Macromol. Symp. ***148,*** *87–102 (1999)*

Epoxy Networks Modified by Unsaturated Oligoesters and Acrylates or Methacrylates

Mihailo Bratychak[§,#], **Witold Brostow**[§] and **Yozef Yatczyshyn**[#]

[#] Department of Analytical Chemistry, Lvivska Politechnika State University, Stepana Bandery 12, 290646 Lviv, Ukraine; mbratych@polynet.lviv.ua

[§] Department of Materials Science, University of North Texas, Denton, TX 76203-5310, USA; brostow@unt.edu

Abstract: We have studied the formation of networks on the basis of an epoxy resin called ED-20, the same resin modified with *tert*-butylhydroperoxide (called ED-20P), unsaturated oligoesters and polyethylenepolyamine in the presence of acrylates and methacrylates at 20°C, 100°C and 130°C. The gel-fraction contents in the blends and the pendulum damping hardness of films made from the blends have been determined. The progress of gelation has been related to the composition, time and crosslinking temperature. The presence of peroxide groups enhances the extent of gelation. When those groups are present, acrylates and methacrylates provide still higher values of the ultimate gel fractions, acting as diluents (lowering viscosity of the initial blends) and simultaneously as crosslinking agents. The pedulum damping hardness tests for organic films performed as a function of time provide results parallel to those obtained by the gel fraction determination via Soxhlett extraction with acetone. Thus, both methods can be used to pursue the progress of gelation.

CCC 1022-1360/99/$ 17.50+.50/0

1. Introduction

Networks on the basis of epoxy resins and unsaturated oligoesters are formed in the presence of polyethylenepolyamine (PEPA), maleic anhydride, styrene, organic hydroperoxides and accelerators of hydroperoxide decomposition [1-3]. Even when network formation is not the primary objective, the presence of reactive groups in the material provides the option of subsequent network creation [4, 5]. However, we have a two-edged sword here; the reactivity results in variation of properties over time. We have dealt before with the issue of time stability of such systems. An epoxy resin based on Bisphenol A (called ED-20) and an unsaturated oligoester was treated with *tert* -butylhydroperoxide epoxy resin (ED-20P) [6]. The amount of ED-20P added varied from 5 to 43 mass %.

To define the scope of this work, let us begin with a brief summary of the procedure developed by us in the preceding paper [6]. We have described there networks on the basis of the ED-20 epoxy resin, the modified ED-20P resin, an unsaturated oligoester and PEPA. We have developed a two-stage process of network formation.

The first stage takes place at room temperature for 24 hours. The network formation occurs as the result of reaction of PEPA molecules with epoxy groups of the ED-20 and ED-20P resins. It is important to note that at this stage the unsaturated oligoester does *not* react with the molecules of the epoxy resins.

The second stage consists in heating the system to a temperature in the range between 100 and 130 °C and maintaining that temperature for 30 - 60 minutes [6]. Under these conditions, decomposition of -O-O- bonds of the ED-20P resin takes place and free radicals are formed. The radicals initiate the polymerization of the unsaturated oligoester and its chemical binding to the crosslinked epoxy resin structure. The fact that the oligoester units become constituents of the networks formed – in addition to the epoxy groups - affects the mechanical properties in a significant and positive way.

The procedure briefly described above has a deficiency: the starting epoxy + oligoester blends exhibit high viscosity. This complicates the formation of thin films and of products with complex configurations on their basis. Therefore, in the present work we explore the addition of acrylates or methacrylates which contain in their structures reactive unsaturated double bonds. We expect that acrylates and methacrylates should lower the viscosities of the above systems - while being able to act as both diluents and the crosslinking agents.

2. Experimental Part

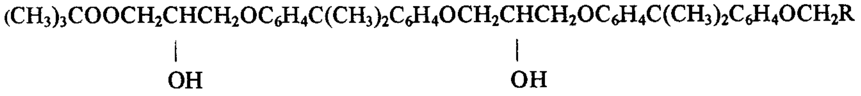
2.3 Analytical Methods

The number-average molecular masses M_n of the synthesized oligomers have been determined by cryometry using benzene as the solvent. The active oxygen content $[O]_{act}$ was determined iodometrically.

