ELSEVIER

Polymer 40 (1999) 3867–3875

polymer

Structure–properties relationship for resols with different formaldehyde/phenol molar ratio

L.B. Manfredi[a], O. de la Osa[b], N. Galego Fernández[c], A. Vázquez[a,*]

[a]*Research Institute in Material Science and Technology (INTEMA)-Mar del Plata University, J.B. Justo 4302-(7600), Mar del Plata, Argentina*
[b]*Cuban Institute of Sugar Cane Derivatives (ICIDCA), Via Blanca, Havana, Cuba*
[c]*Chemistry Faculty, La Havana University, G y Vedado, Havana, Cuba*

Received 19 November 1997; received in revised form 19 May 1998; accepted 11 September 1998

Abstract

The relationship between the structure and the viscoelastic properties of resol resins was studied. Six phenolic resins (resol) were synthesized with different molar ratios of formaldehyde to phenol. These resols were cured by means of temperature and without catalyst. The characterization of the resol was done by means of infrared spectroscopy and chemical methods. From the viscoelastic properties of fully cured resins, characteristic properties such as: storage modulus (E'), tan δ, width of the tan $\delta(\Delta T)$ and damping peak (tan δ) were obtained. The compression modulus and the void content were also determined. A maximum in the methylene bridge and the result of the viscoelastic properties allow us to say that the resol with F/Ph between 1.3 and 1.4 has the highest crosslinking density.

Keywords: Resol; Dynamic-mechanical properties; Phenolic resins

1. Introduction

Phenolic resins were the first thermosetting resins to be synthesized in 1907. This type of resin has been studied again due to its fire-resistance property. They have recently been used in building of means of transport [1]. However, the relationship between the synthesis conditions, the structure and the mechanical properties has not been yet complete clarified [2]. One of the reasons is that the resol has a complicated mechanism of reaction [3,4]. One reaction is the addition of the formaldehyde to ortho- and para-phenol positions. The other reaction is condensation with formation of water and formaldehyde. Two different types of condensation reactions can occur: (a) between the phenol free position and the methylolphenols producing an ether bridge, and (b) between the methylolphenols themselves producing a methylene bridge. Most of the researchers have concluded that the concentration of the ether bridge can be negligible [5,6].

We characterized several resols in solution with variable formaldehyde to phenol (F/Ph) molar ratios before the crosslinking reaction. In order to determine the influence of the chemical structure on the viscoelastic and mechanical properties, different molar ratio for the resols were studied.

2. Experimental

2.1. Materials

Resol-type phenolic resins were prepared at varying formaldehyde–phenol molar ratios (F/Ph): 1.2, 1.3, 1.4, 1.6, 2.0 and 2.5 in the presence of a solution of 40% w/w of NaOH. The pH was kept at 9.0 and the mixture was reacted for 2 hours at 90°C.

Phenol and formaldehyde water solution (37% w/w) was placed in a 1.5-l stainless steel reactor with a low velocity stirrer, thermometer, and reflux condenser. The mixture was neutralized with a solution of boric acid until the pH reached a value of 6.8–7.0. The dehydration of resol was performed inside the same reactor in a vacuum at 75–80°C until total extraction of water. The resols were kept at −10°C after synthesis and until the moment they were used.

The final formaldehyde content was determined by the hydroxylamine method [7]. The solid content was determined by curing the resol at 135°C until constant weight. The free phenol level was measured by means of UV spectroscopy.

Commercial resols from ATANOR S.A. Argentina were also studied: R619 and R435 with a formaldehyde to phenol molar ratio (F/Ph) of 1.0 and 2.0, respectively.

* Corresponding author.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00615-6

Table 1
Results of the charaterization of the resols with different formaldehyde-to-phenol molar ratios

F/Ph	Mn	Mw	% Free formaldehyde	% Free phenol	% Solid
1.2	163.3	266.7	0.33	16.52	86.0
1.4	202.9	307.2	1.77	17.01	76.53
1.6	178.2	280.3	2.38	11.39	78.4
2.0	207.6	305.3	3.17	6.81	82.6
2.5	275.2	379.1	7.43	4.55	82.6

2.2. Methods

In order to characterize the different resols, we have carried out a study using infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and dynamical mechanical analysis (DMA).

Fourier transform infrared (FTIR) was done with a Brüker IFS-45 spectrometer with acquisition conditions being a spectral width of 4000–400 cm^{-1}, 32 accumulations, and 2 cm^{-1} resolution. Uncured resol samples were spread on NaCl windows. For fully cured resol samples, the spectra were recorded in the solid state in KBr pellets. In

