the reactor content was heated to the three chosen reaction temperatures 25, 40, and 60°C. The reaction was carried out for 6 h at each chosen temperature and then for an additional 4 days at room temperature. The first 6 h of the experiment were monitored by the inline FTIR-ATR spectroscopy, using the Mettler Toledo ReactIR-4000 instrument coupled with DiComp diamond probe. IR spectra were collected every 3 min, in the wave number range between 4000 and 650 cm^{-1} at resolution 8 cm^{-1} . The first spectra were collected before formaldehyde addition. At the end of the synthesis the traditional titration method for determining free formaldehyde was carried out.

PUF resin synthesis

PUF resins were synthesized in a 500-mL semibatch reactor fitted with a reflux condenser, a mechanical stirrer, a digital thermometer, and an IR probe.

Three different PUF resins of phenol/formaldehyde/urea molar ratio 1.0/2.5/0.5, 1.0/2.5/1.0, and 1.0/2.5/2.0 were prepared. Each PUF resin with the desired molar ratio was synthesized under acidic (PUF AC; pH = 2) and alkaline (PUF AL; pH = 12) medium. The desired molar amount of solid urea was dissolved in water, charged into a reactor vessel, stirred, and heated to 90°C. Then, the previously synthesized TMeP in aqueous solution was added slowly into the reactor. IR spectra were collected every 2 min, in the wave number range between 4000 and 650 cm^{-1} . The first spectrum was collected before addition of TMeP aqueous solution. After the addition of

TMeP, the reaction was continued under unchanged conditions for at least 2 h. The solid content of all synthesized resins was about 40%.

^{13}C and ^1H nuclear magnetic resonance

The ^1H and ^{13}C NMR spectra were measured using Bruker DPX 300 MHz instrument. Samples for NMR measurement were not purified and dried. D_2O or pyridine was used as a solvent. When D_2O was used as a solvent the ^1H and ^{13}C NMR signals were referred to tetramethylsilane (TMS) as an external standard. For PUF resins soluble in pyridine the ^1H and ^{13}C NMR signals were referred to TMS as an internal standard. Assignment of individual signals was made on the basis of the available literature^{3,13-15,20-22} on PF and PUF resins. A 2.0-s pulse delay time was used with the gated decoupling of protons for quantitative measurements.

Thermogravimetric analysis

Dynamic thermoanalytical measurements were performed on a Mettler Toledo TGA/SDTA 851^e instrument, using maximal resolution method in a temperature range from 25 up to 600°C. The parameters in maximal resolution method were set as follows: maximal heating rate 10 K min^{-1} , minimal heating rate 1 K min^{-1} , high threshold 3 $\mu\text{g s}^{-1}$, low threshold 1 $\mu\text{g s}^{-1}$, factor 2. That means when the weight loss exceeds 3 $\mu\text{g s}^{-1}$, the heating rate was automatically lowered to 5 K min^{-1} (by factor 2).

Samples for TGA testing were dried at room temperature and in a vacuum for a period of 24 h. The initial mass of the sample was ~10 mg. Platinum crucibles (diameter 8 mm) and dynamic air atmosphere with a flow rate of 100 mL min^{-1} were used.

Dynamic scanning calorimetry

The measurements were performed on a METTLER TOLEDO 821^e instrument with intracooler, using the STAR software. In and Zn standards were used for the temperature calibration and for the determination of the instrument time constant. For the heat flow calibration, the In standard was used. To study the crosslinking reactions of TMeP and PUF resins, the measurements in the temperature range from 25 to 280°C, at heating rate 10°C min^{-1} were performed. Medium pressure pans were used to eliminate the endothermic peak of the evaporation of water and other volatile species.

Flexural properties

The method ISO 178 (2001) was used to prepare PUF test specimens and to investigate the flexural behavior by determining the flexural strength at break.

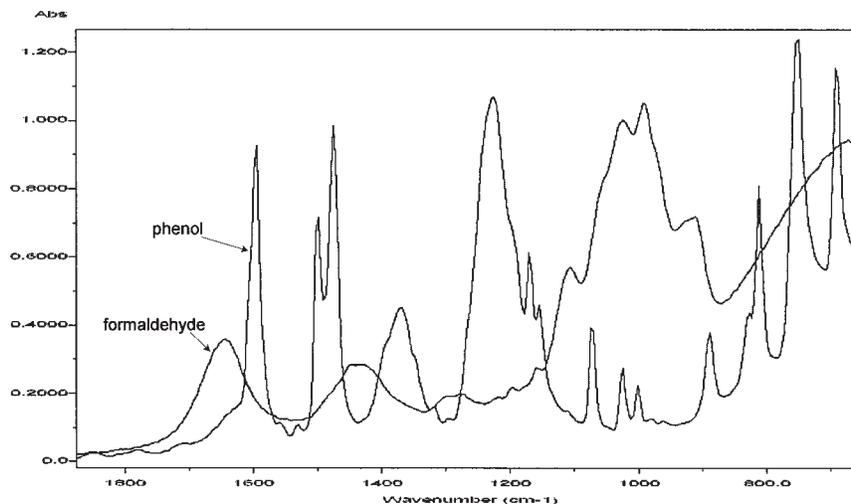


Figure 1 The IR spectra of phenol and formaldehyde aqueous solutions.

RESULTS AND DISCUSSION

TMeP synthesis

FTIR-ATR spectrometry was used to monitor the reaction of phenol with formaldehyde at 25, 40, and 60°C. The assignment of the characteristic peaks of phenol and formaldehyde was done using the previously collected spectra of both reactants in aqueous solution. The spectra of phenol and formaldehyde solutions are presented in Figure 1. The assignment of characteristic peaks was done on the basis of the relevant literature.^{23–26}

The spectra in the wave number range of interest for the TMeP synthesis at 60°C are presented in Figure 2. They were collected every 3 min at a resolution of 8 cm^{-1} , with 64 scans for each spectrum. As shown in Figure 2, the characteristic peaks of phenol at 1586, 1478, 1266, 1165, 992, and 764 cm^{-1} diminished with increasing reaction time. The peaks at 1586 and 1478

cm^{-1} corresponded to the C=C aromatic ring vibrations. The peaks at 1266 and 1165 cm^{-1} corresponded to the C—O asymmetric stretch and C—H in-plane deformations, respectively, while the 992, and 764 cm^{-1} peaks belonged to the C—H out-of-plane vibrations. The peak at 1370 cm^{-1} , which corresponded to the phenol O—H in-plane bend (observable in Fig. 1), was not detected, because of the sodium hydroxide addition and the sodium methylolphenate formation. The aqueous solution of formaldehyde was added into the reactor for ~ 95 min at the beginning of the process; therefore, the characteristic peaks of methylene glycol C—O, O—H, and C—H bends at 1104, 1023, and 992 cm^{-1} , respectively, increased during this period (Fig. 2). After the addition of the formaldehyde solution was completed and the reactor content heated to 60°C, a sharp decrease of phenol and formaldehyde peaks was observed as a result of the reaction. The signal at 1428 cm^{-1} corresponding to the C—H bends

