

JASNA DJONLAGIĆ  
ALISA ZLATANIĆ  
BRANKO DUNJIĆ  
SLOBODANKA MARKOVIĆ

Faculty of Technology and  
Metallurgy, Belgrade

REVIEW PAPER

532.135:678.7

## RHEOLOGICAL STUDY OF THE NETWORK FORMATION OF THERMOSETTING POLYMERS

*The rheokinetics of the curing of thermoset polymers, such as acrylate-terminated unsaturated polyesters, polyurethanes based on unsaturated polyesters and phenol-formaldehyde resins, was studied by rheological analysis. The evaluation of the rheological parameters, such as storage modulus  $G'$  and loss modulus  $G''$ , was recorded. In all cases, the entire polymerization process was presented as  $G'$  versus time curves all of which had a characteristic "S" shapes, indicating autoacceleration of the crosslinking reaction during the formation of the polymer network. Rheokinetic models of the process of network formation of the thermosets were proposed to confirm the autocatalytic character of these reactions, as well as to determine the numerical values of the constants of the rheokinetic equation and the degree of rheological conversion as a function of time. Here it is important to note that the phenomenon of self-acceleration is common to all these different thermoset systems and that the mechanism of self-acceleration results from phase separation and reaction acceleration due to an increased concentration of the reactive groups in the separate microgel phase. The results from the rheokinetic models reveal good agreement with the experimental data over the entire conversion. The information obtained from dynamic mechanical analysis shows that the mechanism of the curing process is essentially determined by the structural parameters of thermosetting polymers.*

Dynamic mechanical spectroscopy, which has been used during the past two decades, is a quite effective method for studying the curing process of thermosetting polymers and for the examination of the viscoelastic properties and transition temperatures of the cured products. Rheological analysis of network formation for three completely different types of thermosetting polymers will be presented here. Although there is large difference in the structure of the starting polymers and in their behavior during the process of curing in the sense of mechanism and kinetic, the physico-chemical phenomena associated with the formation of the crosslinked structures are general and the formation of network can be described by similar mathematical models.

The formation of a polymer network structure can be evaluated from dynamic measurements using a dynamic mechanical spectrometer. Rheological parameters such as the storage  $G'$  and loss modulus  $G''$  and viscosity  $\eta^*$  were recorded. The rheological properties and curing kinetics of the thermoset resins were determined during isothermal curing. For the analysis of unsaturated polyesters and polyurethanes a parallel plate geometry was used, while for the examination of novolac resins rectangular samples of impregnated fabric were found to be more suitable. The rectangular torsion geometry was also used for the examination the viscoelastic properties of cured samples.

The entire polymerization process of network formation can be divided into two parts separated by the gelation point, the point at which  $G'$  equals  $G''$ . In the flow region before the gel point, the viscosity at shear flow is the most informative parameter, while after the gel point, in the rubbery or glass state region, the storage

modulus  $G'$  is more informative. The gel point is one of the most important kinetic characteristics of curing, the viscosity becomes infinitely high but the process continues. In the classical statistical theory of gelation developed by Flory, the gel point is characterized by the appearance in the reactive system of a macromolecule with an infinitely large molecular weight,  $M_w \rightarrow \infty$ . On the other hand, the storage modulus which was lower in magnitude at beginning than the loss modulus, rises more sharply than the loss modulus. It can be also seen that there is large increase of  $G'$ , of several decades, during the cure. While the loss modulus passes through a maximum,  $G'$  enters a plateau. The crosslinked polymer is both infusible and insoluble (Figure 1).

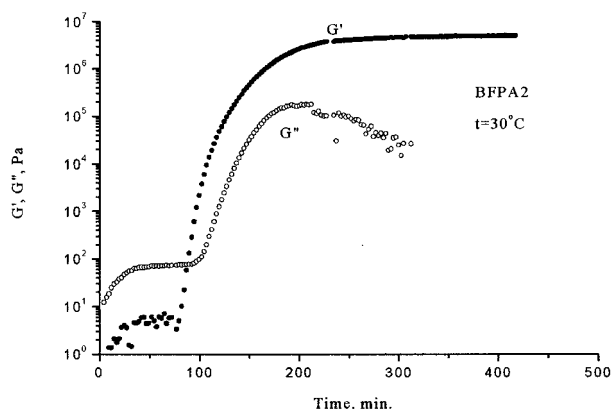


Figure 1. Storage and loss dynamic shear moduli ( $G'$  and  $G''$ ) for the reaction mixture BFPA2, plotted logarithmically as a function of total reaction time at 30°C

Control of the process of network formation is extremely important in the commercial processing of thermosetting plastics. This applies both to the reaction prior the gel point and that subsequent to it. The period after the gel-point is usually referred to as the curing period. A too slow or too rapid crosslinking can be detrimental to the properties of a desired product. For example, for reinforced and laminated products the

bond strength of the components may be low if crosslinking occurs too quickly.

A basic variable in the case of rheological investigations of curing polymers is the dynamic storage modulus,  $G'$ , which is proportional to the crosslink density of the network being formed by chemical bonds and physical entanglements. Its change with time very often exhibits an autocatalytic, S, shape. This effect can be influenced by many different phenomena, such as chemical self-catalysis, the gel-effect, the appearance of local heterogeneities and the parallel course of different reactions. The most important factor determining the time dependence of the rheological conversion described is phase separation. Thus, the superposition of the effects of both chemical crosslinking and morphology change results in the self-acceleration shape of the rheological conversion vs. time dependence. Generally speaking, a rheological analysis of polymerization reactions leading to the formation of a two phase structure cannot be considered without taking into account the morphology of the reactive system [1, 2].

Malkin and Kulichikhin [3] proposed that the rheokinetics of the curing of a heterogeneous reactive system can be described by the following phenomenological equation containing a self-acceleration term:

$$d\beta/dt = k(1 + c\beta)(1-\beta)^n \quad (1)$$

where  $\beta$  is the rheological degree of conversion,  $t$  is time,  $k$  and  $c$  are temperature dependent constants and  $n$  is the reaction order. This equation describes the formation of a two-phase structure by the mechanism of nucleation and growth under the condition that an increase in the concentration of the new phase is determined by the chemical reactions.

In this paper we wish to report on the rheokinetics of crosslinking of three different thermosetting resins:

1. Acrylate-terminated unsaturated polyesters which are low-molecular-weight copolyesters of fumaric, maleic and succinic and phthalic acid dissolved in styrene. These resins can be easily crosslinked by copolymerization with the styrene comonomer. The presence of double bonds at both chain ends diminishes the number of dangling chains and allows the formation of a regular network by crosslinking copolymerization with styrene.

2. Polyurethanes produced by the polyaddition reaction of a low-molecular weight prepolymer, hydroxy-terminated polyesters based on maleic acid and a triisocyanate. The functional groups are present in stoichiometric amounts, which means that side reactions are eliminated. Prepolymer systems generally offer a greater control of the polymerization and crosslinking reaction and, very importantly the structure of the final product.

