

# Application of Different Analytical Methods Used in the Study of the Cross-linking of Resins in Intermediate-Product Used in Manufacturing of Abrasive Articles

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**ABSTRACT:** Determining the degree of the crosslinking of resins in intermediate-product used in the manufacturing of abrasive articles is difficult and complicated because of the presence of different components in the material. The abrasive articles consist of abrasive (e.g., fused alumina), filler (e.g., potassium fluoroborate-KBF<sub>4</sub>, pyrite-FeS<sub>2</sub>), wetting agent (e.g., resol), and binder (e.g., novolak). Proper hardening of intermediate-product is a very important stage dur-

ing production of abrasive tools. The hardening process depends on crosslinking of resins. Following were used to study crosslinking of resins: IGC, washing away method, NMR broad line, DSC, and FTIR methods. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3305–3312, 2009

**Key words:** chromatography; crosslinking; FT-IR; NMR; resins

## INTRODUCTION

Abrasive articles consist of: abrasive (e.g., fused alumina), wetting agent (e.g., resol), binder (e.g., novolak), and filler (e.g., pyrite-FeS<sub>2</sub>, cryolite-Na<sub>3</sub>AlF<sub>6</sub>). The first stage during production of abrasive articles involves wetting of the abrasive by the wetting agent. Then, the binder mixed with fillers is added. Afterwards, the whole intermediate-product is mixed. After mixing, it is conditioned. The last stage is hardening. Factors significantly influencing the quality of the final product are as follows: the quality of abrasive, the coverage of the abrasive by the wetting agent, and the extent of hardening.

Hardening process determines the stability of the final product. Hardening occurred by crosslinking of novolak resin and, to a less extent, by crosslinking of resol. Determination of the degree of the crosslinking of resin in abrasive article is rendered more difficult because of the presence of filler and, most significantly, abrasive in the intermediate-product.<sup>1</sup>

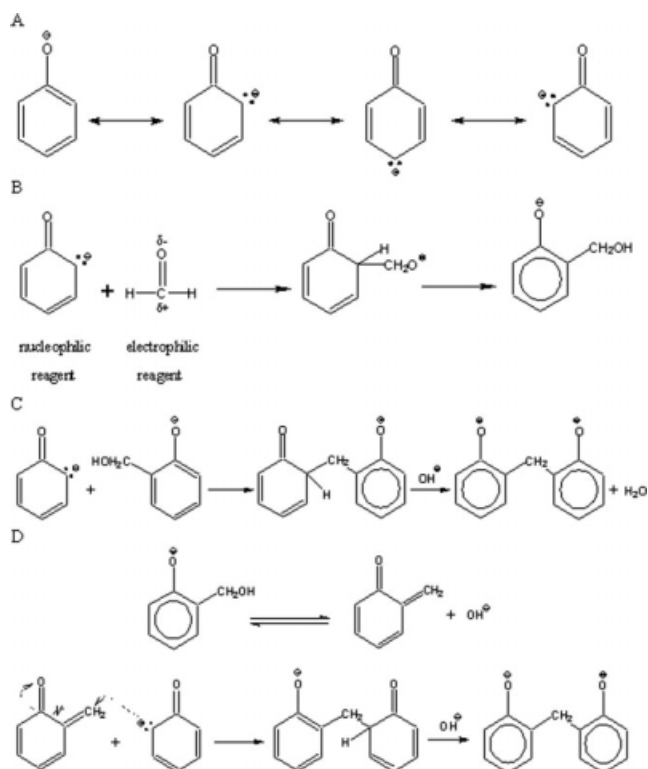
Resol and novolak are phenolic resins. Resol is a liquid resin obtained in the reaction of phenol with

formaldehyde in the basic environment by using excess of formaldehyde (Fig. 1). The nucleophilic phenolic ion [Fig. 1(A)] undergoes the electrophilic substitution by formaldehyde [Fig. 1(B)]. Because of high reactivity of phenol the mixture of hydroxymethylphenol, bis(hydroxymethyl)phenol, and tris(hydroxymethyl)phenol are formed. These hydroxymethyl derivatives of phenol react at higher temperature to resol. The methylene bridges joining the aromatic chains are obtained in the condensation reaction [Fig. 1(C)]. The methylene bridges can also arise in the Michael addition [Fig. 1(D)]. Consequently, the resol is a complex mixture and the part of it may be presented as in Figure 2. Resol is cross-linked at elevated temperature.