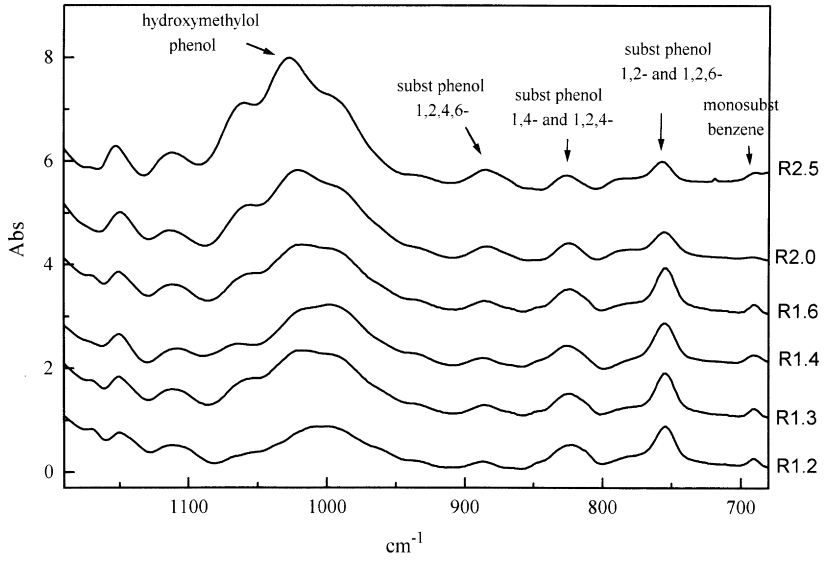

Fig. 1. Spectra of uncured resol with different formaldehyde to phenol molar ratios: 1.2, 1.3, 1.4, 1.6, 2.0 and 2.5.

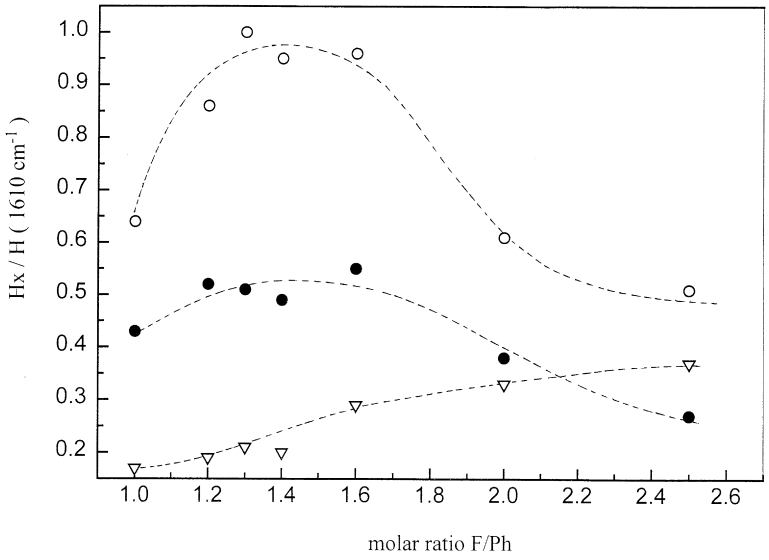

Fig. 2. Changes for the uncured resol in wavelength at: (○) 756 cm^{-1} for 1,2- and 1,2,6-substituted rings; (●) 826 cm^{-1} for 1,4- and 1,2,4-substituted rings; (▽) 888 cm^{-1} for 1,2,4,6-substituted rings.

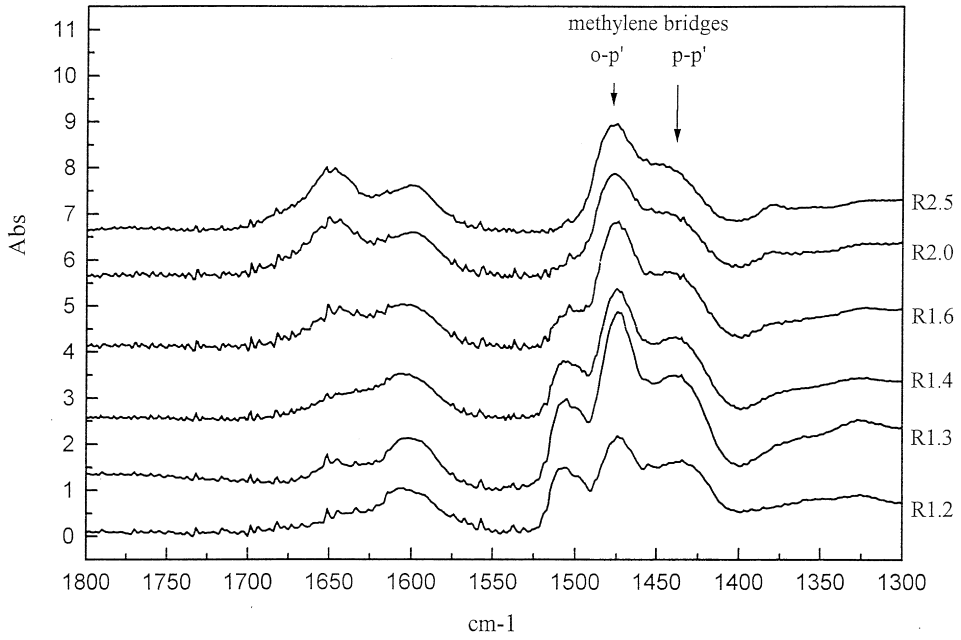

Fig. 3. Spectra for fully cured resols with different formaldehyde-to-phenol molar ratios: 1.2, 1.3, 1.4, 1.6, 2.0 and 2.5.

both cases, a reference band of 1610 cm^{-1} was used. This corresponds to stretching of the aromatic ethylene bond (C=C) in the aromatic ring which seems to be invariant.

The neutralized resins were analysed in a Waters 510 GPC with a refractive index detector and Ultrastyragel 100–100–500 and 1000 Å columns. The injection volume was 10 μl and the flow rate was 1 ml min^{-1}. Measurements were performed in duplicate. The molecular weight averages were referenced to phenol and novolak resin as in a previous work [8].