3. The third group of thermosetting polymers were novolac phenol-formaldehyde resins. They are also low-molecular weight linear or slightly branched products produced in the presence of an acid catalyst with statistical or "high-ortho" positions of the methylene groups between the phenyl rings. Hexamethylenetetramine (HMTA) was used for the curing reaction, which would produce short methylene linkages between phenyl rings from different chains. In this polycondensation reaction the small molecule eliminated is water.

## EXPERIMENTAL PART

### Materials

#### A. Acrylate-terminated unsaturated polyesters

*Synthesis:* The synthesis and structure of the polymaleate (BMPA), polyfumarate (BFPA) and polysuccinate (BSPA) based acrylate-terminated unsaturated copolyesters examined in this study have already been discussed in detail [4].

*Copolymerization procedure of the polyesters with styrene:* The unsaturated acrylate-terminated copolyesters (3.00 g), containing about 0.10 wt.-% hydroquinone, were dissolved in styrene to obtain 67 wt.-% solutions. To each polyester solution, 0.2 wt.-% of dimethylaniline was added as a promoter for the decomposition of the initiator. The copolymerization reactions were started by adding 3 wt.-% of a 50 wt.-% benzoyl peroxide dispersion in dioctyl phthalate.

#### B. Polyurethanes

*Synthesis:* The polymer precursors used in this study were three series of  $\alpha$ ,  $\omega$ -dihydroxy oligo(alkylene maleate)s. The synthesis and characterization of these unsaturated polyesters were described in detail in a previous paper [5].

*The crosslinking agent:* Tris-4-isocyanatophenyl-thiophosphate (Desmodur DRF, Bayer in the form of a 30% solution in ethyl acetate) was recrystallized from ethyl acetate. The NCO content was determined according to ASTM and a NCO content of 26.1 % was found which represents 96.5 % purity.

*Sample preparation:* All the samples for crosslinking were prepared in the same way: the ratio NCO/OH was 1.00. A weighed amount of triisocyanate was dissolved in 0.35 ml of  $\text{CH}_2\text{Cl}_2$ . The solution was then added to a weighed amount of polyester and well mixed. After mixing the reagents, the solvent was evaporated under reduced pressure (1 mm Hg). The so-prepared sample was transferred simultaneously to a Dynamic Mechanical Spectrometer and an FTIR spectrometer. All operations were completed in 12 minutes.

*FTIR measurements:* FTIR spectra were taken of films of unsaturated polyester/triisocyanate reaction

mixtures casted on NaCl plates at programmed time intervals which changed depending on the rate of crosslinking.

### C. Phenol-formaldehyde resins of novolac type

**Synthesis:** The synthesis and structure of the phenol-formaldehyde novolac resins examined in this study have already been discussed in detail [6]. Briefly, six random novolac resins NLO 1–6, with decreasing molar ratio phenol-formaldehyde (1:0.85, 1:0.80 and 1:0.70) were prepared in the presence of two different concentrations of oxalic acid as the catalyst. A high-*ortho* novolac resin (NL-OO') was synthesized using zinc acetate,  $(Zn(Ac)_2)$  as the catalyst.

**Specimen preparation:** Specimens for the rheokinetic examinations were prepared by impregnating cotton strips with novolac resins. The novolac resins with 10 % HMTA were first ground in a ball mill and then 25 % solutions in acetone were made. The cotton strips were soaked in the solutions, dried at room temperature and the procedure repeated. In order to obtain homogeneous and compact samples, the strips were heated in a mold up to 70°C under a pressure of 5 bar. The content of phenolic resins in all samples was around 50 wt-%.

## Procedures

### Rheological measurements

Dynamic rheological data, i.e. storage modulus ( $G'$ ) and loss modulus ( $G''$ ), were recorded during copolymerization using a Rheometrics mechanical spectrometer RMS-605.

The samples of reaction mixtures polyesters and polyurethanes (about 0.80 g) were subjected to dynamic shear between two parallel plates at a constant frequency (6.28 rad/s) and the temperatures of 30, 50 and 70°C. The diameter of the plates was 25 mm and the gap between the plates was about 1.0 mm. Repeated dynamic measurements were taken at programmed 2.5 min. intervals during 420 min. to monitor the build up of the network structure. At the beginning of the experiments, when the reaction mixtures were liquids of relatively low viscosity, the intensity of the strain was 20 %. The initial strain amplitude of 20% was reduced during the cure to ensure a linear viscoelastic response.

The specimens impregnated with novolac resins containing 10 % HMTA, dimensions (25 x 12 x 0.5 mm), were submitted to rectangular torsional deformation in the Cure mode program at 180°C (heating rate to the reaction temperature 50°C/min), at a constant frequency 6.28 rad/s and a strain of 0.1 %. The rheological parameters, i.e. storage modulus  $G'$ , loss modulus  $G''$  and  $\tan\delta$ , were measured and recorded every 0.5 minutes for 45–60 minutes of isothermal heat treatment.

### Mathematical analysis of the results:

The reaction mixtures based on polymaleates (BMPA) and polysuccinates (BPSA) were not crosslinked to the maximum extent after the 420 min. experiments. To determine the maximum value of the storage modulus ( $G'_{\infty}$ ), the experimental plots of  $G'$  vs. time were extrapolated to infinite time by fitting with an asymmetric sigmoid curve using the computer program Table Curve TM 2D. Also, the same program was used to fit the experimental data, i.e.  $dG'/dt-\beta$ , by the selected form of kinetic expression. In this way the kinetic parameters were determined, after confirmation that the experimental and calculated values fitted well.

## RESULTS AND DISCUSSION

A basic variable in the rheological investigations of curing polymers is the dynamic storage modulus,  $G'$ , which is proportional to the crosslink density of the network being formed by chemical bonds and physical entanglements. In the studied cases, the linear  $G'$  versus time curves plotted over the entire polymerization process, had characteristic "S" shapes, indicating autoacceleration of the crosslinking reaction during the formation of the polymer network. From the linear plots of  $dG'/dt$  versus time it can be seen that the rate of increase of the storage modulus with reaction time increased till an inflection point was reached and decreased (Figure 2). The main interest of these analysis was to establish a general rheokinetic law which could describe the whole range of the storage modulus  $G'$  change during curing.