2. 2 Starting Reagents

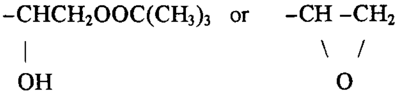
The ED-20 epoxy resin has been supplied by Styrol, Horlivka, Ukraine. It has the number-average molecular mass M_n = 390 and the epoxy number (e. n.) = 20.1 %. We define e.n. as the number of grams of epoxy groups per 100 g of the starting reagents.

The ED-20P modified epoxy resin has the formula



$$(CH_3)_3COOCH_2\underset{\overset{|}{OH}}{CH}CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2\underset{\overset{|}{OH}}{CH}CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2R$$

where R =



$$-\underset{\overset{|}{OH}}{CH}CH_2OOC(CH_3)_3 \quad \text{or} \quad -\underset{\backslash\ O\ /}{CH-CH_2}$$

and has been synthesized as described in [6]. In this case $M_n = 480$, $[O]_{act} = 2.1$ % while e. n. = 5.0 %.

The methacryl-(*bis* -triethyleneglycol)phthalate, called MGF-9 oligoester, has the following formula:

$CH_2=C(CH_3)C(O)O(-CH_2CH_2O-)_3C(O)C_6H_4C(O)(-OCH_2CH_2-)_3\text{-}OC(O)C(CH_3)=CH_2$

It was supplied by Barvnyk, Rubizhne, Ukraine, and has $M_n = 540$.

The triethyleneglycoldimethacrylate, called the TGM-3 oligoester, also from Barvnyk, with $M_n = 280$, has the formula $CH_2=C(CH_3)C(O)(-CH_2CH_2O-)_3C(O)C(CH_3)=CH_2$.

The polyethylenepolyamine (PEPA) was obtained from Oriana, Kalush, Ukraine. The methyl acrylate (MA), butyl acrylate (BA) and butyl methacrylate (BMA) have been supplied by Aldrich Chemical Co., with the main product content of no less than 99.0 %. The triethylamine (TEA) was also from Aldrich.

2.3 Blend Preparation

While degassing is needed sometimes to prevent subsequent bubble formation, it was not needed for our systems. Epoxy + oligoester blends have been prepared by mixing the components at room temperature for 10 -15 minutes, followed by addition of PEPA as the curing agent. In the case of cross- linking performed at the room temperature only, TEA was added to the mixture as the accelerator of peroxy decomposition in the ED-20P resin. The resulting homogeneous mass was cast on plates previously cleaned with acetone.

The crosslinking of blends containing BA and BMA has been carried out on the glass plates in the step-like manner defined above in Section 1. The resulting films had the thickness of ≈ 0.9 mm.

For the purposes of comparison, systems without the modified ED-20P resin have also been investigated. Compositions of the blends studied are listed in Table 1.

Table 1. Compositions of the investigated systems

Number of com-position	Component and its contents, mass parts							
	ED-20 Resin	**ED-20P Resin**	**TGM-3**	**MGF-9**	**BMA**	**BA**	**MA**	**TEA**
K1	100	—	8	—	—	—	—	—
K2	100	—	4	—	4	—	—	—
K3	100	—	4	—	—	6	—	—
K4	100	—	—	8	—	—	—	—
K5	100	—	—	8	4	—	—	—
K6	100	—	—	8	—	4	—	—
K7	100	—	4	—	—	—	6	0.6
K8	100	—	—	8	—	—	4	0.6
K9	100	—	4	—	4	—	—	0.6
K10	100	—	—	8	4	—	—	0.6
I	70	30	4	—	—	—	—	—
II	70	30	4	—	6	—	—	—
III	70	30	4	—	—	6	—	—
IV	95	5	—	8	—	—	—	—
V	95	5	—	8	4	—	—	—
VI	95	5	—	8	—	4	—	—
VII	70	30	4	—	—	—	6	0.6
VIII	95	5	—	8	—	—	4	0.6
IX	70	30	4	—	6	—	—	0.6
X	95	5	—	8	4	—	—	0.6

Note : PEPA contents in all systems was 14 weight parts.