Novolak is obtained in the reaction of phenol with formaldehyde in the acidic environment by using the excess of phenol. Under these conditions the carbonyl group of formaldehyde is protonated [Fig. 3(A)] and formaldehyde becomes electrophilic agent substituting the aromatic ring of phenol [Fig. 3(B)]. The methylene bridges arise in the same way as in the case of resol [Fig. 1(C,D)]. One obtains the mixture of oligomers polycondensation having the methylene bridges laid statistically in the positions *para-para*, *orto-orto*, or *orto-para* giving the structure of novolak presented in Figure 4. Because of the absence of hydroxymethylene groups novolak is cross-linked only after addition of the extra volume of formaldehyde, paraformaldehyde, or urotropine (Fig. 5).

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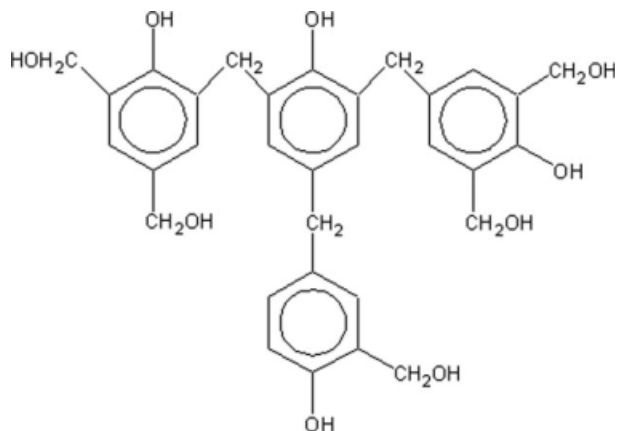
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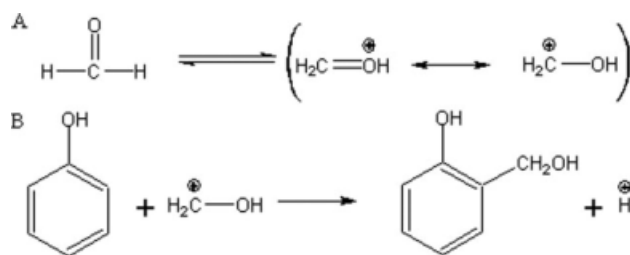
**Figure 1** The reaction of phenol with formaldehyde in the basic environment; A, the resonance structures of phenol in the basic environment; B, the reaction of the obtaining methylene bridges through condensation; C, the reaction of the obtaining methylene bridges through Michael addition.

The inverse gas chromatography (IGC) was used to estimate the degree of crosslinking of resins in the intermediate-product of the abrasive materials. IGC is an extension of classical gas chromatography.<sup>2-4</sup> The modified well-known swelling method was used to verify the results from IGC method.<sup>5,6</sup>

Nuclear magnetic resonance (NMR) broad line was used to describe the behavior of novolak resin and intermediate-product during hardening process. This technique is used to determine the thermal



**Figure 2** The structure of resol.



**Figure 3** The reaction of phenol with formaldehyde in the acidic environment.

transitions during the heating cycle of the sample.<sup>7-9</sup> The second derivative of resonance line is recorded (its linewidth and the second moment). Dependence of these parameters on temperature provides information about the crystal and amorphous phase of studied polymer. The crosslinking of polymer can be also studied by using this method.

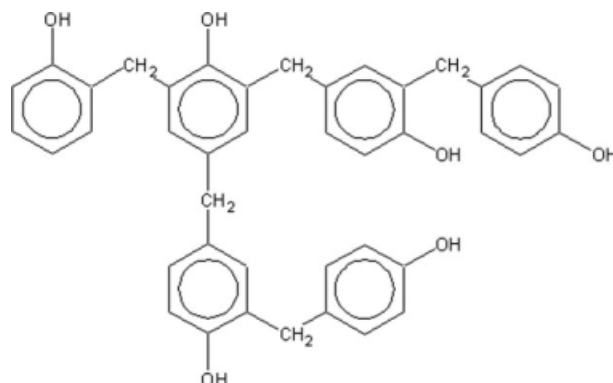
Differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FTIR) were also used to describe qualitatively the hardening process of intermediate-product. These methods are also described in the literature as the useful techniques for studying e.g., crosslinking of polymers.<sup>10-13</sup>

## EXPERIMENTAL

### <sup>1</sup>H NMR broad line

The samples of intermediate-product and novolak were studied. Intermediate-product consists of the following: abrasive (fused alumina, the size of grains—60Mesh), resol as wetting agent (Fig. 2), binder (novolak resin—Fig. 4), and fillers (inorganic compounds: calfix—MgCO<sub>3</sub> + CaCO<sub>3</sub>, lithopone—ZnS + BaSO<sub>4</sub>, slag after-cooper, iron oxide red—Fe<sub>2</sub>O<sub>3</sub>, soot).