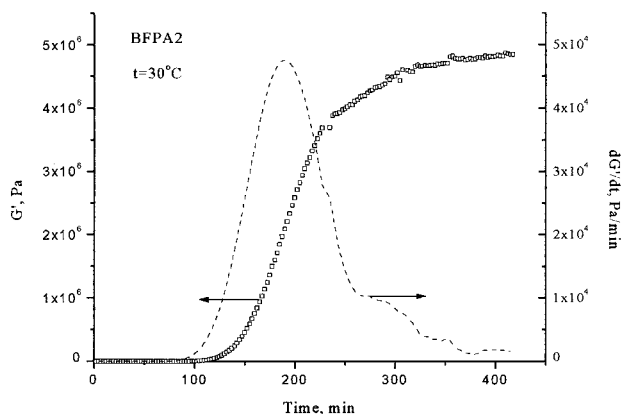


Figure 2. Storage modulus  $G'$  and the rate of its change  $dG'/dt$  for the reaction mixture BFPA2 plotted linearly as function of total reaction time at 30°C

Among physicochemical methods for studying curing process, rheokinetics is the closest to calorimetry, yielding both combined characteristics of the chemical dynamics of the process and morphological changes.

We have applied the same form of expression, which was used in DSC analysis [7–10] for the description of diacrylate polyesters and polyurethane

curing rheokinetics. Actually, the reduced form was used:

$$d\beta/dt = k \beta^m (1 - \beta)^n \quad m + n = 2 \quad (2)$$

where  $\beta$  represents the rheological degree of conversion which is a function of the storage modulus  $G'(t)$  defined as:

$$\beta = (G'(t) - G'_0) / (G'_\infty - G'_0) \quad (3)$$

where  $G'_0$  denotes the value of the storage modulus at zero time, or at the start of the experiment, and  $G'_\infty$  is the value of the storage modulus of the completely crosslinked polymer.

The differential equation (2) has the analytical solution:

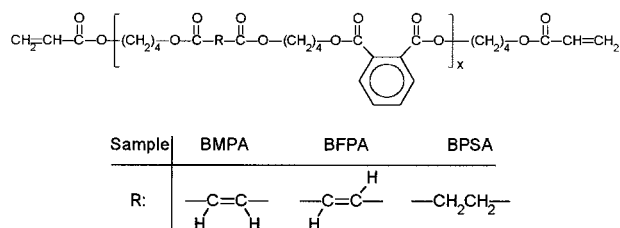
$$\beta = \frac{1-m \sqrt{k(1-m)t}}{1 + \sqrt{k(1-m)t}} \quad (4)$$

This fact makes it possible to compare graphically the experimental and calculated dependencies of the rheological degree of conversion  $\beta$  on time, in an easy way.

Rheological properties, such as the viscosity and dynamic modulus, are very sensitive to variation in the molecular structure of cured oligomers, to phase separation and phase and relaxation transition in the reactive systems, associated with the process of chemical conversion. Rheological data can be used, besides to identify the gel point, to interpret molecular weight, extent of branching and crosslinking density.

### Acrylate-terminated unsaturated polyesters

The structures of the three series of acrylate-terminated copolyesters examined, poly(tetramethylene maleate-co-tetramethylene phthalate) (BMPA), poly(tetramethylene fumarate-co-tetramethylene phthalate) (BFPA) and poly(tetramethylene phthalate-co-tetramethylene succinate) (BPSA) [4], are given below:



The influence of the terminal double bonds, as well as of the cis-trans configuration on the kinetics of curing unsaturated copolyesters was evaluated [11]. The information obtained from dynamic mechanical analysis shows that the mechanism of the curing process is essentially determined by the structural parameters of thermosetting polymers, i.e., concentration of the terminal double bonds, in addition to the cis-trans configuration and its distribution along main chain.

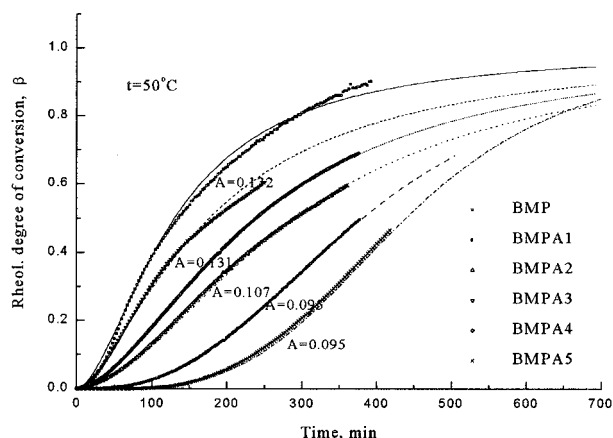


Figure 3. Degree of rheological conversion  $\beta$  versus time of reaction mixtures from the series BMPA at 50°C. Symbols: experimental values of  $\beta$ ; lines: calculated values (see eq. 4). A-molar fraction of acrylate groups

The copolymerization reaction of acrylate-terminated unsaturated copolyesters with styrene is described by a second order phenomenological equation, which takes into account the self-acceleration effect which arises from the superposition of both the chemical reaction and phase segregation. The results from the rheokinetic model reveal a good agreement with the experimental data over the entire conversion (Figure 3). Figure 4. shows that Eq. (2) describes all experimental dependencies  $d\beta/dt$  vs. time in a satisfactory way. This fact made possible the comparison of the cure kinetics of different samples over the whole conversion range. It was shown that characteristic parameters, such as time of  $G'-t$  and  $G''-t$  crossover, time of inflection point and rheological conversion degree at the inflection point,  $\beta_{\text{infl}}$ , are decreasing functions of the acrylate double bond concentration in the polyesters. At the same time, the

Table 1. Some characteristic parameters of curing the unsaturated polyesters at 50°C

Sample	Gel point $t_{G'=G''}$ , min	Inflection point characteristics			$G'_\infty$ MPa
		t, min	$\beta$	$(d\beta/dt) \times 10^3$ , $\text{min}^{-1}$	
BMP	16.3	77.6	0.21	4.75	2.67
BMPA-1	54.0	345	0.32	2.07	0.73
BMPA-2	33.0	195	0.23	2.17	1.07
BMPA-3	22.4	87.6	0.18	3.46	1.43
BMPA-4	25.7	145	0.22	2.59	1.11
BMPA-5	52.0	365	0.37	2.29	0.48
BPSA-3	44.0	—	0.37	1.60	0.53
BPSA-4	41.5	170.1	0.22	1.70	0.19
BFP	5.1	10.1	0.36	83.88	5.57
BFPA-1	13.0	45.1	0.26	24.03	4.94
BFPA-2	29.9	77.6	0.29	10.91	5.12
BFPA-3	16.7	67.6	0.31	16.26	4.67