In contrast to BA and BMA, MA has a relatively low boiling temperature, namely 80°C. This is why crosslinking of blends in the presence of MA has been carried out at the room temperature only; it lasted 4 days. Systems which contain active solvents but do not contain the ED-20P resin (see again Table 1) were also crosslinked at the room temperature for four days.

Structural changes during crosslinking have been followed by two distinct procedures. The first one is based on the gel-fraction determination by extraction of samples with acetone in Soxhlett apparatus for 10 hours, a procedure also used in earlier work [3). The second method is based on measuring indentation hardness of the films. The films were deposited upon standard glass plates. Their hardness has been determined at 20°C with a pendulum-type device using the Buchholz procedure formulated first for paints and varnishes. The German DIN 53153 standard has been followed. That standard is close to the ASTM D-4366 (Hardness of Organic Coatings by Pendulum Damping Tests). The relative hardness reported below is so defined that the hardness of ordinary glass equals to unity.

3. Extraction Results

In an earlier paper some compositions which result in high gel fractions have been found [6). Thus, in the absence of acrylates and methacrylates, high gel-fractions have been achieved using the ED-20 resin, the ED-20P resin and the TGM-3 oligoester in the ratio of 70 : 30 : 4 weight parts. In the case of the system containing the MGF-9 oligoester instead of TGM-3, the respective optimal ratio was 95 : 5 : 8 weight parts. These results from [6) have now been taken into account preparing systems containing acrylates and methacrylates. The systems studied and displayed in Table 1 cover a relatively wide viscosity range.

The changes of the gel-fraction contents with time determined by the Soxhlett extraction are shown in Figures 1 –5 , in each figure for five or six systems.

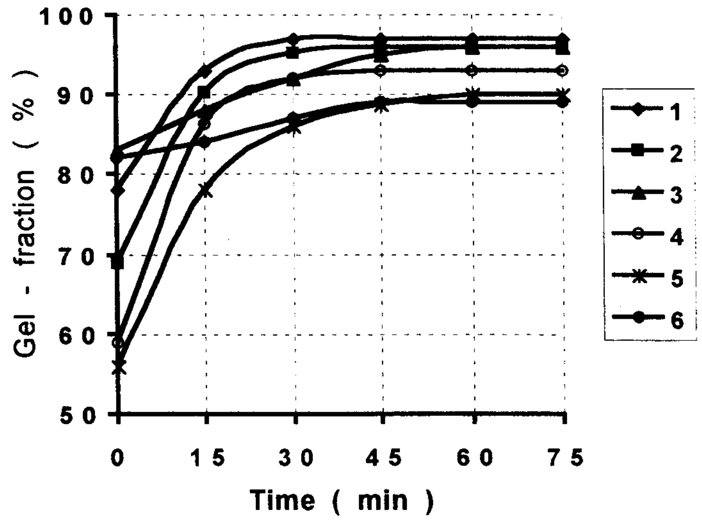


Fig. 1. Dependence of the gel-fraction content on crosslinking time at 100°C for several compositions: II (1), III (2), I (3), K3 (4), K2 (5) and K1 (6); see Table 1.

The highest final gel fraction in Fig. 1 is seen for Blend II which includes the ED-20P peroxide resin, the TGM-3 oligoester, and BMA as the solvent, this in addition to the ED-20 epoxy resin and PEPA, with the last two components present in all systems. The second highest final gel fraction is attained for Blend III, in which instead of BMA we have BA. The third curve from the top is for Blend I which also contains an oligoester, in this case TGM-3.