The temperature used for curing the samples ranged from 20 to 190°C. The cure schedule consist of 7 temperature steps and a ramp of 1°C min^{-1} between each one. The temperatures at each different stage were: 40, 60, 80, 100, 130 and 150°C respectively maintained for 3 hours each and a post-cure at 190°C for 4 hrs.

The final properties of the resols were determined using dynamical mechanical tests.

A Perkin-Elmer DMA-7 unit was used with a fixed frequency at 1 Hz and a heating rate of 5°C min^{-1} in a three-point bending mode. The specimen bars used for these tests were cut from plaques obtained by curing the

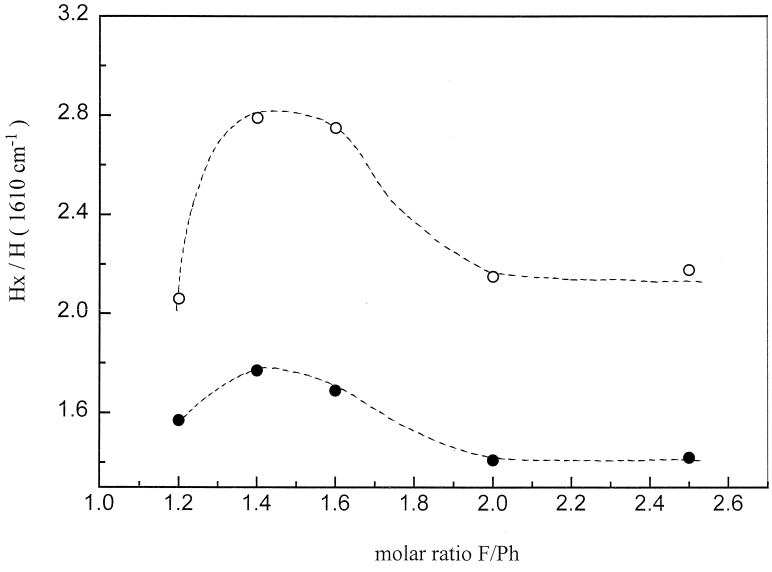

Fig. 4. Changes for fully cured resols in wavelength at: (○) 1480 cm^{-1} for o–p′ methylene bridges; (●) 1450 cm^{-1} for p–p′ methylene bridges.

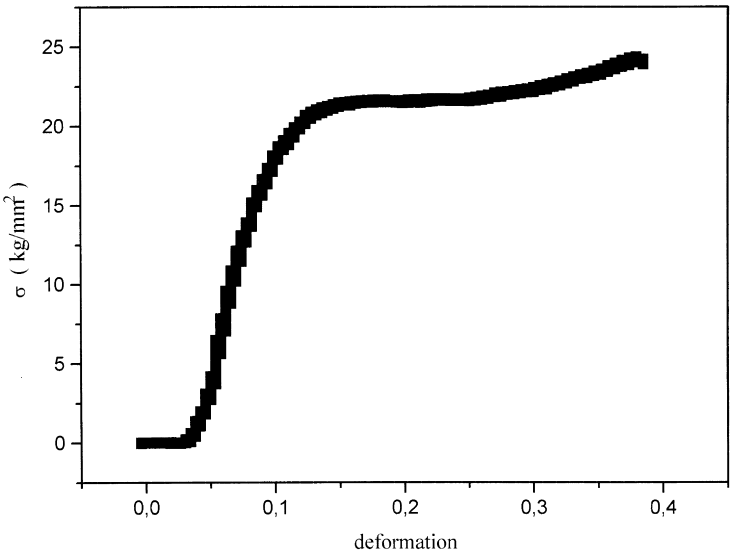

Fig. 5. Typical curve of compression test for a resol.

resol between two thin glasses previously treated with the silicone release agent from Siliar S.A. Argentina.

The compression tests were made with a Shimadzu S-500-c under the ASTM D695-85 with a velocity of 0.5 mm s^{-1}. The cylindrical samples were obtained with a diameter of 5 mm and a height-to-diameter relationship of 1.5–2.0. Acquisition of data was performed by computer and LVDT transducer was used for the displacement measurement.

Samples were prepared adopting metallographic techniques in order to obtain surfaces to be analysed by optical microscopy. The images taken from an optical microscope (Olympus PM63) were digitized and fed to an image analysis computer program (NIH Image 1.61). Within this program the threshold of the image was adjusted so that voids were dark and the rest was light. The percentage of porosity was calculated from this two-dimensional image.