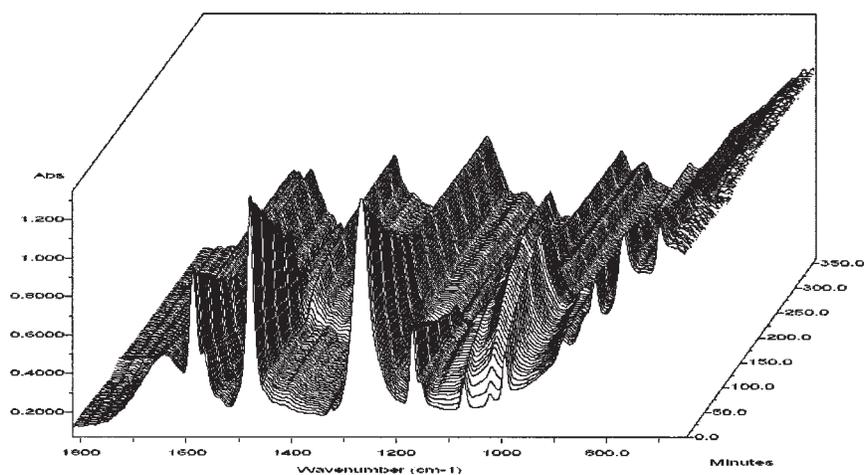


Figure 2 The IR spectra in the wave number range of interest for the TMeP synthesis at 60°C.

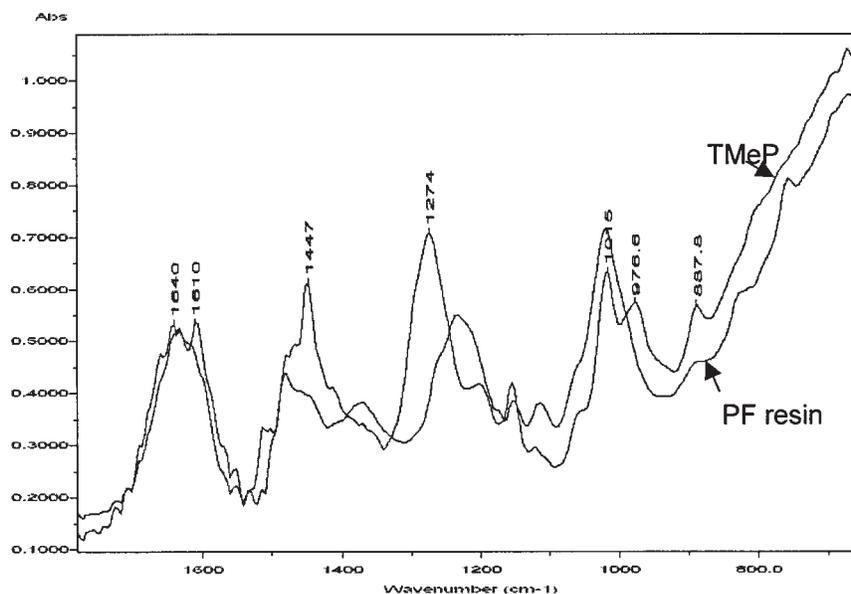


Figure 3 IR spectrum of TMeP obtained after 4 days of reaction at room temperature compared to IR spectrum of a phenol–formaldehyde resin.

(observable in formaldehyde solution spectrum in Fig. 1) shifted to 1447 cm^{-1} due to the addition reaction of formaldehyde on the aromatic ring. The new C—H bends belonged to the reaction product and overlapped with the formaldehyde signal. It can be observed (Figs. 2 and 3) that an additional peak occurred at 1610 cm^{-1} . This peak was attributed to C=C band vibrations of the product aromatic ring. During the reaction, the peaks of O—H and C—H bends shifted from 1023 to 1015 cm^{-1} and from 992 to 976 cm^{-1} , respectively. The presence of one or several methylol groups in the ortho position, favors intermolecular hydrogen bonding. In this case, the vibration is split and there is a shift towards higher wavelengths. The line at 890 cm^{-1} is characteristic of 1,2,4,6-tetrasubstituted rings.

To confirm the absence of PF resin in the product of the reaction at 60°C the IR spectrum of the product (obtained after an additional 4 days of reaction at room temperature) was compared with spectrum of a PF resin in Figure 3. In PF resin spectrum, additional characteristic signals of methylene bridge C—H bend at 1478 cm^{-1} and methylene–ether bridge C—O—C bend at 1116 cm^{-1} were present.

The concentration profiles for phenol, formaldehyde, and the reaction product are drawn in Figure 4. The profiles were generated by the use of ConclRT[®] Opus I software. In the first 95 min, when the formaldehyde solution was added in the reactor at 5°C , the concentration of formaldehyde increased and the concentration of phenol decreased. In 115th minute, when the reaction mixture reached the desired temperature 60°C , the concentrations of phenol and formaldehyde started to decrease. On the other hand, the concentra-

tion of the reaction product (mono-, di-, and trimethylolphenol) increased considerably in this period (115–200 min) of the reaction. Then, the concentration of the reaction product, as shown in Figure 4, increased slowly, because all the phenol already reacted, while the remaining formaldehyde was consumed in reactions of di- and trimethylolphenol formation. After the first 6 h of the experiment the concentration of free formaldehyde in the reaction mixture was $(4.4 \pm 0.5)\%$. The inline end values of the formaldehyde consumption agreed well with those from offline traditional titration method.

The comparison of absorbance profiles of the phenol peak at 1594 cm^{-1} during the reaction at 25, 40, and 60°C is shown in Figure 5. First, the absorbance decreased due to the formaldehyde solution addition. Thereafter, the absorbance decreased due to the phenol reaction with formaldehyde. It is clearly observable that at 60°C the reaction rate was considerably higher and that the concentration of phenol after 6 h of reaction was lower. As it was observed earlier (Fig. 3), the condensation reaction between methylol groups did not occur and the methylene or methylene–ether bridges of PF resin were not formed at 60°C .

The chemical structure of all the TMeP synthesized after 4 days of additional reaction at room temperature was investigated using FTIR–ATR spectrometry. The spectra of TMeP were practically identical.