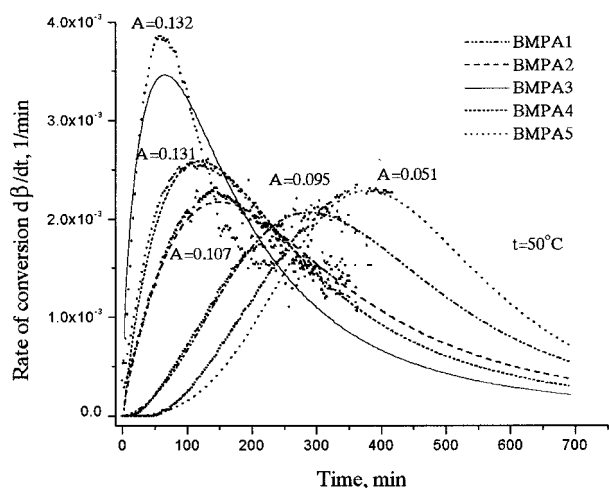


Figure 4. Curing rate  $d\beta/dt$  versus curing time for the BMPA series at  $50^\circ\text{C}$ . Symbols: experimental values of  $\beta$ ; lines: calculated values,  $A$ —molar fraction of acrylate groups

Table 2. Kinetic parameters of the unsaturated polyesters at  $50^\circ\text{C}$  curing given by fitting the experimental data with the expression  $d\beta/dt = k\beta^m(1-\beta)^{(2-m)}$

Sample	Kinetic parameters			Molar fraction of acrylate C=C bonds
	$k \times 10^3 \text{ min}^{-1}$	$m$	$n$	
BMP	13.27	0.419	1.581	—
BMPA-1	7.22	0.636	1.364	0.095
BMPA-2	6.37	0.458	1.542	0.107
BMPA-3	8.81	0.355	1.645	0.132
BMPA-4	7.38	0.436	1.564	0.131
BMPA-5	8.51	0.732	1.268	0.051
BPSA-3	5.93	0.720	1.280	0.065
BPSA-4	4.81	0.430	1.570	0.051
BFP	310	0.723	1.277	—
BFPA-1	75.53	0.519	1.481	0.104
BFPA-2	36.06	0.570	1.430	0.096
BFPA-3	56.40	0.627	1.373	0.091

Molar fraction of acrylate groups ( $A$ ).

rate of rheological conversion at the inflection point  $(d\beta/dt)_{\text{infl}}$ , increased (Table 1).

The influence of the polyester double bond configuration was shown by comparing the values of the rate constants  $k$  from the phenomenological equation describing the curing process (Table 2). The values of  $k$  for the polyfumarate based reaction mixtures were 6 to 10 times higher than the  $k$  values for mixtures based on the *cis*-isomer. This is a confirmation that the *trans*-disubstituted double bonds are more reactive than their *cis*-isomers (Figure 5). Namely, the fumarate unsaturations reacted quantitatively during

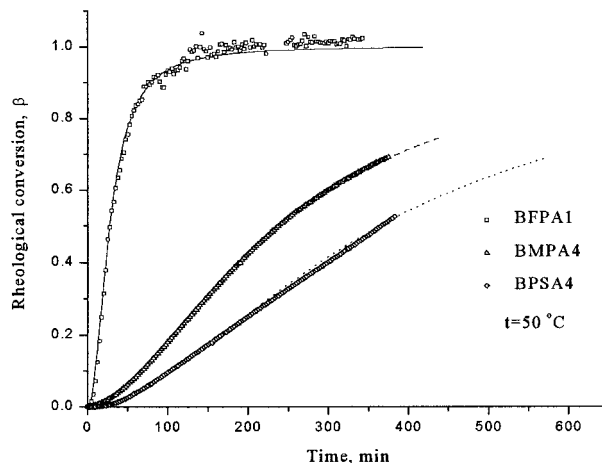


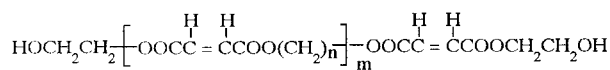
Figure 5. Degree of rheological conversion  $\beta$  versus time at  $50^\circ\text{C}$  for acrylate-terminated polymaleate (BMPA-4), polyfumarate (BFPA-1) and polysuccinate (BPSA-4) Symbols: experimental values of  $\beta$ ; lines: calculated values

copolymerization with styrene, resulting in very dense networks, while the maleate bonds along the polyester chains reacted only partially, resulting in higher degrees of swelling [12]. The rheokinetic model is not only important for a better understanding of structure–property relationships, but it is also fundamental in optimizing the cure time, concentration of the initiator, curing temperature and the properties of the final product.

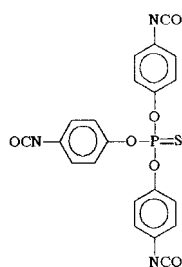
The constant  $k$  followed an Arrhenius type temperature dependence so the calculation of the apparent activation energy of the curing process was possible for samples of polymaleates cured at several different temperatures.

### Polyurethanes based on unsaturated polyesters

Polyurethane model networks with polyester elastic chains have been synthesized by the stoichiometric end-linking of a reaction hydroxy terminated prepolymer and a trifunctional isocyanate crosslinker. The prepolymers were bifunctional hydroxy terminated polyesters of known molecular weight, i.e.  $\alpha$ ,  $\omega$ -dihydroxyoligo(alkylene maleate)s, while tris-4-isocyanatophenylthiophosphate (Desmodur DRF) was the crosslinking agent. Three-dimensional polyurethane networks were produced in the polyaddition crosslinking reactions, while a control of the length and of the number of elastic chains was provided. Fourier transform infrared (FTIR)–spectroscopy was used to describe the chemical kinetics of network formation, i.e., to establish the order of the reaction before the gel point and extent of reaction at the gel point. Hydroxyl terminated stereoregular polymaleates could be used as prepolymers in synthesis of the model polyurethane networks due to their high flexibility of the polymer chains and telechelic structures [5].



n = 4, 6 and 8  
 n = 4, PBM(OH);  
 n = 6, PHM(OH);  
 n = 8, POM(OH)



Tris-4-isocyanatophenylthiophosphate (Desmodur DRF)

The change in the rheological properties of the curing reaction mixture is directly proportional to the extent of the reaction. For example, the gel time could be determined according to different criteria [13–15]. One criterion is the peak maximum in the tangent angle of mechanical loss  $(\tan\delta)_{\max}$  where there exists the maximum difference between the elastic and viscous behavior of the reaction mixture. The other criterion is the crossover of  $G' - t$  and  $G'' - t$  curves, when the system show the same level of elastic and viscous behavior, which means that the same quantity of energy is stored and dissipated. Or it could be determined as the intersection point tangent on the curve  $G'$  (100 kPa) and the base line ( $G'' = 0$ ).

We accepted the criterion corresponding to the crossover between the  $G'$  and  $G''$  curves, i.e., the point at which the system exhibits not only elastic but also viscous behavior, when a similar amounts of energy are stored and dissipated. This criterion is not a general criterion for determining the gel point and the gel point coincides with the crossover only when the storage and loss moduli are proportional to  $\omega^{1/2}$  for stoichiometrically balanced network polymers, and networks with excess crosslinker, as was reported by Winter [16,17]. The gel time values obtained for curing  $\alpha$ ,  $\omega$ -dihydroxy terminated polymaleates with a trisocyanate crosslinker under isothermal condition shows a dependence on the molecular weight of the prepolymer as well as on chain flexibility (Table 3).