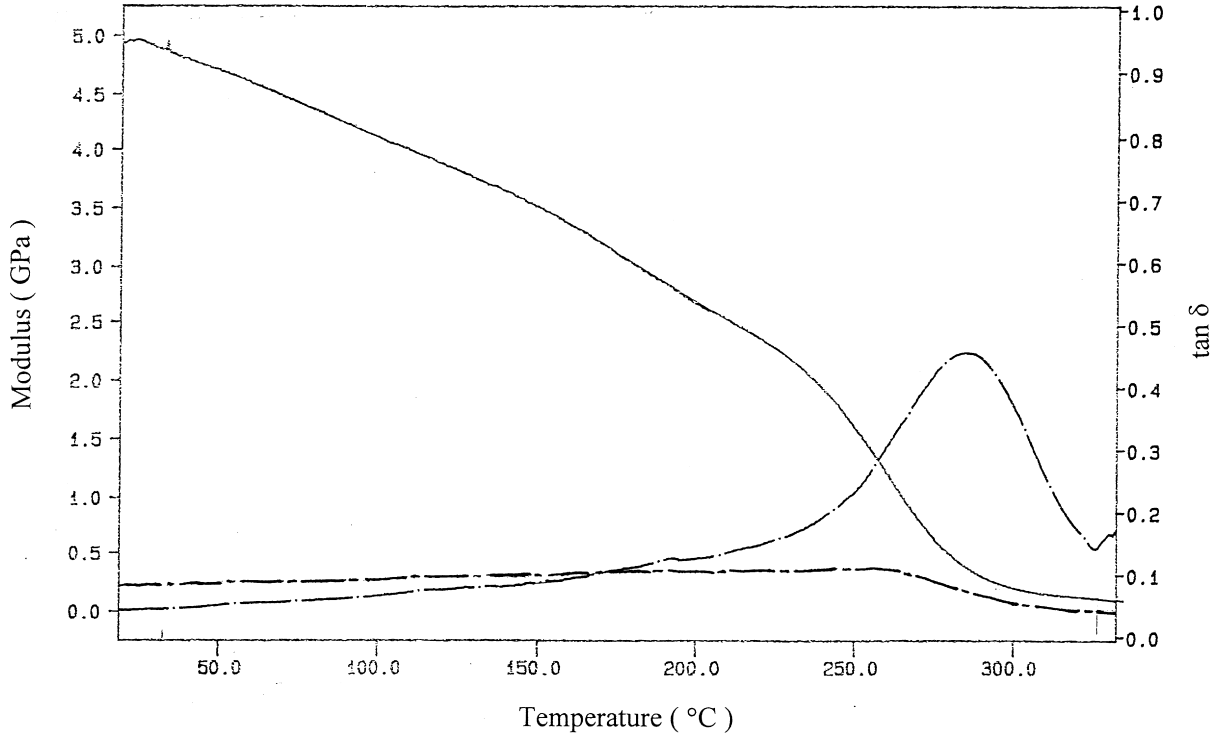

Fig. 6. Typical curve of dynamical mechanical analysis for a resol showing: (———) storage modulus, E'; (– · –) tan δ; (— - —) loss modulus, E''.

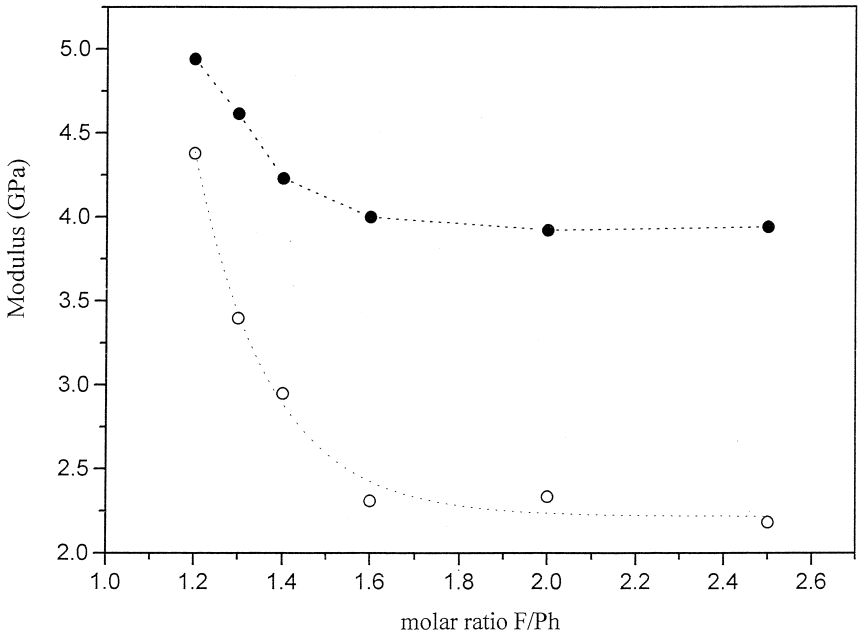

Fig. 7. Storage modulus measured in dynamical mechanical analysis (○), in compression tests (●) as a function of formaldehyde-to-phenol molar ratio.

3. Results and discussion

Different resols were characterized by means of the average molecular weight, free content of formaldehyde and phenol, and solid content. The result is shown in Table 1. The average molecular weight increases with the F/Ph ratio, together with the free formaldehyde content.

Grenier-Loustalot et al. [9,10] have identified the phenolic compounds in the resol resins under different conditions. They have assigned the different wavelengths in the spectra of the different compounds, based on a model compound and on spectroscopic studies of substituted benzene [11]. The mono-, di- and tri-hydroxymethylolphenol content and the relative reactivities of the free sites of the phenol compounds were determined. The assignment of each peak permits the quantification of each compound after the prepolymerization and after the crosslinking reaction.

Fig. 1 shows the spectra for different uncured resols. The out of plane C–H deformation in the monosubstituted benzene ring appears at 690 cm^{-1}. The peak at around 756 cm^{-1} corresponds to a 1,2-disubstituted benzene ring, and a 1,2,6-trisubstituted benzene ring. The peak at 826 cm^{-1} is attributable to 1,4- and 1,2,4-substitution, and the 888 cm^{-1} peak was identified as a 1,2,4,6-trisubstituted benzene ring. Fig. 2 shows the results for resols with different molar ratio of F/Ph. The addition reactions on the free para-position occur in almost the same proportion as in each ortho-position of the phenol ring [12]. A maximum quantity of disubstituted phenol was found for the F/Ph ratio between 1.3 and 1.4. However, the quantity of the trisubstituted phenol compounds increases with the F/Ph ratio, as a consequence of the higher degree of conversion.