PUF resin synthesis

PUF resins were synthesized by adding TMeP, obtained after 4 days of reaction between formaldehyde

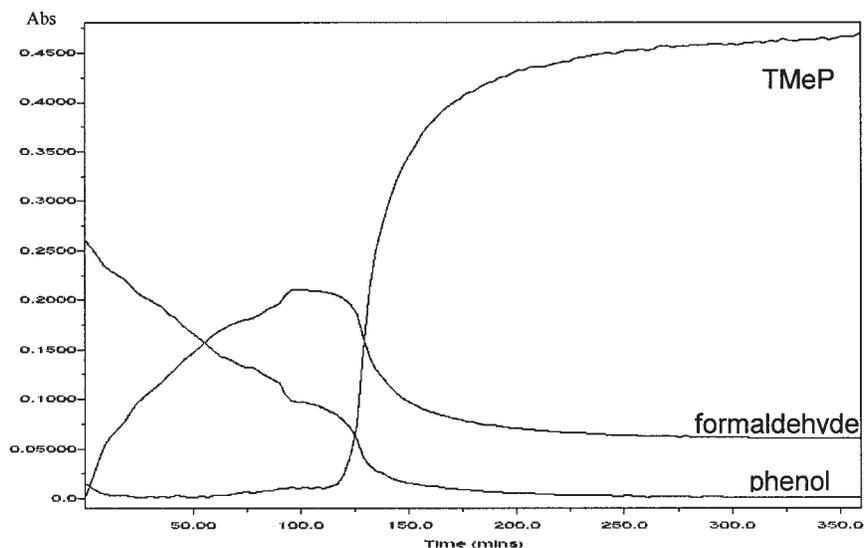


Figure 4 The concentration profiles in weight % for phenol, formaldehyde, and reaction product during TMeP synthesis at 60°C.

and phenol, to the aqueous urea solution. FTIR-ATR inline spectrometry was used to monitor the reaction of urea with TMeP at 90°C, under acidic (pH = 2) and alkaline (pH = 12) conditions. Three PUF resin synthesis with phenol/formaldehyde/urea molar ratios of 1.0/2.5/0.5, 1.0/2.5/1.0, and 1.0/2.5/2.0 were monitored. The resins were labeled as PUF 1.0/2.5/0.5 AC, 1.0/2.5/1.0 AC, and 1.0/2.5/2.0 AC for the synthesis under acidic, and PUF 1.0/2.5/0.5 AL, 1.0/2.5/1.0 AL, and 1.0/2.5/2.0 AL for the synthesis under alkaline conditions.

The spectra in the entire wave number range for the PUF 1.0/2.5/1.0 AC and PUF 1.0/2.5/1.0 AL synthesis are presented in Figure 6. The spectra were collected every 2 min, at a resolution of 8 cm^{-1} , with 64 scans for each spectrum. As shown in Figure 6(A), the characteristic peaks of methylene C—H asymmetric vibrations at 2937 and 2879 cm^{-1} and scissors vibrations at 1482 cm^{-1} , which belong to the methylene bond linkage between TMeP and urea, increased with reaction time. The strong increasing peaks at 1548 and 1513 cm^{-1} corresponded to the N—H in-

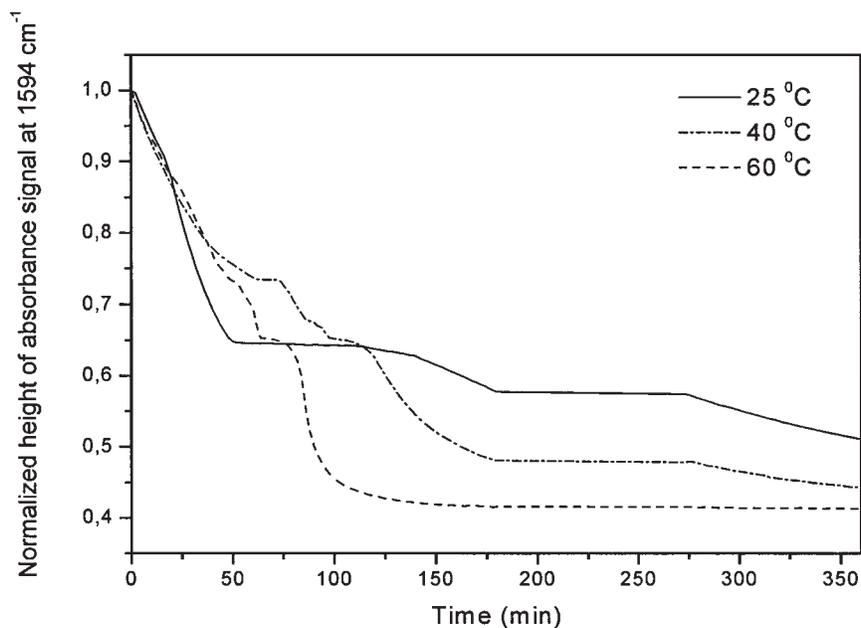


Figure 5 The comparison of absorbance profiles of phenol peak at 1594 cm^{-1} during the reaction at 25, 40, and 60°C.

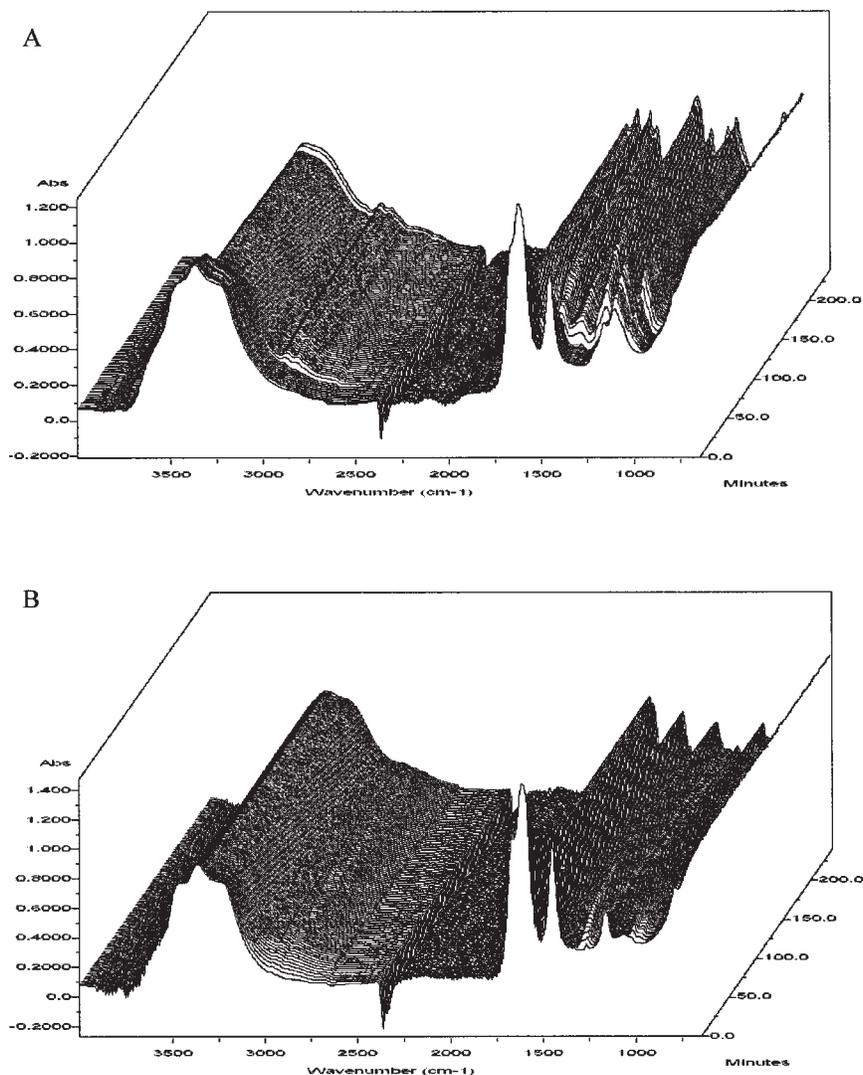


Figure 6 The IR spectra in the entire wave number range of interest for the PUF 1.0/2.5/1.0 synthesis in acidic (a) and alkaline (b) conditions.