In a previous paper [18], we proposed that in the crosslinking reaction of polymers, three stages could be distinguished: pre-gelation, gelation and post-gelation. In the pre-gelation stage, the molecular weight and branching of the oligomers increase as a result of the coupling reactions. True gelation is the stage between the point at which  $G'$  equals  $G''$  and the point at which  $dG'/dt$  reaches its maximum (i.e. the inflection point). During this stage, gel and sol coexist in the reaction mixture and further coupling reactions not only enhance the crosslink density of the gel but also progressively

Table 3. Some characteristic parameters of curing unsaturated polyesters with trisocyanate,  $\tau$  is the characteristic time determined from FTIR measurements, i.e. the time to gel point, the gel point and the inflection point and degree of reaction ( $p$ ) determined by FTIR.

Sample	$\bar{M}_n$ GPC	$\tau$ (FTIR)		Gel point		Inflection point characteristics		
		$\tau$ , min	$p$ (IR)	$t_{G'=G''}$ , min	$p$ (IR)	$\tau$ , min	$\beta$	$p$ (IR)
PBM(OH)1	1750	20	0.78	27	0.84	50	0.238	0.935
PBM(OH)2	1900	26	0.75	52	0.87	88	0.251	0.92
PBM(OH)3	2600	55	0.75	67	0.77	97	0.355	0.81
PHM(OH)1	1700	12	0.73	18	0.87	25	0.233	0.95
PHM(OH)2	2700	12	0.78	25	0.94	42	0.514	0.99
PHM(OH)3	3800	23	0.83	152	–	192	0.504	–
POM(OH)1	1900	13	0.83	15	0.89	20	0.365	0.95
POM(OH)2	2300	11.5	0.76	15	0.85	20	0.242	0.94
POM(OH)3	3300	12	0.74	19	0.91	25	0.233	0.95

transform the sol fraction into gel. Post-gelation crosslinking follows after the inflection point (Figure 1). The importance of post-gelation curing is shown by the fact that over 70 % of the storage modulus of a maximally crosslinked polymer  $G_\infty$  is gained during the post-gelation period. It is also evident that the duration of post-gelation curing is several times longer than the duration of gelation.

The results of a kinetic study of the crosslinking reaction for three series of  $\alpha$ ,  $\omega$ -dihydroxy poly(alkyl maleate)s and a trisocyanate crosslinker are presented in Table 3. The reaction follows simple second-order kinetics until the extent of the reaction reaches 75 %. The gel point is reached when the extent of reaction is between 87–91%. The characteristic time  $\tau$  shows, as well as the gel time, a dependence on the molecular weight of the prepolymer and on chain flexibility. Below the gel point, the characteristic time  $\tau$  is determined from the slope of the linear part of the function  $1/(1-p)$  versus time  $t$ . For conversion above the gel point, a positive deviation from second order kinetics, i.e., an increase in the overall reaction rate, is observed.

It can be concluded that the rate of crosslinking is dependent on the concentration of NCO (or OH) groups (i.e. on the molecular weight of the polyester glycol) and on the number of carbon atoms in the repeating unit. The influence of the molecular weight of the prepolymer is illustrated in Figure 6 where the crosslinking of three samples of poly(hexamethylene maleate)s is shown. The results obtained for polyesters with the same molecular weight but synthesized with different dibromoalkanes are shown in Figure 7.

The rate of crosslinking as a function of molecular weight for the three series of polyesters is shown in Figure 8, from which it can be seen that the rate of crosslinking decreases in the order poly(octamethylene maleate) > poly(hexamethylene maleate) > poly(butylene maleate). As the NCO concentration was

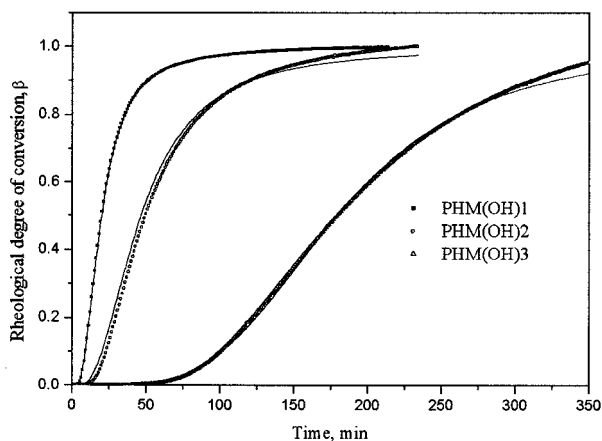


Figure 6. The influence of molecular weight of prepolymer on the crosslinking rate for PHM series. Symbols: experimental values of  $\beta$ ; lines: calculated values

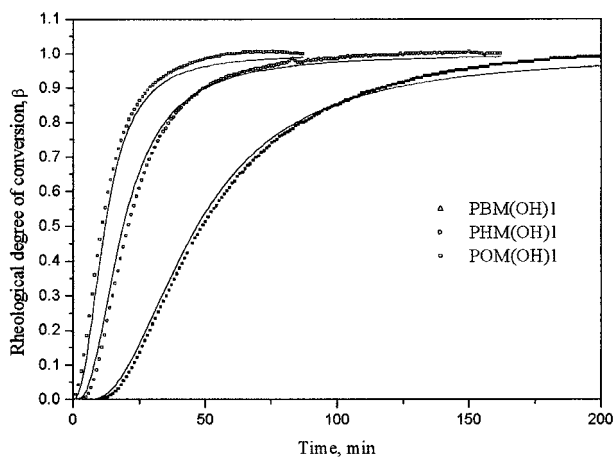


Figure 7. The influence of the chain flexibility of the prepolymer on the rate of crosslinking. Symbols: experimental values of  $\beta$ ; lines: calculated values

approximately equal for all the samples, the difference in the rate of crosslinking is due only to the difference in chemical composition. We think that poly(octamethylene maleate) has the greatest chain mobility and that this contributes to the rate of crosslinking in the gel.