The measurements were carried out by using home-made continuous wave spectrometer with automatic stabilization of <sup>1</sup>H field level and



**Figure 4** The structure of novolak.

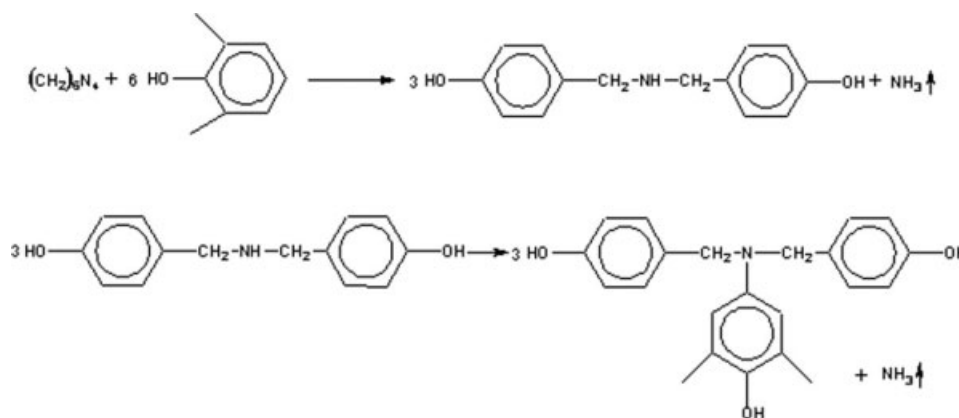


Figure 5 Crosslinking of novolak resin under influence of urotropine.

frequency in the temperature range 40–180°C. The second derivative of resonance line was recorded every 10°C increase. The samples were kept for 2 h at 120°C and 180°C each. The measurements were carried out in air.

### DSC

DSC curves for intermediate-product, novolak with and without urotropin, resol, and urotropin were collected under the following conditions:

equipment: thermogravimeter Setaram, France, 1.53d version;  
 atmosphere: air;  
 heating range: –20 to 400°C;  
 heating rate: 5°C/min.

DSC experiments for novolak with urotropin as well as without urotropin, resol, and urotropin were carried out to determine all the thermal transition proceeding in the intermediate-product.

### FTIR

Two samples of intermediate-product were studied: the one after 2 h of crosslinking at 120°C and the second one after final crosslinking (2 h) at 180°C. It was not possible to study intermediate-product before hardening because of the presence of abrasive (aloxite). The measurements were carried out using spectrophotometer model IFS 66v/S, Bruker, Germany. The reflection method was used.

### IGC

Six samples of intermediate-product were studied: 1a, 1b, 1c (one mixing) and 2, 3, 4 (different mixing). “One mixing” means that samples were taken from a mixer during one production process. “Different

mixing” means that the samples were taken from a mixer during other (consecutive) production processes. The samples from several mixing processes were studied to check homogeneity of intermediate-product and reproducibility of mixing process. Intermediate-product consists of abrasive—aloxite with granulation 60, nonaqueous resol resin, novolak resin, and the mixture of fillers (inorganic compounds). The measurements were carried out by using chromatograph Chrom5 with FID detector. The intermediate-product was heated to 120°C and kept for 2 h. Then, it was heated to 180°C and kept for 2 h at this temperature. The retention parameters (specific retention volume,  $V_g$ ) were determined at the temperature 25°C for intermediate-product before crosslinking, after initial crosslinking at 120°C and after final crosslinking at 180°C. The size of chromatographic column was 2 m length and 3 mm internal diameter. Helium was a carrier gas with the flow rate of 15 mL/min. Pentane, hexane, heptane, octane, ethanol, methanol, diethyl ether, 1,2-dichloroethane and acetone were used as test solutes.

Flory-Huggins interaction parameter,  $\chi_{12}^\infty$ , was calculated according to the following equation:

$$\chi_{12}^\infty = \ln\left(\frac{273.15 \cdot R}{P_1^0 \cdot V_g \cdot M_1}\right) - \frac{P_1^0}{R \cdot T} \cdot (B_{11} - V_1^0) - 1 \quad (1)$$

where:  $R$ , the gas constant—8.314 [J/molK];  $P_1^0$ , the vapor pressure of the test compound at the temperature of the measurement [Pa];  $V_g$ , the absolute retention volume of the test solute [ $\text{m}^3/\text{g}$ ];  $M_1$ , molar mass of the test solute [g/mol];  $T$ , the temperature of the measurement [K];  $V_1^0$ , the molar volume of the test solute [ $\text{m}^3/\text{mol}$ ];  $B_{11}$ , the second virial coefficient calculated according to the following equation:

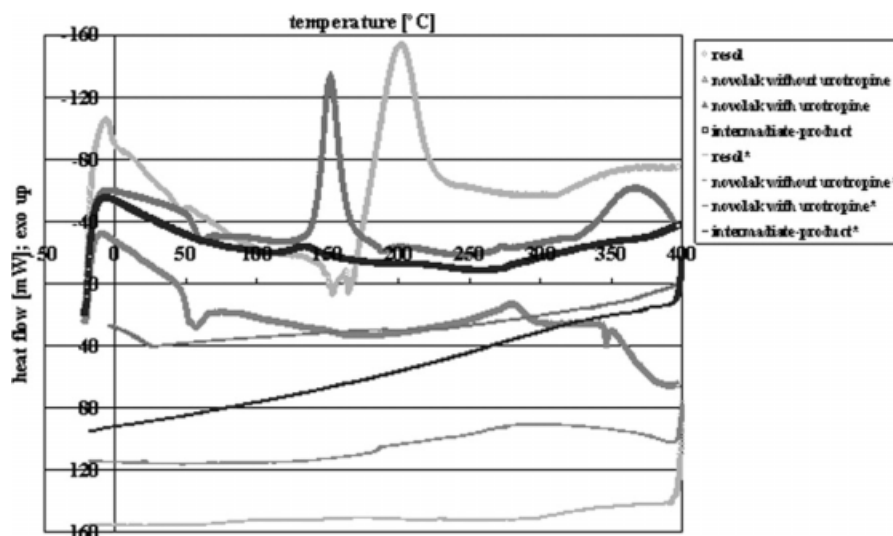


Figure 6 DSC curve for intermediate-product, novolak resin without and with urotropin, resol resin; \*cooling.

$$B_{11_1} = V_{c_1} \cdot \left[ 0.25 - 1.5 \cdot \left( \frac{T_{c_1}}{T} \right) \right] \quad (2)$$

$V_{c_1}$ , critical molar volume of the test solute [ $\text{m}^3/\text{mol}$ ];  $T_{c_1}$ , critical temperature of the test solute [K].

The degree of the crosslinking of resin in intermediate-product was estimated on the basis of the value of  $\chi_{12}^\infty$  parameter for nonhardened and hardened intermediate-product (explanation of this method is provided in section “Results and Discussion”).

### Washing away method

The samples of intermediate-product hardened at 180°C were placed for three days in six different solvents: octane, acetonitrile, ethanol, acetone, chloroform, diethyl ether, and ethyl acetate. Then, they were dried and weighed.

## RESULTS AND DISCUSSION

DSC, NMR broad line, and FTIR methods were used for qualitative determination of the hardening process of intermediate-product. IGC method was used to determine the degree of the crosslinking of resin in intermediate-product quantitatively. The washing away method was used to verify IGC results.

The thermal transitions occurring in the intermediate-product were determined by using DSC method (Fig. 6). To identify all thermal transformation in the intermediate-product the transitions curves were determined for the components of the intermediate-product that are expected to change in the range of studied temperatures. These are novolak resin with urotropin (urotropin is crosslinking agent), novolak

without urotropin, urotropin, and resol (Figs. 6, 7). DSC results showed that the main transformations taking place in the intermediate-product are related to novolak. Thermal effect for intermediate-product is weaker than for resins because of the small amount of resins ( $\sim 15\%$  of novolak and 3% of resol). Glass transition of novolak occurs in temperature range from  $-10$  to  $80^\circ\text{C}$ . The novolak resin melts in the temperature range  $60$ – $110^\circ\text{C}$ . This is not seen in the intermediate-product. This might be caused by the presence of fillers as well as by small amount of novolak in the intermediate-product. The first crosslinking of novolak takes place at  $110$ – $140^\circ\text{C}$ . The main crosslinking of novolak occurs in the temperature range  $130$ – $180^\circ\text{C}$ . However, in the intermediate-product novolak crosslinks at lower temperatures,  $120$ – $150^\circ\text{C}$ . This effect might result from by presence of fused alumina grains and fillers in the intermediate-product. It might catalyze and speed up to some extent crosslinking of novolak as it is in case of  $\text{Zn}^{2+}$  ion.<sup>14</sup> Crosslinking of resol