Roczniak et al. [13] identified the region between 1500 and 1400 cm^{-1} as characteristic for the deformation vibrations of –CH– bonds in $-CH_2-$ groups and some differences can be noticed. These differences can yield information as to the structure of methylene bridges. Fig. 3 shows the FTIR spectra for different resols after the crosslinking reaction. The band at approximately 1450 cm^{-1} was assigned to methylene bridges in p–p′, the band at 1460 cm^{-1} was assigned to the methylene bridge in o–o′ and the band at 1480 cm^{-1} was assigned to the o–p′ position. These bands are higher for the completely cured resols than for the prepolymer or uncured resols. It is an indication that more crosslinking reaction occurs in the curing step than during the synthesis of the resols. The application of this analysis to the resols allows us to determine that the quantity of p–p′ bridge is higher than that of the o–p′ bridge, and that the o–o′ bridge was not found in the resols (Fig. 4). A higher proportion of methylene bridge was found for the molar ratio of F/Ph between 1.3 and 1.4.

Fig. 5 shows a typical curve of the compression test. The modulus in compression at room temperature decreases when the F/Ph ratio increases. Dynamic mechanical analysis of the cured resol was performed and Fig. 6 shows a typical curve. The storage modulus (E') determined by means of dynamical mechanical analysis in the glass state (room temperature) has a lower value than that obtained by the compression test, Fig. 7.

The pictures of the measured samples were obtained by optical microscopy (Figs 8–10). The percentage of voids was determined and the results are shown in Table 2. The model of modulus takes into account the volume fraction of voids [14,15]. However, it is similar in all samples. As a consequence, the variation in the modulus is not influenced by the voids. Other effects such as packaging density or free

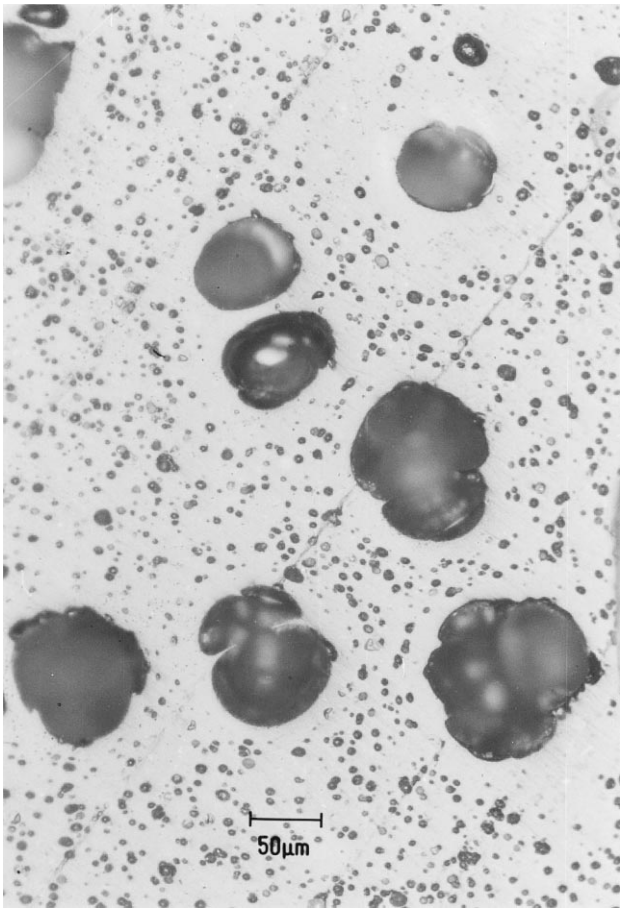

Fig. 8. Picture obtained by optical microscopy of the fully cured resol with a formaldehyde-to-phenol molar ratio of 1.2.

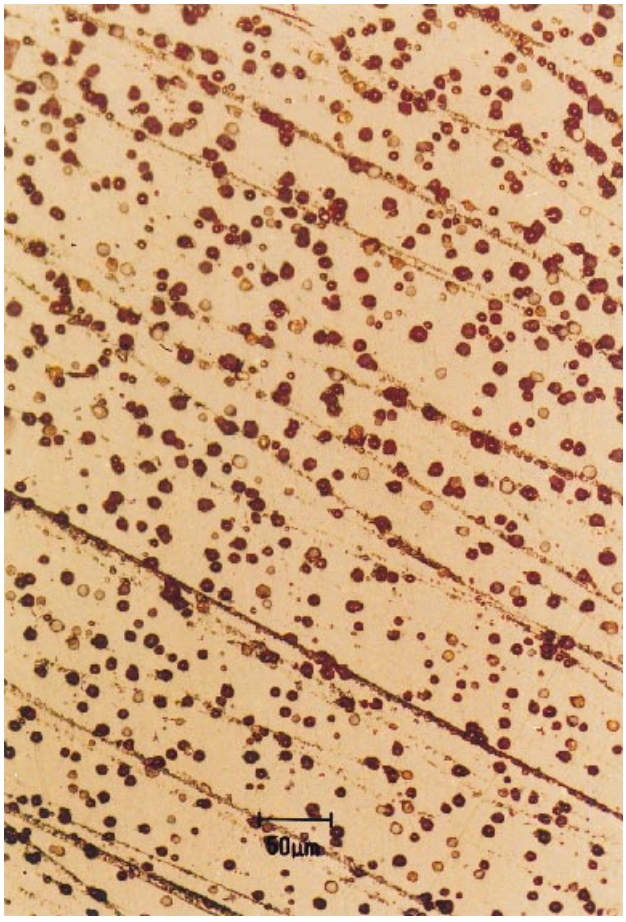

Fig. 9. Picture obtained by optical microscopy of the fully cured resol with a formaldehyde-to-phenol molar ratio of 1.6.