In order to obtain better understanding of the physical meaning of the inflection point on the  $G'$  vs  $t$  curve (i.e. the maximum of rheological rate of crosslinking), the curing reactions were followed by FTIR. The results presented in Table 3 show that the chemical conversion increased very rapidly during the initial stage of the curing reaction, while an appreciable rheological conversion could be detected near the gel point. The results confirm that the uncatalysed reaction between NCO and OH was unusually rapid, and, due to the high reaction rate, it was only possible to follow the reaction from 40 % (in the case of poly(butylene methylene maleate) and from 55 % (in the case of poly(octamethylene maleate)). In general, the extent of the reaction was greater than 50 % during the 12 min necessary for the operations of mixing and evaporation of the solvent. The

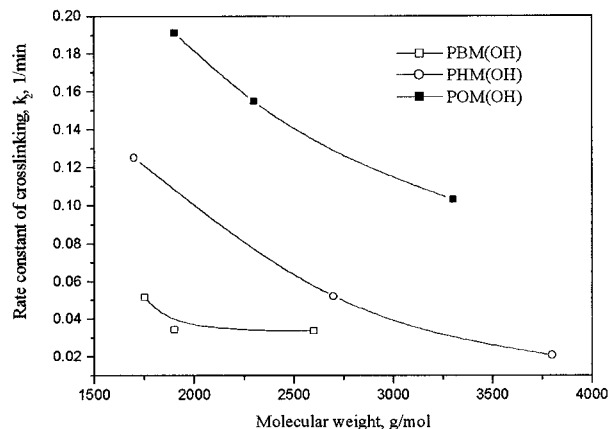


Figure 8. The influence of molecular weight of the polyester prepolymer on the crosslinking rate

chemical degree of reaction ( $p$ ) at the inflection point on the  $G'$  vs.  $t$  curves (i.e. at the beginning of post-gelation crosslinking) increases as the rate of cure increases. Thus, in the case of the PBMs  $p_{inf}$  at the inflection point varies from 0.81 to 0.93, in the case of the PHMs from 0.95 to 0.99 and for the POMs it is around 0.95.

In a previous paper [18], we associated the inflection point with the moment when the sol content ( $w_s$ ) falls below a certain value, so that from that moment on the increase of  $G'$  is only the consequence of increasing crosslink density, and not of the transformation of liquid sol into solid gel. The results obtained in the series of PBMs confirm that the sol content, calculated as:  $w_s = (1/p^2 - 1)^3$ , is always below 5 weight % at the inflection point. In the two other series PHMs and POMs, due to the faster rate of crosslinking, the fraction of the sol content is even lower.

The rate constants for the reaction of NCO with OH groups are also given in Table 4. For the series of poly(butylene maleate) the values of the rate constant  $k_2$  are in the range from 0.03 to 0.05  $\text{min}^{-1}$ , while the rate

Table 4. Kinetic parameters of crosslinking hydroxyl-terminated polymaleates with triisocyanate given by fitting the experimental data with the expression  $d\beta/dt = k_2 \beta^m (1-\beta)^{2-m}$

Sample	$\bar{M}_{nGPC}$	Inflection Point		$k_2 \times 10^2$ , l/min	m	n=2-m
		$\beta$	$\times 10^3$ $d\beta/dt$ $\text{min}^{-1}$			
PBM(OH)1	1750	0.262	16.5	5.17	0.514	1.486
PBM(OH)2	1900	0.299	10.2	3.44	0.594	1.406
PBM(OH)3	2600	0.384	9.2	3.39	0.749	1.251
PHM(OH)1	1700	0.256	39.8	12.51	0.522	1.478
PHM(OH)2	2700	0.268	16.4	5.21	0.526	1.474
PHM(OH)3	3800	0.355	5.6	2.09	0.713	1.287
POM(OH)1	1900	0.28	58.2	19.12	0.562	1.438
POM(OH)2	2300	0.25	49.0	15.48	0.521	1.479
POM(OH)3	3300	0.256	34.2	10.31	0.492	1.508

Table 5. Rheokinetic parameters of the novolac resins cured at 180°C obtained by fitting the experimental data with the expression  $d\beta/dt = k(1 + c\beta)(1 - \beta)^2$

Sample	Kinetic parameters		Molar ratio formaldehyde/phenol	Content of isomer o-o', %
	k, min <sup>-1</sup>	c		
NLO-1	0.023	13.74	0.73	26.05
NLO-2	0.025	15.32	0.80	27.20
NLO-3	0.042	10.27	0.85	30.61
NLO-4	0.021	12.24	0.70	25.81
NLO-5	0.025	13.79	0.78	25.64
NLO-6	0.034	13.42	0.85	26.58
NLOO'1	0.069	5.32	0.85	70.17
NLOO'2	0.106	3.95	0.69	78.00

constant for poly(octamethylene maleate)s are four times higher (Table 4). The values for the PHMs series lie between the two extreme cases.

The combination of both FTIR spectroscopy and dynamic mechanical spectroscopy [19] is a powerful tool in monitoring changes in the chemical and rheological conversion during polyurethane network formation. The crosslinking reaction was very rapid even at room temperature and followed second order kinetics until the extent of the reaction of 75%, which corresponds approximately to the gel point. The obtained rheological data permitted the description of the whole crosslinking process. The equation,  $d\beta/dt = k_2 \beta^m (1 - \beta)^{2-m}$ , which includes a self-acceleration term, describes the whole process well. The rate constant,  $k_2$  is also dependent on the segmental mobility. The chemical extent of reaction was determined by FTIR analysis which permitted the calculation of the sol content at the beginning of the post-gelation curing, i.e., at the inflection point. It confirmed that the sol content was less than 5 wt %, and that in post-gelation crosslinking all the functional groups are attached to the network, and that the reaction rate depends exclusively on the segmental mobility.

### Phenol-formaldehyde novolac resins

Novolac resins have a linear or slightly branched chain structure, in which the phenolic rings are linked by methylene bridges. They are of relatively low molecular weight up to approximately 2000. These resins are soluble and permanently fusible, i.e. thermoplastic, and are cured only by the addition of a hardener, almost exclusively with hexamethylenetetramine (HMTA), to give insoluble and infusible products. The kinetics of the curing reactions strongly depend on the nature and amount of reactive positions on the phenol ring. The influence of the composition, structure and content of unreacted ortho and para positions in the phenol ring on the rheology and curing behavior of novolac phenol-formaldehyde resins have been analysed. Typical random commercial phenol-formaldehyde novolac resins, with decreasing ratios of phenol/formaldehyde

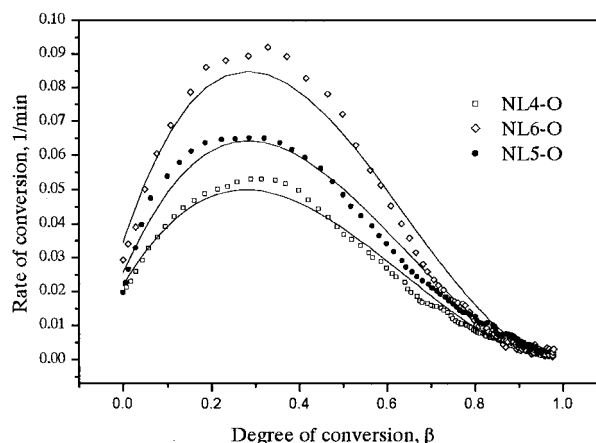


Figure 9. Rate of change of the rheological conversion  $d\beta/dt$  versus the rheological degree of conversion  $\beta$  for the NLO-4, NLO-5 and NLO-6 reaction mixtures at 180°C. Symbols: experimental values, lines: calculated values

from 1:0.75 to 1:0.85, were prepared in the presence of oxalic acid at two different concentrations (NLO 1-6). A high-ortho novolac resin (NL-OO') was synthesized in the pH range 4-6 using zinc acetate (ZnAc<sub>2</sub>), as catalyst. Random novolac resins synthesized with higher concentrations of oxalic acid have higher molecular weights, broader molecular weight distributions and higher reactivity in the curing reaction with HMTA.