plane bend vibrations and the peak at 760 cm^{-1} corresponded to the wag vibration of the urea bond. When the 3D spectra obtained during synthesis under acidic conditions (Fig. 6(A)) are compared with the 3D spectra obtained under alkaline conditions (Fig. 6(B)), a difference in the magnitude of the signals characteristic for PUF resin can be observed. The IR spectra of final PUF 1.0/2.5/1.0 AC and final PUF 1.0/2.5/1.0 AL resins are presented in the Figure 7. The magnitude of the characteristic peaks of methylene C—H asymmetric vibrations at 2937 and 2879 cm^{-1} and scissors vibrations at 1482 cm^{-1} , which belong to the bond linkage between TMeP and urea, as well as signals at 1548 and 1513 cm^{-1} corresponded to the N—H in-plane bend vibrations are weak. The peak observed at 1227 cm^{-1} in the IR spectrum of PUF synthesized under acidic conditions corresponded to the C—O stretch vibrations of phenolic rings and

shifted to higher wave numbers under alkaline conditions. At the same time, the peak at 1351 cm^{-1} of O—H on phenolic ring was not observable due to the sodium methylolphenate formation, under alkaline conditions. The peak at 1061 cm^{-1} corresponding to the C—O—C ether methylene bridges is clearly observable in IR spectrum of PUF resin synthesized under acidic conditions and barely observable in IR spectrum of PUF 1.0/2.5/1.0 AL. From these results, it can be concluded that PUF resins synthesized under alkaline conditions had a lower degree of cocondensation as expected.

The profiles for total concentration of TMeP methylol groups, urea, and the total concentration for methylene and methylene-ether bridges of PUF are shown in Figure 8. The profiles were generated using ConcIRT[®] Opus I software. In the first 20 min of the synthesis, under acidic conditions [Fig. 8(A)], when

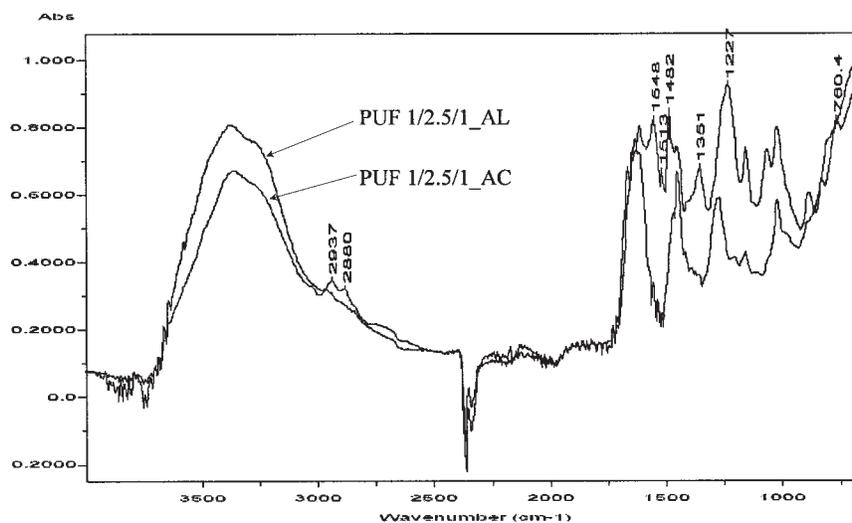


Figure 7 IR spectra of PUF resin obtained under acidic (PUF 1.0/2.5/1.0 AC) and under alkaline (PUF 1.0/2.5/1.0 AL) conditions.

the TMeP aqueous solution was added in the reactor, the total concentration of methylol groups increased and the concentration of urea decreased. After all the TMeP aqueous solution was added the total concentration of methylol groups started to decrease and the total concentration of methylene and methylene–ether bridges in PUF resin started to increase. It was estimated, that almost all the free urea reacted in 30 min of the synthesis, while the methylol groups of TMeP continued to react till the end of experiment. We assume that a certain amount of urea reacted with free formaldehyde and the remaining part with methylol groups of TMeP at the same time. After all free urea was consumed, the methylol groups of TMeP continued to react with urea NH_2 groups already bonded to TMeP and at the same time the reaction between methylolphenol groups could not be avoided.

The reaction rate between urea and TMeP under alkaline conditions is considerably lower; therefore, a slower flow rate of TMeP addition was used to avoid an extended reaction between methylolphenol groups [Fig. 8(B)]. The TMeP aqueous solution was added in the reactor for 120 min. In this period, the total concentration of TMeP methylol groups increased and the concentration of urea decreased. Almost all the free urea was consumed after the addition period. The total concentration of PUF resin methylene and methylene–ether bridges started to increase approximately after 15 min of the synthesis.

It is believed that urea reacted with free formaldehyde to form methylolurea. In comparison with PUF resin synthesis under acidic conditions, the self-condensation reaction between methylolurea groups as well as self-condensation reaction between methylolphenol groups was favorable in the synthesis of PUF resin under alkaline conditions. The cocondensation

reactions between the methylol group and urea occurred in smaller portions. The PUF resins synthesized under alkaline conditions were soluble in water indicating that the degree of condensation was low and the number of methylol groups was high. This was achieved by using high formaldehyde to phenol ratios, the appropriate catalyst, and an appropriate amount of urea.