volume should be taken into account, but they were not studied in this work. From the pictures, it was observed that the distribution of the voids is similar with excess of formaldehyde or phenol. Both pictures (Figs 8 and 10) show two types of voids with bimodal distribution of void size. An excess of either phenol or formaldehyde and water, see Fig. 8 and Fig. 10, respectively, produces a bimodal distribution of void sizes. This may be related with the thermodynamic phase separation coming from free phenol, free formaldehyde or water, together with the reaction kinetics. This effect will be studied in future works.

The main transition temperature, $T\alpha$, increases up to 1.2 and after this value it is quite constant (Fig. 11). The value of the transition temperature for the resol with F/Ph equal to 1.2, presents a maximum value but also superimposed on the degradation reaction. Several authors [3,4] have found that degradation reactions occur close to 300°C.

This result agrees with the maximum in methylene bridges found in Fig. 4 and with the explanation of a maximum crosslinking in the network. The theoretical stoichiometric molar ratio of F/Ph should be at 1.5, because the theoretic functionality of phenol is 3. However, using the gel conversion obtained experimentally [16,17] and the theoretical model of Flory–Stockmayer [18], the real functionality of the phenol is 2.38 ± 0.05 and the stoichiometric molar ratio is 1.19 [2]. As a consequence, the network with higher crosslinking should be the one with an F/Ph ratio close to 1.2. In our case, the resol with 1.2 did not present the higher crosslinking and the corresponding molar ratio is between 1.3 and 1.4, depending on the properties that we are measuring. The width of the tan δ measured at the middle height, ΔT, shows a maximum value between 1.3 and 1.4 which is an indication of a higher distribution of chain lengths and a higher crosslinking density in comparison with the other F/Ph molar ratios (Fig. 12).

Table 2
Percentage of voids of the resols with different formaldehyde-to-phenol ratios

F/Ph	Void content
1.2	0.212
1.4	0.212
1.6	0.191
2.0	0.134
2.5	0.192

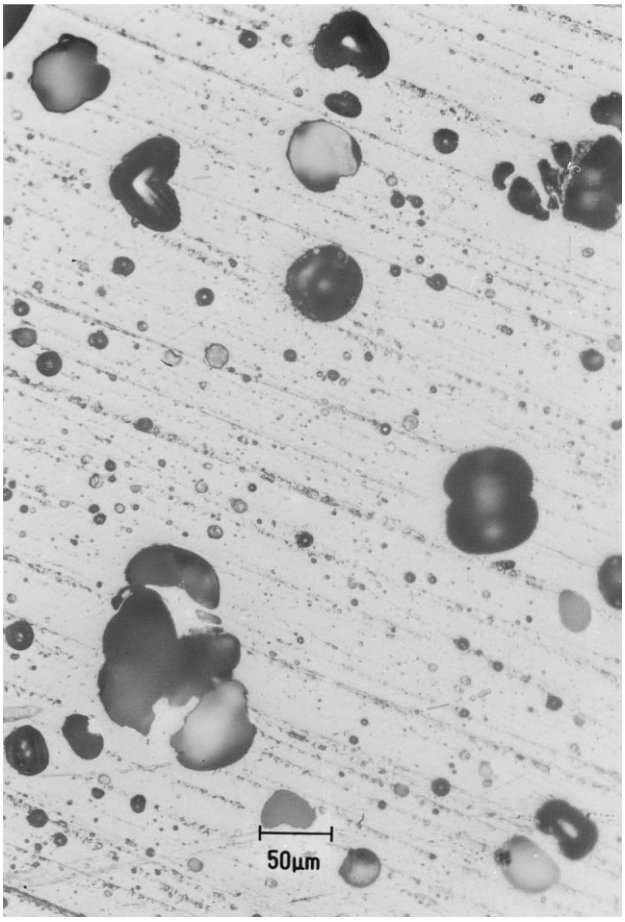

Fig. 10. Picture obtained by optical microscopy of the fully cured resol with a formaldehyde-to-phenol molar ratio of 2.0.

The damping of the network or height of tan δ and loss modulus, E'', show a minimum value (Fig. 13). It also supports the theory of a more highly crosslinked resol for the F/Ph value and a more rigid network structure. The rubber modulus, E'_r shows very high values, and these values do not correspond to rubber behaviour. The rubber theory of elasticity could not be applied in this case. However, the maximum of this value is shown between 1.3 and 1.4 of F/Ph molar ratio (Fig. 14).

Commercial resols show the same behaviour as the ones synthesized in this study. As a consequence, the molar ratio of F/Ph is more important in determining the network crosslinking than the synthesis conditions (temperature, catalyst concentration or time) in the pre-polymer production.

4. Conclusions

The influence of the resol molar ratio F/Ph on the final viscoelastic properties and final structure, measured by infrared spectroscopy, was studied. Methylene bridge concentration depends on the phenol position involved and it has the following sequence: p–p′ > o–p′ > > > o–o′. The total concentration of methylene bridge was measured and the results agreed with the literature. It was found that a resol with a molar ratio, F/Ph, of between 1.3 and 1.4 has the highest total methylene bridge concentration and as consequence, the highest crosslinking density.