The integral of equation (1) gives the dependency  $\beta = f(t)$  in the implicit form:

$$\frac{\beta}{\beta + 1} + \frac{c}{1 + c} \ln \frac{1 + c\beta}{1 - \beta} = (1 + c)kt \quad (5)$$

It can be seen from Figure 9, that good agreement between the experimental and calculated dependencies of the rate of conversion over the entire conversion is obtained. This confirms that the proposed rheokinetic model is good and that the self-acceleration character of these processes is a consequence of the chemical reaction of crosslinking and of morphological changes.

Difference in the reactivity of novolac resins was ascertainable from rheokinetic analysis [20]. Thus, the reaction rate constant  $k$  from the phenomenological expression increases regularly with increasing molar ratio of formaldehyde to phenol, going from 0.021 to 0.042 min<sup>-1</sup> for the series of random novolac NLO 1-6. The values of the self-accelerating constant,  $c$ , varies between 10 and 15 for the same series of novolac resins and does not show any apparent dependency on the molar ratio (Figure 10).

However, it is possible to see that in the region of low molar ratio (until 0.8) of formaldehyde to phenol, the self-acceleration constant  $c$  increases with increasing molar fraction of formaldehyde. In the region of higher molar ratio in the case of the more reactive novolac resins, like NLO-3 and NLO-6 the value of the self-acceleration constant  $c$  decreases. This is especially pronounced with the novolac NLO-3, which



of all the random samples has the highest number of o-o' methylene linkages and the highest reactivity.

One of the aims of this work was to quantify the differences in the reactivity between random and high-ortho novolac resins. The rate constant  $k$  of curing high-ortho novolac resins were 1.6 to 2.5 times higher compared with the most reactive random novolac resin NLO-3, while the values of the self-acceleration constant  $c$  were the lowest for the novolac resin with the highest content of o-o' methylene bridges.

The characteristics parameters of curing novolac resins at 180°C, such as the time of gel point, i.e., the time of the maximum of  $\tan\delta$ ,  $t(\tan\delta)_{\max}$ , the time of the attainment of the inflection point  $t(\beta_{\text{infl.}})$ , the rheological conversion  $(\beta_{\text{infl.}})$ , and its rate at the inflection conversion  $(d\beta/dt)_{\text{infl.}}$  are presented in Table 6. It may be noted that the gel time, as well as the time and conversion at the inflection point are dependent on both the novolac composition, i.e., the molar ratio of formaldehyde to phenol, and the content of the o-o' isomer. It can also be seen that the curing rate maximum is higher and the conversion at the curing rate maximum lower for the high-ortho than for the fastest random novolac NLO-3. Also, from Table 6, it can be seen that the  $dG'/dt$  maximum for the high-ortho novolac is reached before that for the fastest random novolac resin NLO-3.

The self-acceleration model  $d\beta/dt = k(1 + c\beta)(1 - \beta)^2$  can be used when the maximum reaction rate appears at around 30% conversion, as is the case in the curing reaction of random novolacs. The reason for the derivation of the calculated from the experimental data in the curing reaction of high-ortho novolac resins (Table 6) may be due to fact that the reaction at 180°C is very fast without an induction time so that the maximum of the curing rate occurs at around 25% conversion.

It seems that the molar ratio formaldehyde to phenol (fraction of formaldehyde) is the main variable which governs the reactivity of novolac resins, especially random ones (Figure 10). On the contrary, it can be seen that the rate constant values of high-ortho novolac

Table 6. Some characteristic rheological parameters of the curing novolac resins at 180°C

Sample	Gel point ( $\tan\delta$ ) <sub>max</sub> , min	Characteristics of the inflection point			G' <sub>∞</sub> , Pa
		t <sub>infl.</sub> , min	β <sub>min<sup>-1</sup></sub>	dβ/dt	
NLO-1	4.4	6.5	0.29	0.061	4.43 10 <sup>8</sup>
NLO-2	2.5	5.15	0.30	0.071	6.99 10 <sup>8</sup>
NLO-3	0.5	3.9	0.26	0.093	6.12 10 <sup>8</sup>
NLO-4	5.0	7.7	0.31	0.052	4.75 10 <sup>8</sup>
NLO-5	2.5	5.8	0.30	0.064	3.00 10 <sup>8</sup>
NLO-6	1.0	4.1	0.29	0.092	6.36 10 <sup>8</sup>
NL-OO'1	1.0	3.0	0.25	0.107	3.75 10 <sup>8</sup>
NL-OO'2	0.5	3.0	0.26	0.125	3.74 10 <sup>8</sup>

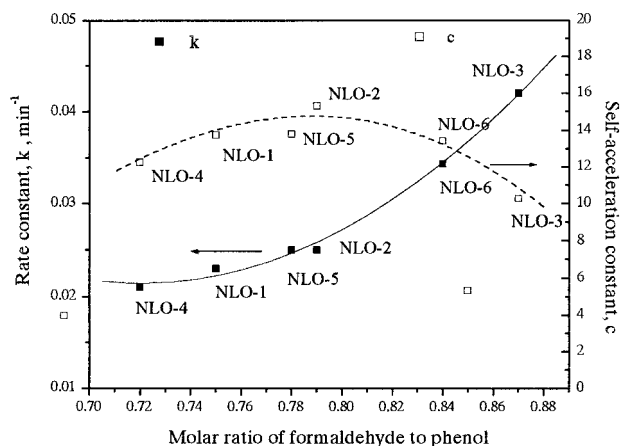


Figure 10. Effect of the novolac composition on the rate constant of curing  $k$  and the self-acceleration constant  $c$  for the series NLO 1-6 (Table 2)

resins are higher than expected on the base of the molar fraction of formaldehyde. From the dependency of the rate constant on the content of o-o' isomer, which is an indirect measure of the unsubstituted para positions per phenolic ring, it can be seen that random novolacs with a greater content of the o-o' isomer show higher values of the rate constant. For high-ortho novolac resins, this is even more pronounced, which is obviously the influence of the high fraction of free para positions, which are more reactive than the ortho position in the curing reaction (Table 5).

The constants of the curing reaction follow an Arrhenius type temperature dependence. The results confirm that the value of the activation energy of the curing process decreases with increasing reactivity of novolac resins. It was also shown that not only does the rate constant, but also the self-acceleration constant depend on temperature. The rheokinetic parameters obtained by this analysis could permit the simulation of the curing both inside and outside the experimental range of temperatures. The time of the gel point, as well as the time to the inflection point were shorter with increasing temperature.