^{13}C and ^1H nuclear magnetic resonance

Figure 9 represents the ^{13}C NMR spectra of the TMeP synthesized under alkaline conditions, with the formaldehyde/phenol ratio 2.5/1.0. The most characteristic chemical shifts, which corresponded to the functional groups, are listed in Table I. The chemical shift of methanol, which is a stabilizer in formaldehyde solution, occurred at 49.3 ppm. Small signals around 56 ppm were assigned to the methyl carbons in hemiformal ($\text{CH}_3\text{OCH}_2\text{OH}$), signals at 80.0–90.0 ppm belonged to the methyl carbons in hemiformal ($\text{CH}_3\text{OCH}_2\text{OH}$), whereas the chemical shift at 87.7 ppm corresponded to oxymethylene ($\text{HOCH}_2\text{OCH}_2\text{OH}$). The intensity of the chemical shift at 82.3 ppm, which belonged to formaldehyde, was very small. Chemical shifts in the range of 64.4–64.6 ppm belonged to the *para*-methylol groups, whereas chemical shifts in the range of 61.4–62.0 ppm belonged to the *ortho*-methylol groups. Signals in the chemical range of 118.9–131.1 ppm listed from higher to lower magnetic field, 118.9–119.2, 125.2–126.7, 128.0–128.1, 128.9–129.8, and 130.2–131.1, belonged to the unsubstituted *ortho*, unsubstituted *para*, substituted *ortho*, unsubstituted *meta*, and substituted *para* aromatic carbons, respectively. Signals in the chemical range of 160.7–171.4 ppm were assigned to the C-atom of the aromatic ring of phenol; they shifted towards the lower

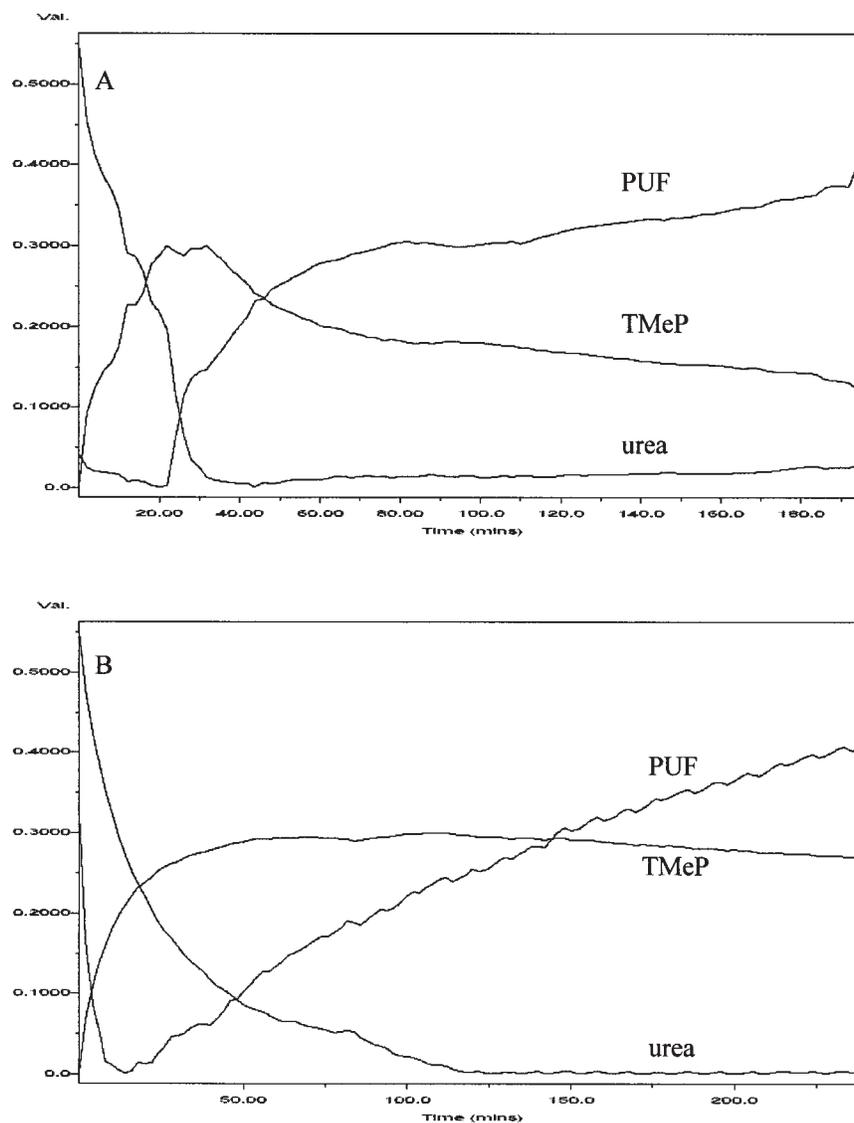


Figure 8 The concentration profiles in weight % for TMeP, urea, and PUF during PUF 1.0/2.5/1.0 synthesis in acidic (a) and alkaline (b) conditions.

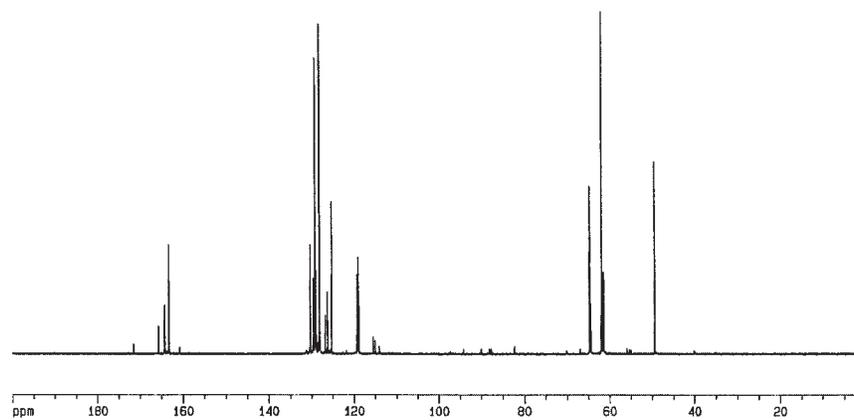


Figure 9 ¹³C NMR spectrum of the TMeP after 4 days of reaction of phenol with formaldehyde.

TABLE I
¹³C NMR Assignments for TMeP

Structures	Chemical shifts (ppm)
Phenolic carbon HO-C	160.7–171.4
Aromatic carbons	
Unsubstituted ortho	118.9–119.2
Substituted ortho	128.0–128.1
Unsubstituted meta	130.2–131.1
Unsubstituted para	125.2–126.7
Substituted para	128.9–129.8
Methylol groups	
<i>o</i> -CH ₂ OH	61.4–62.0
<i>p</i> -CH ₂ OH	64.4–64.6

magnetic field due to the formation of sodium phenolate. No peaks of methylene–ether linkages at 69–73 ppm and methylene linkages at 40–50 ppm were observed, indicating there was no reaction between methylolphenol groups during TMeP synthesis. From the ¹³C NMR spectrum of TMeP it can be concluded that there are higher proportions of methylol groups substituted at ortho than at para position.