Several conclusions can be drawn from these results. First, all systems which do not contain the ED-20P peroxide resin (K1, K2 and K3) have lower final gel fractions than the blends which contain that resin (I, II, and III). Thus, and in fact as expected, the presence of the peroxide groups enhances the extent of network formation. Second, BMA (Blend II, curve 1) produces in this respect better results than BA (Blend III, curve 2). Both these blends have higher ultimate gel fractions than Blend I (curve 3) which contains neither BMA nor BA. Thus, curves 1 – 3 show that our objective of viscosity lowering by the addition of acrylates and methacrylates and thus achieving higher degrees of gelation has been accomplished. We shall see whether the extraction results for other systems will support this conclusion.

The situation in the absence of peroxide-containing ED-20P resin is somewhat different. Here BA (Blend K3, curve 4) is more effective in gelation than BMA (Blend K2, curve 5). Here again, however, Blend K1 which contains neither BA nor BMA has the lowest final degree of gelation. Thus, the acrylate and butylacrylate diluents enhance the extent of gelation.

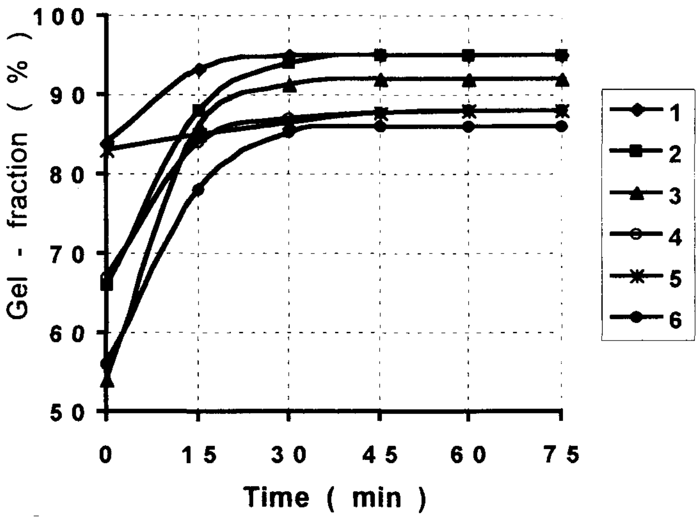


Fig. 2. Dependence of the gel-fraction content on crosslinking time at 100°C for several compositions: IV (1), VI (2), K6 (3), V (4), K4 (5) and K5 (6); see Table 1.

Let us now consider Fig. 2, starting with the comparison of the curves 5 and 6. The difference between the compositions of these two blends is the presence of the BMA acting as a diluent in the K5 system (curve 6). We see that the solvent lowers considerably the initial gel fraction and much less the final gel fraction. This result seems to be contradictory to what we have seen in Figure 1, but K4 and K5 both do not contain ED-20P. Compare similarly the curves 5 and 3. Here the difference is the presence of BA in K6 (curve 3). Initially, that diluent has an analogous effect as BMA, but the final gel fraction is higher than in K4 without BA. The highest initial as well as final gel fraction is seen for the Blend IV (curve 1); in contrast to the blends just considered, this one does contain the peroxide ED-20P resin. The final gel fraction in Blend VI is for all purposes the same as in Blend IV.

The results presented in Figures 1 and 2 pertain to 100°C. In Fig. 3 we show results for the same systems as in Fig. 1 but for 130°C; the symbols for the blends are the same. As expected, the temperature increase resulted in an overall increase of ultimate degree of gelation. However, the order of the systems is basically the same. Again, the lowest curve is that for K5 which does not contain ED-20P.