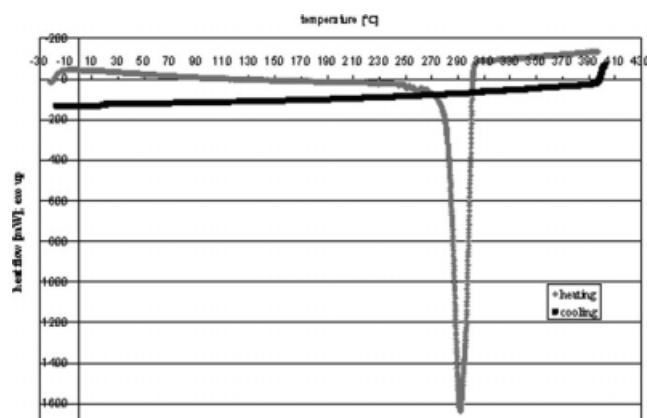
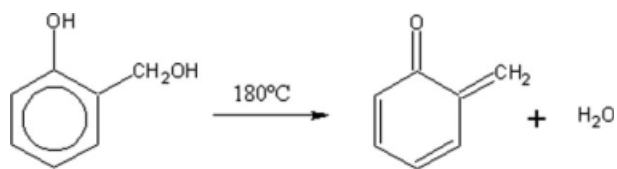
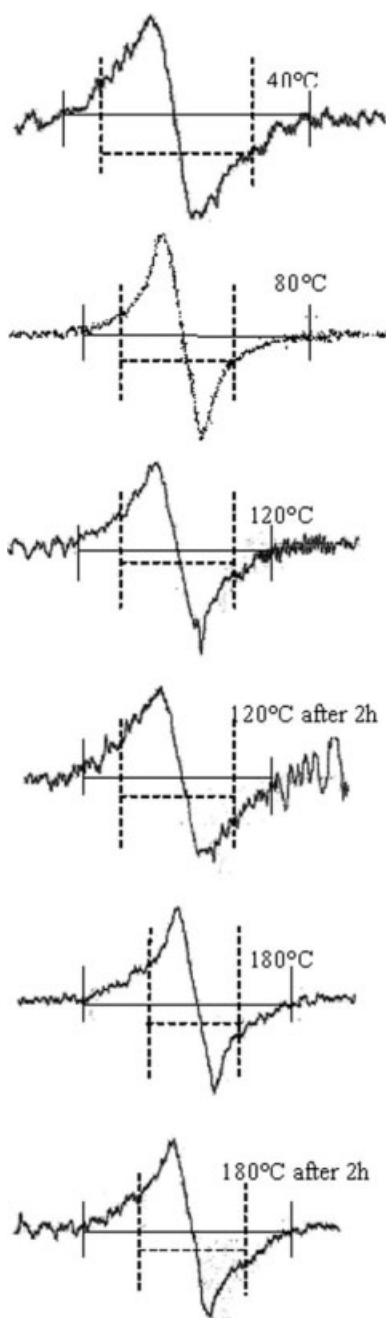


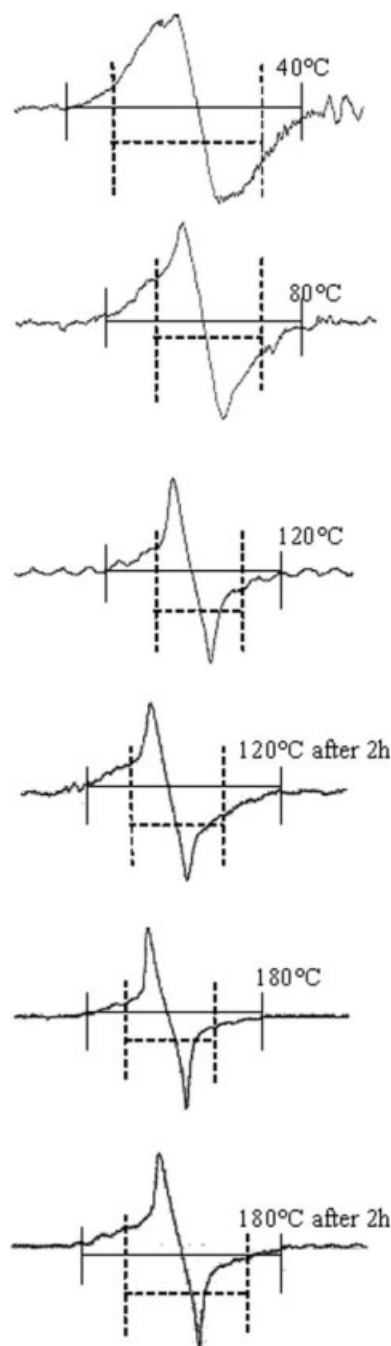
Figure 7 DSC curve for urotropin.