The ¹³C NMR spectra of the PUF 1.0/2.5/1.0 AC and PUF 1.0/2.5/1.0 AL resin synthesized under acidic and alkaline conditions were presented in Figure 10. The assignments of the most characteristic

TABLE II
¹³C NMR Assignments for PUF Resins³

Structures	Chemical shifts (ppm)
Methylol groups	
<i>o</i> -Ph—CH ₂ OH	61.2, 61.9
<i>p</i> -Ph—CH ₂ OH	64.7
—NH—CH ₂ OH	63.7, 64.3, 66.8
—N(CH ₂ OH)	74.5
Methylene group between phenols	
<i>o,o</i> -Ph—CH ₂ —Ph	29.6
<i>o,p</i> -Ph—CH ₂ —Ph	37.4
<i>p,p</i> -Ph—CH ₂ —Ph	40.6
Benzylether group between phenols	
<i>o</i> -Ph—CH ₂ —O—CH ₂ —Ph	69.1
<i>p</i> -Ph—CH ₂ —O—CH ₂ —Ph	72–73
Cocondensed methylene group	
<i>o</i> -Ph—CH ₂ —NHCO—	40.6
<i>o</i> -Ph—CH ₂ —N(CH ₂ —)CO—	46.4
<i>p</i> -Ph—CH ₂ —NHCO—	42.4
<i>p</i> -Ph—CH ₂ —N(CH ₂ —)CO—	49.2
Methylene group between ureas	
—NH—CH ₂ —NH—	47.2
—NH—CH ₂ —N(CH ₂ —)—	54.5, 55.6
—N(CH ₂ —)—CH ₂ —N(CH ₂ —)—	58.1, 58.7
Phenolic carbon HO—C	159–170
Urea residue —CO—	163–165.5

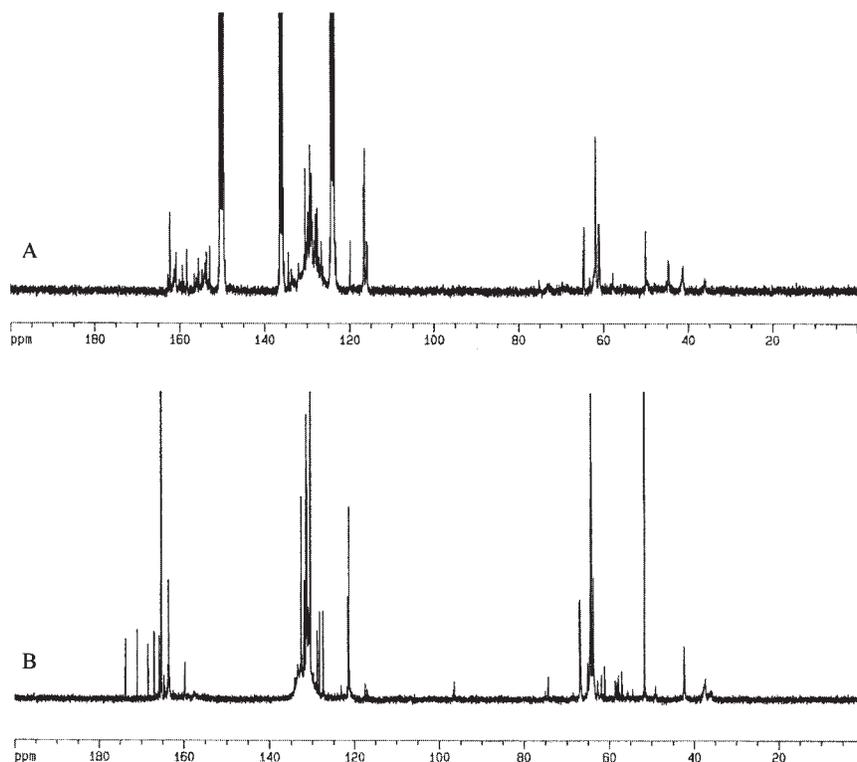


Figure 10 ¹³C NMR spectrum of the PUF 1.0/2.5/1.0 resin in acidic (a) and alkaline (b) conditions after 3 h of reaction of urea with TMeP at 90°C.

chemical shifts for PUF resin are listed in the Table II. The PUF spectra had characteristic signals of the high molecular weight resin plus additional signals of the urea component. The effect of the high molecular weight compounds can be observed as broad signals. The characteristic signals of free formaldehyde and hemiformal listed above in the text were not detected in ^{13}C NMR spectra for both resins. The free formaldehyde was successfully removed, as the added urea reacted with residue free formaldehyde present in the reaction mixture. As shown in Figure 10, the main difference between ^{13}C NMR spectra of PUF 1.0/2.5/1.0 AC and PUF 1.0/2.5/1.0 AL are the signals due to the methylol groups (58–63 ppm), methylene, and dimethylene ether bridges (35–50 and 65–75 ppm, respectively). Every methylene bridge, which has a different chemical environment, has a different chemical shift. The comparison of these two spectra is difficult because two different solvents were used. The solvent also has an effect on the chemical shifts of various carbons. The carbon signals (C_1) of phenolic rings, in which the reaction has taken place at ortho positions, have lower chemical shift values than the ones that reacted at para positions. Free ortho and para carbons occur at 115 and 119 ppm, respectively.

From a comparison of the ^{13}C NMR spectrum of PUF resins synthesized under acidic and alkaline conditions the following conclusions can be made: There were relatively high proportions of unsubstituted aromatic carbons in ortho and para positions. PUF resin synthesized under alkaline conditions had a higher proportion of free or unsubstituted para positions and smaller proportions of unsubstituted ortho positions, while PUF resin synthesized under acidic conditions had a smaller proportion of unsubstituted para positions and higher proportions of unsubstituted ortho positions; The formation of dimethylene ether bridges was much higher in PUF resins synthesized under acidic conditions, which was also confirmed by IR measurements. As is well known the condensation of two hydroxymethyl groups to form a dibenzylether linkage can occur near neutral or acid pH values, but it is rare in the alkaline environment used to produce most resins. Increasing the pH in alkaline medium favors the formation of methylene bridges. The presence of methylene bridges of para–para type in PUF resins synthesized under acidic conditions was higher and there were no *ortho–ortho*-methylene bridges found in the ^{13}C NMR spectra of both resins. These results are in agreement with the results from the literature,⁸ where the authors stated that the *para*-methylol group has a stronger reactivity with urea than the *ortho*-methylol group. There is also a significant difference in the chemical shifts of phenoxy carbons. The chemical shifts of phenoxy carbons of PUF resins synthesized under acidic conditions were between 153 and 163 ppm and of PUF resins synthesized

under alkaline conditions were between 160 and 175 ppm.

The ^{13}C NMR spectrum of PUF 1.0/2.5/2.0 AL resin had the same signals as the PUF 1.0/2.5/1.0 AL spectrum. The spectra differed only in the signal intensity of methylene groups between ureas and free methylol groups. With increasing molar ratio between urea and TMeP the signal intensity of methylene groups between ureas increased, while the signal intensity of free methylol groups decreased. In ^{13}C NMR spectrum of PUF 1.0/2.5/0.5 AL, resin peaks of methylene groups between phenols, which were absent in PUF 1.0/2.5/1.0 AL and PUF 1.0/2.5/2.0 AL spectra, at 21–28 ppm were observed. This indicated that the molar ratio between urea and TMeP should be higher than 0.5 to synthesize a cocondensed PUF resin, but it is enough to eliminate free formaldehyde.