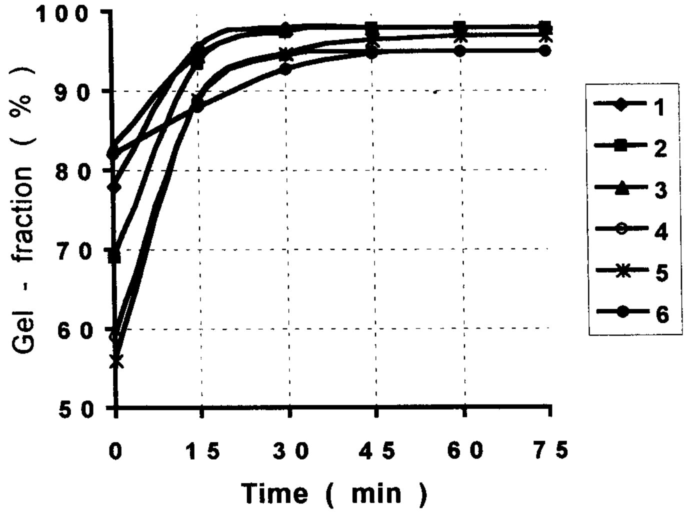


Fig. 3. Dependence of the gel-fraction content on crosslinking time at 130°C for several compositions: II (1), III (2), I (3), K3 (4), K2 (5) and K1 (6); see Table 1.

Figure 4 is the analog of Fig. 2 in that it represents results for the same systems but for 130°C. Again, the final gel fractions are generally higher while the same sequence of the final degrees of gelation is preserved.

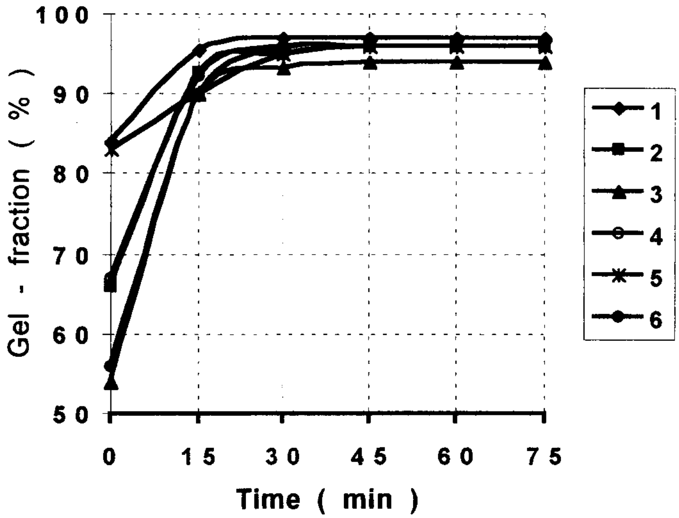


Fig. 4. Dependence of the gel-fraction content on crosslinking time at 130°C for several compositions: IV (1), VI (2), K6 (3), V (4), K4 (5) and K5 (6); see Table 1.

As noted above, we have also performed crosslinking at 20°C but introducing additionally TEA. The respective results for five systems are displayed in Fig. 5.

The curve with the highest gel-fraction contents in Fig. 5 pertains to Blend VII. It contains 30 weight parts of ED-20P, the highest amount we have used. It also contains TGM-3 as well as MA. The lowest curve is that for Blend K7 which does not contain ED-20P; the final gel-fraction des not reach 70 %. We infer that the results of room temperature curing largely confirm those obtained at 100°C and 130°C. The presence of peroxide groups seems to play the most important role, followed by the presence af acrylate or methacrylate diluents. We shall see in the next Section whether the hardness test results will also support these findings.

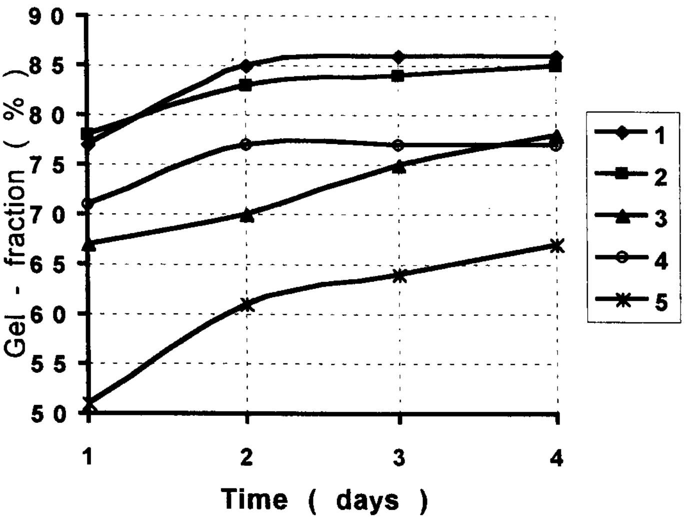


Fig. 5. 20°C gel-fraction vs. crosslinking time for: VII (1), IX (2), X (3), VIII (4) and K7 (5).