**Figure 8** Arising of *orto* and *para* methylenequinones in the reaction of crosslinking of resol at 180°C.

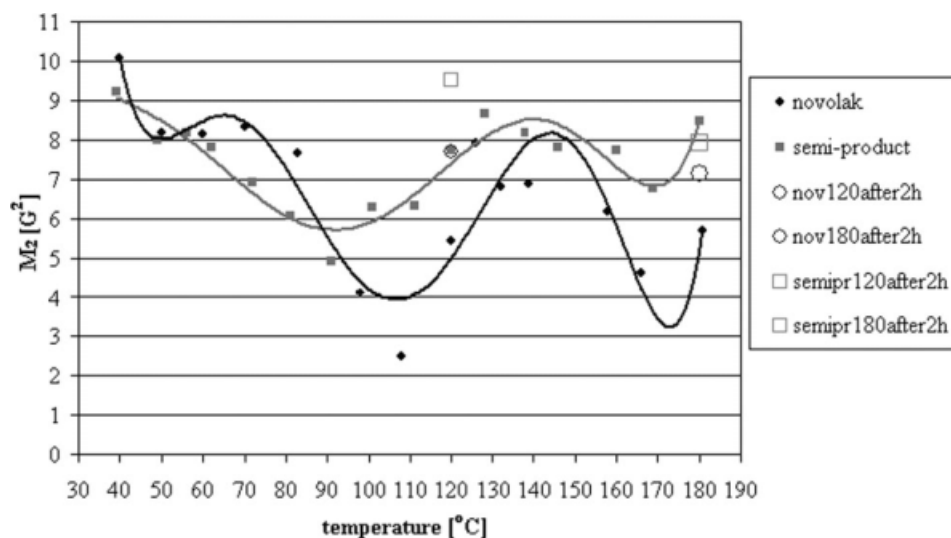


**Figure 9** The second derivative of resonance line for intermediate-product at various temperatures; — means the broad line component, ----- means the narrow line component.



**Figure 10** The second derivative of the resonance line for novolak resin at various temperatures.

observed at 210°C has a relatively minor effect on the intermediate-product due to the small amount of resol (just 3%) present in the material. Above 270°C activity of urotropin is visible. Analysis of DSC curve for urotropin indicates that it melts, decomposes, and causes continued crosslinking of novolak. Novolak resin crosslinks under influence of urotropine (Fig. 5). Resol crosslinks under influence of the temperature. At 180°C the reaction of dehydration takes place (Fig. 8).



**Figure 11** The dependence of the second moment of the line on the temperature—comparison novolak with intermediate-product; “nov120after2h” means the measurement for novolak resin at 120°C after heating it at this temperature for 2 h; “nov180after2h” means the measurement for novolak resin at 180°C after heating it at this temperature for 2 h; “semipr120after2h” means the measurement for intermediate-product at 120°C after heating it at this temperature for 2 h; “semipr180after2h” means the measurement for intermediate-product at 180°C after heating it at this temperature for 2 h.

NMR broad line experiment provides additional information on the structure of resin. Temperature dependence of the second derivative of resonance line assists in establishing the characteristic transformations that occur during hardening process of intermediate-product. The transition curves are presented in Figure 9 for intermediate-product and in Figure 10 for the novolak resin.

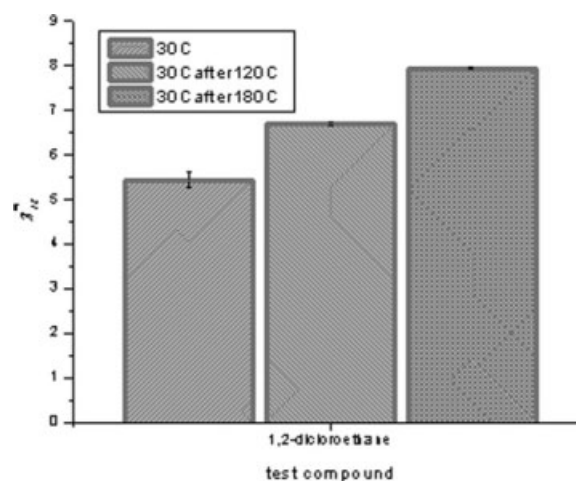
Two components of the resonance line are identified for novolak resin as well as for intermediate-product. The narrow line component is connected with amorphous region. The broad line component indicates the presence of crystalline area where the chains of the polymer are stiff.

The shape of the curve of the second derivative line changed with temperature. Moreover, the line for novolak resin is definitely clearer than for the intermediate-product. This is caused by the presence of fillers and especially by the presence of abrasive in the intermediate-product.