From the viscoelastic properties measured as a function of the different resol molar ratio, F/Ph, an observation was made of a minimum in the loss modulus value, E'', as well as in the tan δ height or damping value. A maximum in the

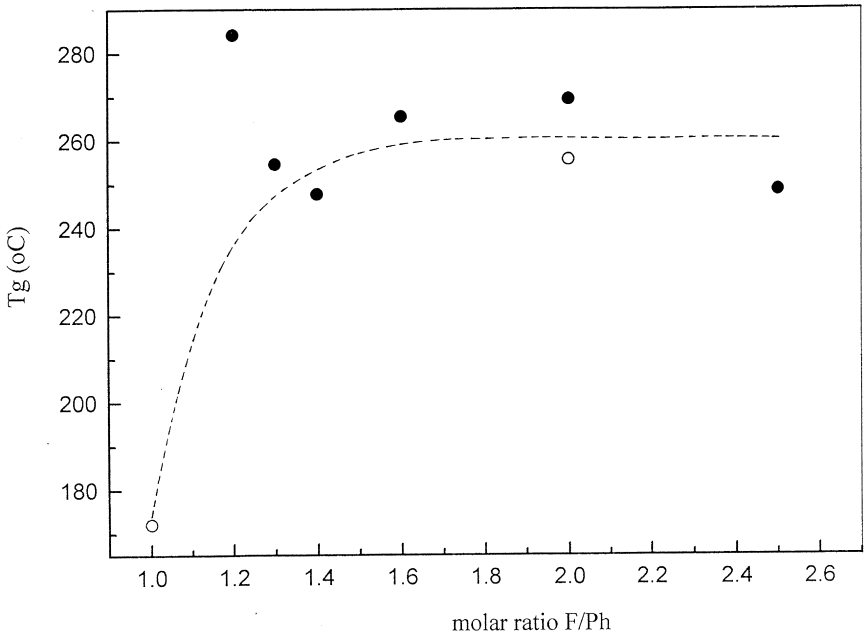

Fig. 11. Main transition temperature (T_g) as a function of the formaldehyde-to-phenol molar ratio for the resols: (●) synthesized, (○) commercial products.

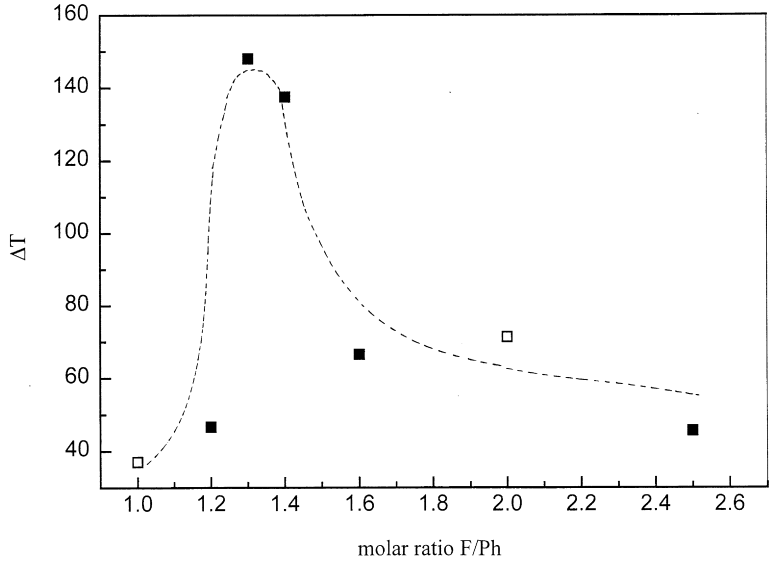

Fig. 12. Width of the tan δ (ΔT) as a function of the formaldehyde-to-phenol molar ratio for the resols: (■) synthesized, (□) commercial products.

glass transition temperature, T_g, and in the rubber modulus of elasticity, E'_r, were also found. These viscoelastic properties values are coincident with a resol molar ratio F/Ph of between 1.3 and 1.4, depending on the properties that we are measuring.

Considering the results obtained by infrared spectroscopy and the viscoelastic measurements for resols with different molar ratio of F/Ph, it can be concluded that the real phenol functionality is close to 2.7.

Commercial resols crosslinked in the absence of catalyst and with different molar ratios of F/Ph, were characterized. The main determining factor in the final properties appears to be the molar ratio of F/Ph in the crosslinking reaction.

Acknowledgements

The authors gratefully acknowledge CONICET for financial support and thank ATANOR S.A. Argentina for the resols used in the present work. Discussions with Prof. I. Mondragón Egaña and Prof. J.M. Kenny are gratefully acknowledged.