4. Hardness Results

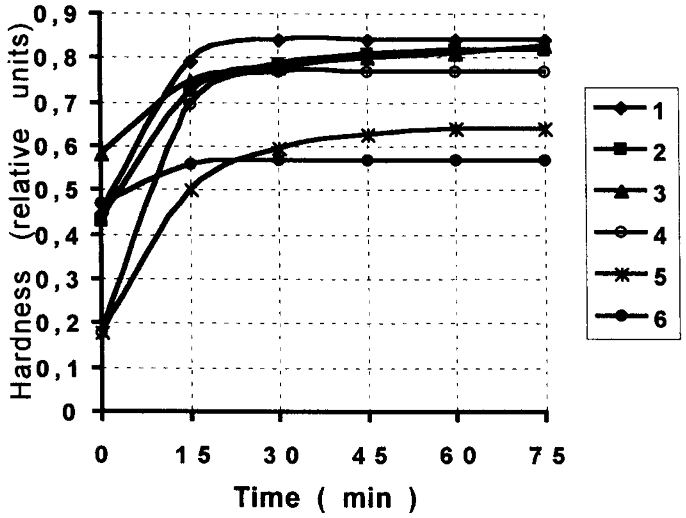


Fig. 6. Dependence of the Buchholz hardness on crosslinking time at 100°C for several compositions: II (1), III (2), I (3), K3 (4), K2 (5) and K1 (6).

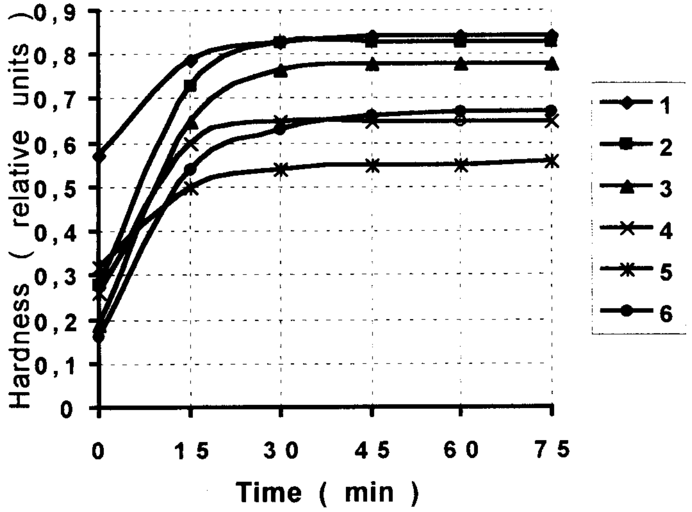


Fig. 7. Dependence of the Buchholz hardness on crosslinking time at 100°C for several compositions: IV (1), VI (2), K6 (3), V (4), K4 (5) and K5 (6).