The dependence of the width of the resonance line on the temperature is important. Changes of the width of the broad line component are not clear for novolak as well as for intermediate-product. However, more visible change could be observed for the second moment of the line (Fig. 11). The dependence of the second moment of the resonance line on the temperature for intermediate-product and novolak is shown in Figure 11 and it will be used in further analysis. Visible change of the second moment of the line takes place at 110°C. Heating of the samples at 120°C, as this is during production of abrasive articles, causes the increase of the value of the second moment from value 2.5 G to value 7.6 G. This is

attributed to the chemical changes connected with crosslinking of resin. It can be seen that the heating at 180°C (the second important temperature during heating the intermediate-product in production of abrasive tools) causes already considerable change of the value of the second moment of the line. The main crosslinking process occurs at 180°C according to reaction given in Figures 5 and 8.

FTIR method was found to be unsuitable for examination of transformations occurring in the intermediate-product because of the presence of fused alumina, which affected the quality of the spectra.



**Figure 12** Parameter  $\chi_{12}^{\infty}$  for intermediate-product (1a) determined at 30°C before crosslinking (30C) and after crosslinking at 120°C (30Cafter120C) and final crosslinking at 180°C (30Cafter180C).

**TABLE I**  
The Values of the Degree of the Cross-Linking of Resin Determined for Samples 1a, 1b, 1c and 2, 3, 4—IGC Method (Test Compound—Octane)

Material	The cross-linking, DC <sub>x</sub> [%]	
	120°C	180°C
1a	28.4 ± 1.0	93.4 ± 2.0
1b	25.8 ± 1.2	83.9 ± 3.4
1c	34.2 ± 0.9	80.7 ± 3.2
2	44.4 ± 0.8	89.3 ± 2.4
3	35.9 ± 0.6	92.5 ± 1.2
4	44.1 ± 0.9	94.6 ± 3.8

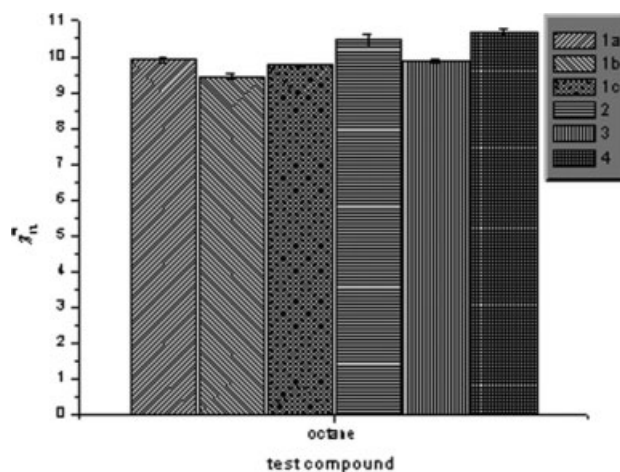
On the basis of NMR broad line as well as DSC studies and information from literature<sup>14–17</sup> the degree of crosslinking was determined quantitatively by using of IGC at two characteristic temperatures during the crosslinking process, i.e., 120°C and 180°C. Crosslinking of resin probably starts at 120°C while complete crosslinking of the resin occurs in the vicinity of 180°C.

The idea of the IGC experiment is presented in Figure 12. Flory-Huggins parameter,  $\chi_{12}^{\infty}$ , which describes interaction between intermediate-product and test compound, was used for determination of the degree of the crosslinking of the resins. The higher value of the  $\chi_{12}^{\infty}$  parameter denotes weaker interactions between studied material and test compound. It was found that the resins before crosslinking interacts stronger with test compound than after crosslinking (Fig. 12). Thus, the values of  $\chi_{12}^{\infty}$  parameter are higher for intermediate-product after crosslinking than for intermediate-product before crosslinking. As it is shown in Figure 12 the value of  $\chi_{12}^{\infty}$  is the lowest before crosslinking at 30°C, increasing after crosslinking at 120°C and is the highest after final crosslinking at 180°C. The degree of the crosslinking of resins can be calculated according to the following equation:

$$DC_x = \frac{\chi_{12,T,x}^{\infty} - \chi_{12,n,x}^{\infty}}{\chi_{12,180,rm}^{\infty} - \chi_{12,n,rm}^{\infty}} \times 100(\%) \quad (3)$$

where DC, the degree of crosslinking;  $x$ , material for which the degree of the crosslinking is calculated; rm, reference material (standard); T and 180, condition (temperature) of the crosslinking;  $n$ , noncrosslinked material.