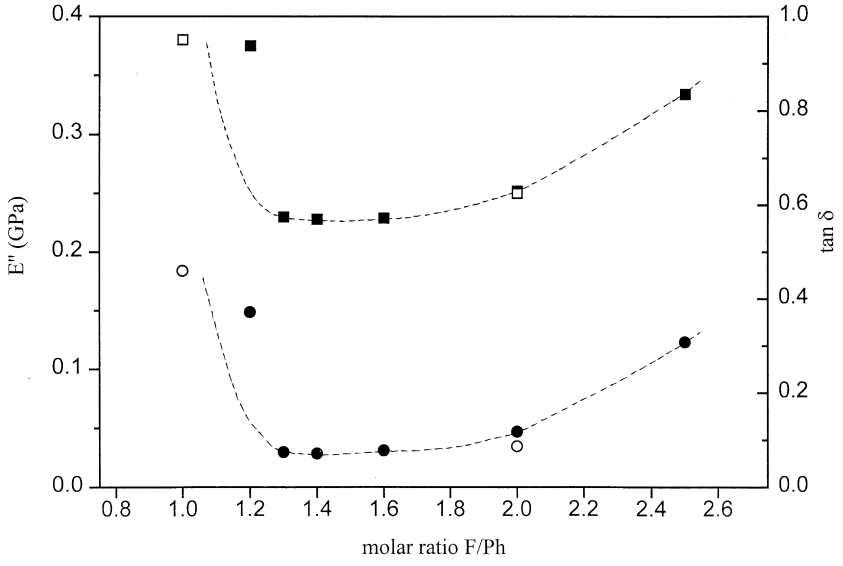

Fig. 13. Loss modulus (E'') for the resols: (■) synthesized, (□) commercial products; and the height of tan δ for the resols: (●) synthesized, (○) commercial products.

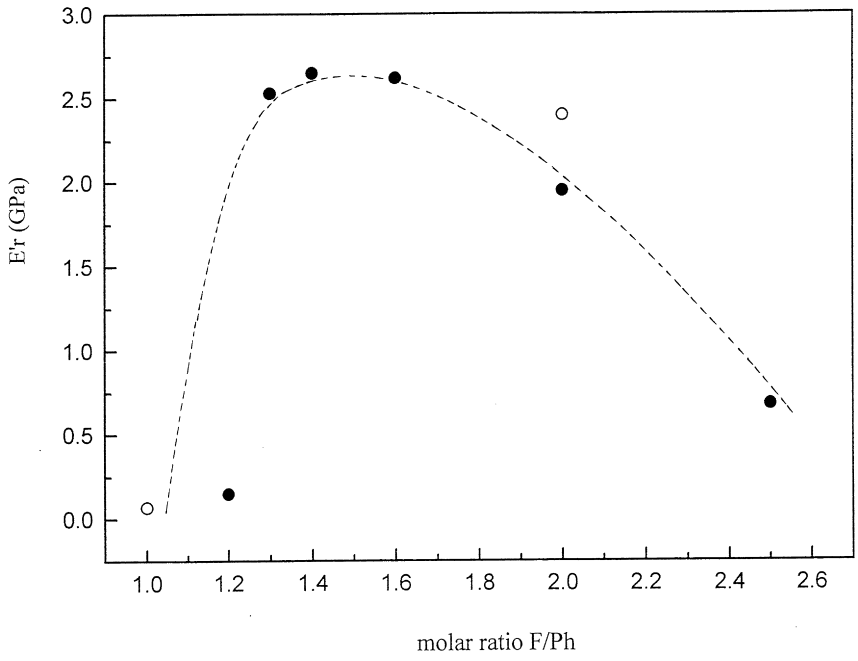

Fig. 14. Rubber modulus (E'r) as a function of formaldehyde-to-phenol molar ratio for the resols: (●) synthesized, (○) commercial products.

References

[1] Brown N, Linnert E, Bühl D. Composites 1996;14:29.
[2] Moragues J. Analyse Etude Cinetique et Transformations Structurales de Resols. Relations Structure-Properties. PhD Thesis. INSA, Lyon, France, l994
[3] Knop A, Pilato L. Phenolic Resins. Berlin: Springer-Verlag, 1985
[4] Kopf PW, Little AD. In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI, editors. Encyclopedia of Polymer Science and Engineering. Vol 11. New York: Wiley and Sons, l988.
[5] Grenier-Loustalot MF, Larroque S, Grenier P, Bedel D. Polymer l996;37(6):955.
[6] Jones RT. J. Polym. Sci. l985;21:1801
[7] Haslam J, Soppet W. J Appl Chem 1953;3:328.
[8] Oyanguren PA. Polmeros Entrecruzados Producidos por el Curado de Novolacas Epoxidadas. Tesis Doctoral, UNMdP, 1992.
[9] Grenier-Loustalot MF, Larroque S, Grenier P, Leca J, Bedel D. Polymer 1994;35(14):3046.
[10] Grenier-Loustalot MF, Larroque S, Grenier P, Leca J, Bedel D. Polymer 1994;35(14):955.
[11] Grenier-Loustalot MF, Larroque S, Grenier P. Polymer 1996:37(4):639.
[12] Zsavitsas A, Beaulieu A. Am Chem Soc Div Org Coat Plast, Chem Pap 1967;27:100.
[13] Roczniak C, Biernacka T, Skarzynski M. J Appl Polym Sci l983;28:531.
[14] Qian JY, Pearson RA, Dimonie VL, Shaffer OL, E-Aasser MS. Polymer l997;38(1):2.
[15] Danusso F, Tieghi G. Polymer l986;27:1385.
[16] Drumm LF, Lebranc JR. In: Solomon DH, editor. Step Growth Polymerization. New York: Marcel Dekker, l972.
[17] Vázquez A, Adabbo HE, Williams RJJ. Ind Eng Chem Prod Res Dev l984;23(3):375.
[18] Stockmayer NH. J Chem Phys l943;11:45.