Thermogravimetric analysis

Thermogravimetric analysis was performed on dry PUF resin samples synthesized under acidic and alkaline conditions. In Figure 11 the thermograms of the three PUF resins are shown, and percentage of weight retained is plotted against temperature. All three PUF resins synthesized under acidic conditions displayed similar degradative mechanisms at lower temperatures, the first stage was attributed to the evolution of water and the second to the evaporation of volatile species loosely bound to the phenolic backbone. At higher temperatures (400–500°C) the weight loss of PUF resins was attributed to the bulk degradation of the PUF matrix. It can be seen that the PUF 1/2.5/0.5 AC resin began to lose weight markedly near 430°C, whereas the PUF 1/2.5/1 AC and PUF 1/2.5/2 AC began to lose weight at 500°C. The degradation behavior of the PUF 1/2.5/1 AC and PUF 1/2.5/2 AC is indistinguishable. The PUF 1/2.5/0.5 AC degraded at lower temperatures than the PUF resins with higher amounts of urea (PUF 1/2.5/1 AC, PUF 1/2.5/2 AC). We believe that PUF resins with higher amounts of urea had a higher degree of condensation.

PUF resins synthesized under alkaline conditions displayed different degradative behavior as compared with PUF resins synthesized under acidic conditions. At lower temperatures, the weight loss of all three PUF resins synthesized under alkaline conditions was attributed to the evaporation of water and to the volatilization of species loosely bound to the phenolic backbone. In the thermogram for PUF 1.0/2.5/2.0 AL, a major weight loss was observed at 450°C. This weight loss was due to PUF degradation. The bulk degradation of PUF resins with smaller amounts of urea appeared at higher temperatures. No severe weight losses were detected for PUF 1.0/2.5/0.5 and PUF 1.0/2.5/1.0 resins in this temperature range.

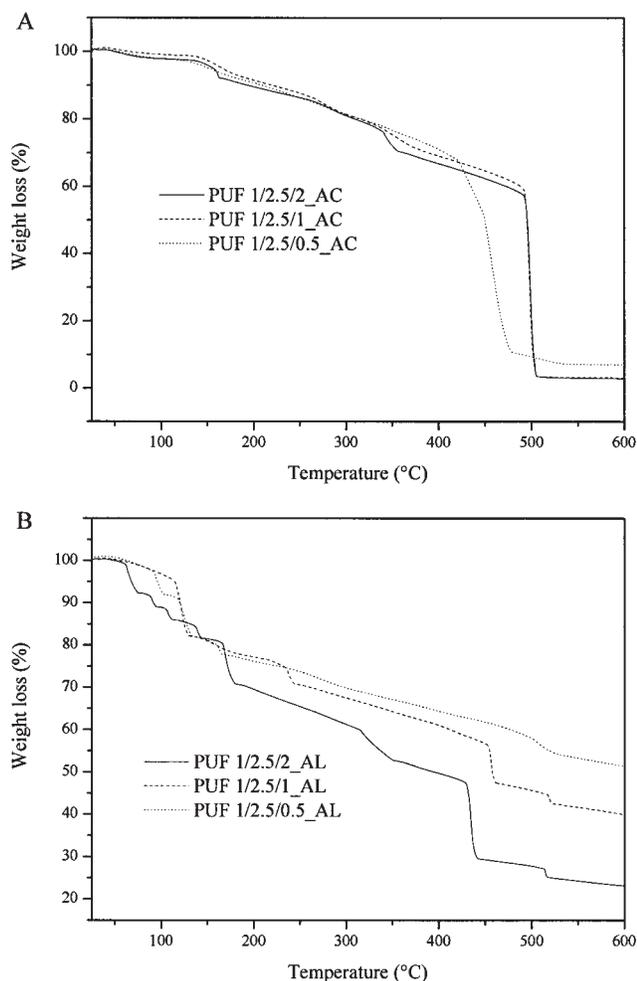


Figure 11 Thermograms of the three PUF resins obtained by thermogravimetric analysis; (a) acidic conditions, (b) alkaline conditions.

Therefore, it can be concluded that the PUF resin with a higher content of urea was less stable due to the urea bond decomposition. The weight loss at $\sim 150^{\circ}\text{C}$ detected in samples with a higher content of urea was attributed to the evaporation of residue water and another weight loss at 330°C was attributed to the degradation of excess urea. From a comparison of the thermogravimetric analysis of PUF AC and PUF AL we can conclude that the former resins had a lower degree of condensation. On the basis of the NMR results, it might be proposed that PUF AL (particularly those with smaller amounts of urea) had a higher portion of PF bonds.

Dynamic scanning calorimetry

The crosslinking reactions of PUF resins of different urea content were studied using DSC. The thermograms of PUF 1.0/2.5/0.5 AC, PUF 1.0/2.5/1.0 AC, PUF 1.0/2.5/2.0 AC as well as PUF 1.0/2.5/0.5 AL, PUF 1.0/

2.5/1.0 AL, and PUF 1.0/2.5/2.0 AL synthesized under acidic and alkaline conditions are shown in Figure 12. During the curing processes the PUF resins underwent gelation and vitrification, because of the increased molecular weight and the formation of a crosslinked network. Regarding the chemical structure of the PUF resins, determined previously by NMR method, numerous chemical reactions could simultaneously take part as well. As it has been already accepted,² the curing rate of PUF resins is faster than that of PF resins. This effect can also be observed from Figure 12. In a comparison of the DSC scanning curves of the PUF resins synthesized under alkaline conditions with different amounts of urea, the thermogram of PUF 1.0/2.5/0.5 (shown in the figure) consisted of two overlapped exothermic peaks indicating curing reactions in the temperature range from 90 to 220°C . It is believed that there were two dominant reactions involved, the first being the addition reaction and then the condensation reaction. The first peak corresponded to the addition reaction between formaldehyde and the aromatic ring or urea, while the second peak corresponded to the cocondensation and condensation reactions between methylolphenol and methylolurea groups. The DSC curves of these two reactions overlapped. However, the first peak is absent in the DSC curves of PUF resins with higher amounts of urea, suggesting that only condensation reactions occur in the curing process of these PUF resins. From this it can be concluded that urea successfully reacted with free formaldehyde indicating that the addition reactions were almost complete and that the condensation reactions are the main reactions during the curing of PUF 1.0/2.5/1.0 and PUF 1.0/2.5/2.0 resins. The curing reactions for PUF 1.0/2.5/0.5 and PUF 1.0/2.5/1.0 resins were extended to 220°C , while the curing reaction for PUF 1.0/2.5/2.0 resin was complete at $\sim 170^{\circ}\text{C}$. As it can be observed in the DSC thermogram of PUF 1.0/2.5/2.0 AL the resin decomposition started already at about 175°C . This result is in accordance with results obtained by thermogravimetric analysis, which indicated that the PUF 1.0/2.5/2.0 AL was less stable due to the urea bond decomposition and urea hydrophilic properties.