The degree of the crosslinking was determined by using IGC method for six samples of intermediate-product. These samples were taken from (i) the one batch, i.e., samples 1a, 1b, and 1c were collected from the same mixer but from different places therein; (ii) from different mixing processes, e.g., 1a, 2, 3, 4. Intermediate-product leading to the product having good mechanical properties (durability on



**Figure 13** The value of  $\chi_{12}^{\infty}$  parameter determined at 30°C for six samples of intermediate-product after crosslinking at 180°C.

the tearing, higher efficiency of work) was used as the reference material. Values of the degree of the crosslinking calculated according to IGC method are presented in Table I. The degree of crosslinking is definitely higher at 180°C. Sample 4 has the highest DC<sub>x</sub> value. This is in agreement with the  $\chi_{12}^{\infty}$  highest value for this sample after crosslinking at 180°C (Fig. 13). Results for samples 1a-1c indicate that this batch of intermediate-product is not homogeneous. As a result of nonhomogeneity of the batch of intermediate-product samples 1a-1c are characterized by different values of  $\chi_{12}^{\infty}$  expressing the magnitude of interactions of these samples with octane used as test solute (Fig. 13). Moreover, the samples from different batches also exhibit different properties (compare values of  $\chi_{12}^{\infty}$  parameter for samples 1a and 2, 3, 4). It may lead to variation in final product quality. The enhance of abrasive material quality could be achieved by more careful preparation (better mixing) of component forming intermediate-product.<sup>1,18</sup>

IGC method was verified by modified swelling method. Sample 4 was chosen for these studies and different solvents were used. The swelling was not observed but washing away of the noncrosslinked resin was found (Table II).

**TABLE II**  
The Mass of Dried Sample 4 of Intermediate-Product,  $m_d$  and After Washing,  $m_w$

Solvent	120°C		180°C	
	$m_d$ (g)	$m_w$ (g)	$m_d$ (g)	$m_w$ (g)
Octane	1.2934	1.2800	1.0752	1.0728
Ethanol	1.3273	1.3103	1.1587	1.1567
Acetone	1.1185	1.1051	0.7164	0.7145
Chloroform	1.1555	1.1414	1.0027	1.0023
Diethyl ether	1.0657	1.0528	1.7370	1.7350

**TABLE III**  
**The Values of DC<sub>w</sub> and DC<sub>x</sub> for Intermediate-Product (Sample 4) Determined by Using Different Solvents**

Solvent	DC <sub>w</sub> (%)		DC <sub>x</sub> (%)	
	120°C	180°C	120°C	180°C
Octane	65.5	92.6	28.4 ± 1.0	93.4 ± 2.0
Ethanol	57.3	94.2	26.8 ± 0.8	83.6 ± 2.4
Acetone	60.1	91.2	36.2 ± 0.9	88.3 ± 2.2
Chloroform	59.3	98.7	49.5 ± 1.3	78.8 ± 2.4
Diethyl ether	59.6	96.2	42.5 ± 0.6	84.5 ± 2.1

On this basis the degree of the crosslinking was calculated. The degree of the crosslinking by washing away method was calculated by using eq. (4):

$$DC_w = \frac{m_d \cdot P - (m_d - m_w)}{m_d \cdot P} \times 100\% \quad (4)$$

where  $P$  is the content of resin in studied material.  $P$  was equal to 0.03 in these experiments;  $m_d$ , the mass of dried sample of intermediate-product;  $m_w$ , the mass of sample of intermediate-product after washing.

The values of DC<sub>w</sub> and DC<sub>x</sub> determined for Sample 4 while using different solvent are presented in Table III. The values determined by washing away method are larger than by IGC method, especially at 120°C. The "overestimation" of the DC<sub>w</sub> values could be attributed to the difficulty in the "washing away" of the noncrosslinked resin from intermediate-product. The decrease of the washed-away resins results in the increase of  $m_w$  (eq. 4) and finally increase of DC<sub>w</sub> value. IGC might be treated as more accurate method as the small molecules of test solutes easily find the access to the noncrosslinked resin. The interaction of the test solute with noncrosslinked resins leads to the decrease of DC<sub>x</sub>. The legitimacy of the proposed eq. (3) seems to be proved.

## CONCLUSIONS

Results presented in this article showed that IGC method can be successfully used for determination of the degree of crosslinking of the resin in intermediate-product used for the production of abrasive

articles. It is important to describe the crosslinking process of intermediate-product both qualitatively and quantitatively. NMR broad line and DSC methods are useful for qualitative characterization of this process. FTIR method is not suitable because of the presence of the fused alumina in the examined material. The additional difficulty is connected with the preparation of intermediate-product sample for FTIR method examination.

The crosslinking of resins in abrasive articles intermediate-product can be satisfactorily described by using combination of NMR broad line, DSC, and IGC methods. These methods provide very useful information concerning parameters of the hardening process, e.g., suggested temperature.

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