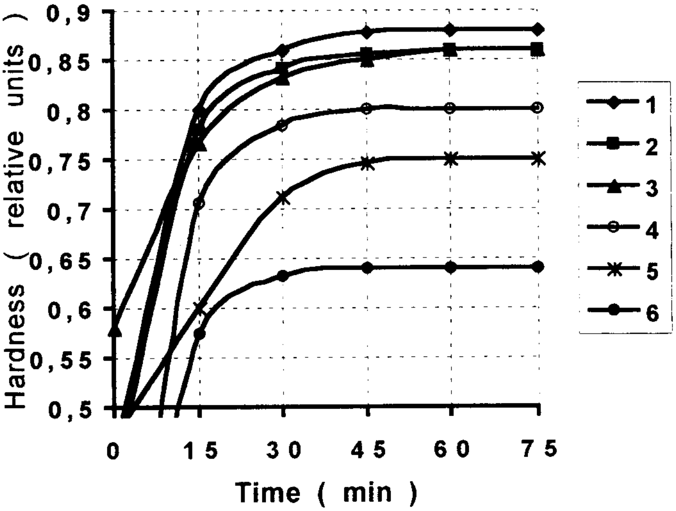


Fig. 8. Dependence of the Buchholz hardness on crosslinking time at 130°C for several compositions: II (1), III (2), I (3), K3 (4), K2 (5) and K1 (6).

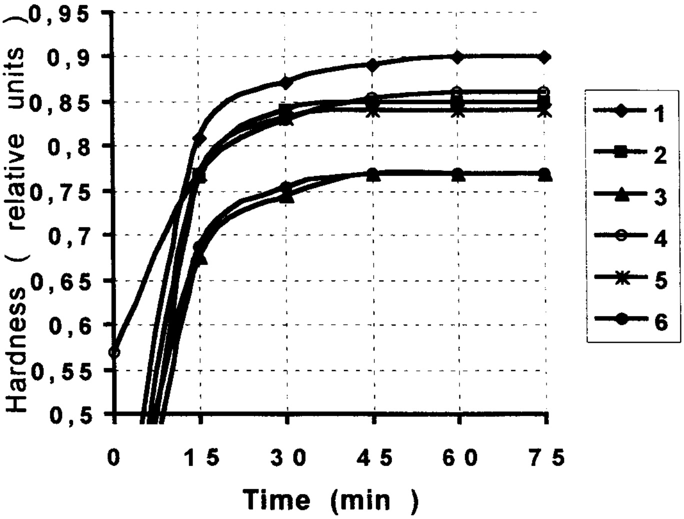


Fig. 9. Dependence of the Buchholz hardness on crosslinking time at 130°C for several compositions: IV (1), VI (2), K6 (3), V (4), K4 (5) and K5 (6).

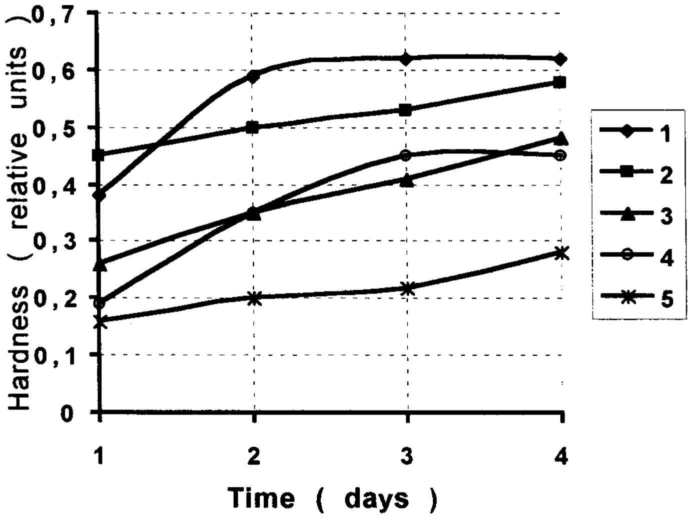


Fig. 10. Dependence of the Buchholz hardness on crosslinking time at 20°C for several compositions: VII (1), IX (2), X (3), VIII (4) and K7 (5).

The first question pertaining to the results of the hardness tests displayed above is: do they show parallel trends to those determined by the extraction ? Figures 6 – 10 are, respectively, analogs of Figures 1 – 5 since they provide results for the same systems. Inspection of the corresponding pairs of Figures shows that the hardness results do parallel the gel fractions determined by the Soxhlett acetone extraction. This is particularly striking when comparing figure pairs 1 with 6, 2 with 7, as well as the room temperature results in Figures 5 and 10. Thus, tentative conclusions on the roles of various constituents of the blends - reached on the basis of the extraction results - are now confirmed by two independent experimental techniques. Moreover, for the purpose of pursuing changes of the gel fraction with time, the pedulum damping hardness test can be used as a substitute for the more cumbersome and time consuming solvent extraction procedure.