These results indicate that dynamic mechanical measurements on cotton strips impregnated with phenol-formaldehyde resins, followed by careful rheological analysis, can be a powerful tool in the characterisation and design of thermosetting resins and in the determination of the properties of the final products.

## CONCLUSIONS

Cure characterization methods, i.e. dynamic mechanical spectroscopy used single or in combination with FTIR, discussed in conjunction with kinetic models can transform raw data into useful cure kinetic information. These rheokinetic models allow the subsequent prediction of thermosetting curing behavior as a function of formulation variables and time-temperature profiles and,

thereby, establish the relationship of cure behavior to end-use properties. Radically initiated reactions, like that of styrene with unsaturated polyesters, gel very early in the reaction, while a stepwise system, like the examined polyurethanes and phenolics, typically gel at 70 % or higher conversion. The process of network formation of thermosets was described by second or third order phenomenological equations, which take into account the self-acceleration effect that arises from the superposition of both a chemical reaction and a phase separation.

## REFERENCES

- [1] A.Ya. Malkin, S.G.Kulichikhin, *Rheokinetics, Rheological Transformation in Synthesis and Reaction of Oligomers and Polymers*, Hüthig & Wepf Verlag, 1996, 170.
- [2] K. Dusek, *Polymer Network'91*, K. Dusek & S.I.Kuchanov (Eds), VSP, Utrecht, 1992, 1-6.
- [3] A.Ya. Malkin, S. G. Kulichikhin, *Reologiya v protsessah obrazovaniya i prevrashcheniya polimerov*, Khimiya, Moscow, 240,(1985)
- [4] A. Zlatanić, J. Djonlagić, *Macromol. Chem. Phys.* **198**, 1775 (1997)
- [5] B. Dunjić, M.O. Sepulchre, M. Sepulchre, N. Spassky, J. Djonlagić, *Makromol. Chem.Phys.*, 199, 1051 (1999).
- [6] S. Marković, J. Djonlagić, J. Zakrzewska, B. Dunjić, J. Serb. Chem. Soc., **64**(3), 177 (1999).
- [7] M.R. Kamal, S. Sourour, *Polym. Eng. Sci.* **13**, 59, (1973)
- [8] S.Y. Pusatcioglu, A.L. Fricke, J.C. Hassler, *J. Appl. Polym. Sci.* **24**, 937-946, (1979)
- [9] C.D. Han, K.W. Lem, *J. Appl. Polym. Sci.* **28**, 3155-3183, (1983).
- [10] C.D. Han, K.W. Lem, *J. Appl. Polym. Sci.* **29**, 1879-1902, (1984).
- [11] A. Zlatanić, B. Dunjić, J. Djonlagić, *Macromol. Chem. Phys.* **200**, 2048 (1999)
- [12] A. Zlatanić, J. Djonlagić, B. Dunjić, *Macromol. Chem. Phys.* **199**, 2029 (1998).
- [13] J.K. Gillham, J.A. Benci, *J. Appl. Polym. Sci.*, **18**, 951 (1974).
- [14] J.M. Laza, C.A. Julian, E. Larrauri, M. Rodriguez, L.M. Leon, *Polymer*, **40**, 35(1998).
- [15] C.W. Macosko, *Brit. Polymer J.*, **17**, 239 (1985).
- [16] H.H. Winter, F. Chambon, *J. Rheol.* **30**, 367 (1986).
- [17] H.H. Winter, *Polym. Eng. Sci.*, **27**, 1698 (1987).
- [18] M.S. Jacović, J. Djonlagić, M. Sepulchre, M.O. Sepulchre, N. Spassky, *Makromol. Chem.* **193**, 2113 (1992).
- [19] T. Provder, *Journal of Coating Technology*, **61**, No 770, 33, (1989).
- [20] S. Marković, B. Dunjić, A. Zlatanić, J. Djonlagić, *Hem. Ind.* **53** (11) 349 (1999).

## IZVOD

### REOLOŠKO IZUČAVANJE UMREŽAVANJA TERMООČVRŠĆAVAJUĆIH POLIMERA

(Pregledni rad)

Jasna Djonlagić, Alisa Zlatanić, Branko Dunjić, Slobodanka Marković  
Tehnološko – metalurški fakultet, Karnegijeva 4, 11000 Beograd

Za izučavanje umrežavanja termoočvršćavajućih polimera kao što su nezasićeni poliestri sa završnim akrilatnim grupama, poliuretani na bazi nezasićenih poliestara i fenol-formaldehidne smole korišćena je reološka analiza. Reakcija umrežavanja polimera praćena je preko promene reoloških parametara kao što su modul sačuvane energije  $G'$  i modul izgubljene energije  $G''$  i  $tg\delta$  u ogleđima smicanja između paralelnih ploča ili u ogleđima uvijanja. U svim slučajevima, promena modula sačuvane energije od vremena pokazuje karakterističan "S" oblik, što je posledica samoubrzavanje reakcije umrežavanja. Važno je naglasiti da je efekat samoubrzavanja zajednički za sve ispitane termoočvršćavajuće smole i da se efekat samoubrzavanja javlja kao posledica ne samo hemijske reakcije formiranja poprečnih veza u oblasti posle nastajanja gela već i promene morfologije. Predloženi reokinetički modeli umrežavanja termoočvršćavajućih smola omogućili su određivanje brojčanih vrednosti konstanti brzine reakcije, kao i konstante samoubrzavanja i zavisnosti reološke konverzije od vremena. Rezultati dobijeni iz reokinetičkih modela pokazuju dobro slaganje sa eksperimentalnim rezultatima u čitavom opsegu konverzije. Informacije dobijene iz dinamičko-mehaničke analize pokazuju da je mehanizam umrežavanja određen elementima strukture termoočvršćavajućih smola.

Izučavani su uticaj prisustva dvostrukih veza na krajevima lanaca i duž osnovnih lanaca kao i njihove konfiguracije na sam proces umrežavanja nezasićenih poliestara. A na seriji nezasićenih stereoregularnih teleheličnih poliestara maleinske kiseline sa završnim hidroksilnim grupama praćena je reokinetika obrazovanja poliuretana pomoću triizocijanata. Takođe je analiziran uticaj hemijskog sastava odnosno strukture na seriji statističkih i novolacnih fenolnih smola sa visokim sadržajem orto-orto položaja na reakciju umrežavanja sa heksametilentaaminom.

Ključne reči: reokinetika • dinamička mehanička analiza • reakcije umrežavanja • termoočvršćavajući polimeri • novolacne smole • poliuretani • poliestri •  
Key words: Rheokinetics • Dynamic mechanical analysis • Curing reaction • Thermosetting polymers • Novolac resins • Polyurethanes • Polyesters •