In a comparison of the DSC scanning curves of the PUF 1.0/2.5/0.5 AC, PUF 1.0/2.5/1.0 AC, PUF 1.0/2.5/2.0 AC resins synthesized under acidic conditions with different amounts of urea show only one peak of curing. For this type of PUF resins only the condensation and cocondensation reactions occurred, even though addition reactions can occur simultaneously due to the released formaldehyde at the condensation reactions.

Flexural properties

The flexural properties of cured PUF resins synthesized under alkaline conditions were measured according to the ISO 178 (2001) method. Determined

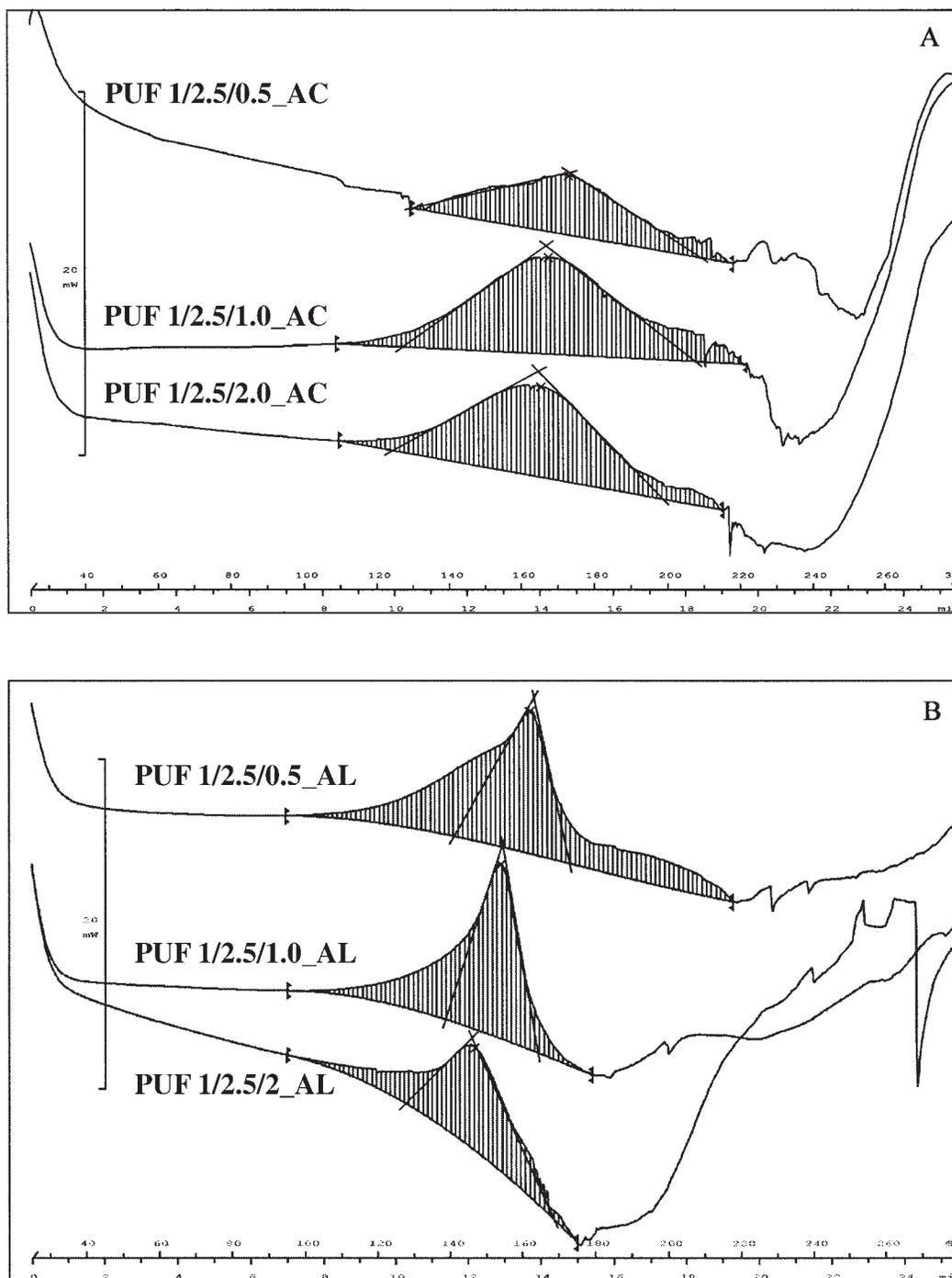


Figure 12 Thermograms of the three PUF resins obtained by differential scanning calorimetry; (a) acidic conditions, (b) alkaline conditions.

flexural strength at break values are given in Table III. The flexural strength at break increased with urea content. The addition of urea units in the network decreased the density of phenolic rings, which contributed to the rigidity of the network.²

CONCLUSIONS

Inline FTIR-ATR spectroscopy was found to be a successful and informative analytical tool for determining

TABLE III
Flexural Properties of Cured PUF Resins Synthesized in Alkaline Conditions

PUF resin	Flexural strength at break (N/mm ²)
PUF 1.0/2.5/0.5.AL	150
PUF 1.0/2.5/1.0.AL	195
PUF 1.0/2.5/2.0.AL	210

individual phenol, formaldehyde, and urea conversions as well as intermediate and final product composition. The TMeP intermediate was synthesized at three different temperatures (25, 40, and 60°C). It was observed that the intermediate product was actually a mixture of different methylolphenols; the presence of methylene linkages between phenolic rings was not detected.

When the synthesis of PUF resin from TMeP and urea under acidic conditions was followed by inline FTIR–ATR technique, the cocondensation reactions between the methylol group and urea occurred. Under acidic conditions no self-condensation reactions between methylol groups as well as between urea were identified.

On the other hand, under alkaline conditions the cocondensation between the methylol group and urea, and the self-condensation of urea occurred. At lower molar ratios (PUF 1.0/2.5/0.5 AL) of urea and phenol, the self-condensation reaction of methylol groups also proceeded. The presence of these linkages was confirmed by ¹³C NMR spectroscopy.

The structural changes during the synthesis undoubtedly arose from the use of different synthesis conditions. It seemed that the high pH influenced the composition of the synthesized product. Between two phenol rings or between phenol and urea no *ortho-ortho*-methylene bridges were found in the analysis of PUF resins synthesized at different conditions; therefore, it can be concluded that the *para*-methylol group had a stronger reactivity with urea than the *ortho*-methylol group.

By NMR and FTIR–ATR techniques, it was confirmed that all the free formaldehyde present in the TMeP reacted with the added urea. The flexural strength of cured PUF resins at break increased with increasing urea content. The thermal stability of PUF resins was investigated by thermogravimetric analysis. The PUF 1.0/2.5/2.0 resin with the highest urea content had the lowest thermal stability. Therefore, an optimal molar ratio between phenol, formaldehyde, and urea has to be chosen for a specific practical application.

From this we can conclude that the PUF resins synthesized under acidic conditions compared to the PUF resins synthesized under alkaline conditions had a higher degree of condensation.

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