Analyzing now the hardness results alone, we find that the blends which contain the peroxy-modified ED-20P resin exhibit higher values of hardness. The same materials also show better adhesion to glass and metal surfaces. As for the systems which do not contain ED-20P, increasing of crosslinking temperature promotes the increase of hardness and of the final gel-fraction.

5. Discussion

Analyzing the solvent extraction and hardness results above, we have noted good properties obtained in the presence of the modified epoxy resin ED-20P. All results show that three-dimensional polymerization of unsaturated oligoesters in the presence of a reactive solvent and crosslinking of the epoxy resins take place both in control blends and in those which contain ED-20P. However, in the cases of control systems (the K series) two separate three-dimensional polymer networks are formed. The first one is epoxy resin ED-20 crosslinked with the use of PEPA. The second is the product of three-dimensional polymerization of the TGM-3 oligoester (or else of the MGF-9 oligoester) in the presence of BA or BMA. Interpenetration seems to be the primary mode, but a certain extent of grafting caused by the peroxide is presumably taking place also. We hope to deal in more detail with this issue in a later paper.

In the Blends I – VI which contain ED-20P, both PEPA and ED-20P act as crosslinking agents, with the dominant role of PEPA. Moreover, at room temperature a partial decomposition of -O-O- bonds of the ED-20P resin takes place - in addition to the crosslinking process. The presence of tertiary nitrogen atoms in PEPA promotes the decomposition. Free radicals formed as a result of that decomposition initiate the process of three-dimentional polymerization of the unsaturated oligoester and the reactive solvent. The radicals associate themselves chemically to the ED-20 and ED-20P resins while those resins undergo crosslinking because of the presence of PEPA. As a result, BMA or BA molecules become chemically attached to the surfaces of the crosslinked epoxy resins.

Comparing the result for systems with and without TEA, we find that the decomposition of -O-O- bonds in the ED-20P resin is accelerated by the presence of TEA.

The introduction of acrylates and methacrylates into the epoxy + oligoesteric systems decreases the viscosity of the starting blends. Thus, thinner films and polymeric components with a better control of dimensions can be made. We conclude that the primary objectives of this work as defined at the end of Section 1 have been acccomplished.

Acknowledgments

Partial financial support for this work has been provided by the State of Texas Advanced Technology Program (Project # 063594-077). The research has been performed under the agreement of cooperation between the University of North Texas (UNT), Denton, and the Lvivska Politechnika State University (GULP). We appreciate detailed discussions with Michael Hess of UNT and of the Gerhard Mercator University, Duisburg, and with Kevin P.

Menard of the Perkin-Elmer Corp. and UNT. An equipment donation by the Perkin-Elmer Corp., Norwalk, Connecticut, is gratefully acknowledged.

References

1. S. L. Rosen, *Fundamental Principles of Polymeric Materials*, Wiley, New York (1993).
2. M. Hess and R. Kosfeld, in *Polymeric Materials Encyclopedia,* vol. 3, edited by J. C. Salamone, CRC Press, Boca Raton, FL (1996)
3. M. Bratychak and W. Brostow, *Polymer Eng. & Sci*. **39**, in press (1999)
4. E.B. Mano, *Polimeros como Materiais de Engenharia*, Editora Edgard Blücher, São Paulo (1991)
5. L. Bazyliak, M. Bratychak and W. Brostow, *Mater. Res. Innovat*. **3**, in press (1999)
6. M. Bratychak, W. Brostow and Y. Yatczyshyn, *Visnyk Lviv. Politech.* **342**, 204 (1998)
7. M. M. Bratychak, Y. G. Medviedievskih and R. V. Kuczer, *Ukr. Him. Zh.* **49**, 879 (1983)