Vinyl Ester and Unsaturated Polyester Resins in Contact with Different Chemicals: Dynamic Mechanical Behavior

A. VALEA, M. L. GONZALEZ, I. MONDRAGON

Departamento Ingeniería Química y del Medio Ambiente, Escuela Universitaria Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1 B, 20011 San Sebastián/Donostia, Spain

Received 13 January 1998; accepted 1 May 1998

ABSTRACT: A prior study has shown for a vinyl ester resin that the adequate choice of the curing conditions becomes completely necessary to reach the maximum glass transition temperature. In the same study, the variations produced in the dynamic mechanical properties because of exposure to different solvents were related to the chemical structure of both the resin and solvent. This investigation was undertaken in an attempt to analyze the effects of solvent exposure on the viscoelastic properties of resins currently used for applications in which the resin is kept in contact with the solvents. Several vinyl ester resins as well as various unsaturated polyester resins immersed in different liquids were investigated. The influence of exposure time to the solvent as well as that for the temperature were characterized using dynamic mechanical analysis. The chemical structure of the resin was found to be determinant in the changes produced after solvent exposure. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 21–28, 1999

Key words: vinyl esters, polyesters, chemical resistance, dynamic mechanical

INTRODUCTION

Thermosetting resins are often used in applications for which an aggresive liquid is in touch with the cured resins. These applications include solvent reservoirs, tanks, and others. The reason for employing these resins relies on their chemical inertness to a great number of solvents.¹ However, choosing of the to-be-used resin has to be made taking into account a series of factors such as full incompatibility to the liquid to be used and storage temperature but also long-term behavior.² The latter factor is not often taken in account, therefore, problems appear during the life in service of the product. On the other hand, for a great percentage of these applications, hand layup molding techniques are used, and very often postcuring is not made at suitable conditioning, so leading to noncompletely crosslinked materials which can be more easily attacked by the liquid put into contact with them.³⁻⁶

Dynamic mechanical properties after solvent exposure were investigated in this study for several vinyl ester and unsaturated polyester resins advisable for the above-referred applications. The used liquids were monochlorobenzene (MCB), sulfuric acid (H_2SO_4), and a test liquid for simulating petroleum (TLSP) that, according to AFNOR, was constituted by 50% toluene, 33% octane, 15% methanol, and 2% isobutanol, in volume. In the case of vinyl esters, the variation of the dynamic mechanical properties upon cure conditions was also analyzed. For sulfuric acid exposure, the influence of solvent soaking was studied for several exposure times and as well for different cure conditions for an urethane vinyl ester resin.

Correspondence to: A. Valea.

Journal of Applied Polymer Science, Vol. 71, 21-28 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/010021-08

EXPERIMENTAL

The resins used in this study as well as some of their physical characteristics are shown in Table I. Viscosity was measured in a Brookfield viscometer at 25°C. Density values were obtained using the Ford vessel normalized method. For the acid index determination, the DIN 53402 standard was used. The styrene weight content was calculated by evacuating the styrene from the resin in an air-circulating oven at 110°C for 2 h.

The amounts of the catalyst, a solution of methyl ethyl ketone peroxide (MEKP), and accelerator, a solution of cobalt octoate, used were the same as those used in a prior study.⁷ For several resins, the accelerator content was varied from 0.20 to 0.50 wt % but no noticeable variations were observed in the dynamic mechanical properties. The mixing procedure and impregnation of a glass fiber mat from Vetrotex as well as the pathway to prepare $20 \times 20 \times 0.25$ -cm plaques were previously described.⁷ Curing temperatures for each resin are stated below.

Exposure to MCB was carried out at room temperature by solvent soaking the resins previously postcured at 180°C for 3 h; with the exception of Derakane 470-36, all samples lost their physical integrity at longer exposure times. For TLSP exposure, specimens were immersed in the liquid at 50°C up to 31 days for the urethane vinyl ester and 10 h for the bisphenol-A epoxy-based vinyl ester. In the case of exposure to sulfuric acid (70 wt % solution), soaking times were 15, 30, and 50 days.

Dynamic mechanical measurements were performed in bending in a Polymer Labs DMTA instrument by using $37 \times 12 \times 2.5$ -mm samples. Tests were run at 1 Hz and a heating rate of 3°C/min. The glass transition temperature, T_g , was taken as that corresponding to the maximum value of the loss factor in the α relaxation region during the scan. The height of the α relaxation, h_{α} , was taken at the T_g . The rubber modulus, E_r , was taken as the value of the elastic modulus at a temperature 30°C higher than the T_g .

RESULTS AND DISCUSSION

A previous study⁷ reported the influence of both cure conditions and type of solvent on the dynamic mechanical behavior of a phenolic–epoxy-

Table I Chi	Table I Characteristics of the Thermosetting Resins Used	ing Resins Used						
Grade	Type	Supplier	Viscosity (mPa s)	Density (g/cm ³)	Acid Index	Styrene Content (%)	$T_{lpha} \left(T_{cure} ight) _{(\circ { m C})}$	h_a
DERAKANE 470-36	Phenolic-novolac epoxy-based vinyl ester	Dow Chemical (distributed by Quimidroga, Barcelona, Spain)	185 ± 5	1.06	8.5 ± 0.5	36	168 (175)	0.40
ATLAC A- 382	Propoxylated bisphenol-A fumarate-based polyester	DSM (Zwolle, The Netherlands)	500 ± 50	1.03	6.5 ± 1	48	138 (180)	0.37
ATLAC A- 580	Urethane-based vinyl ester	DSM	400 ± 50	1.04	$4.5~\pm~0.5$	46	120 (180)	0.70
PALATAL A-430	Bisphenol-A epoxy-based vinyl ester	Basf (Barcelona, Spain)	$450\ \pm\ 20$	1.07	8.0 ± 2	39	124 (180)	0.50
PALATAL A-420	Terephthalic acid + standard glycol)-based polyester	Basf	750 ± 50	1.10	10 ± 2	40	143 (180)	0.32
SYNOLITE 593	(Isophthalic acid + standard glycol)-based polyester	DSM	800 ± 80	1.20	13 ± 2	39	119 (180)	0.34

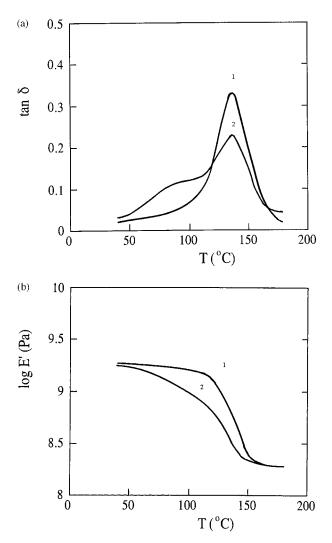


Figure 1 Dynamic mechanical behavior after exposure to MCB for ATLAC A-382: (a) loss factor; (b) storage modulus; (1) original sample; (2) after 6 h in MCB.

based vinyl ester, DERAKANE 470-36, showing the significance of postcuring and that of the chemical structure of the solvent. Dynamic mechanical variations upon temperature for the unsaturated polyester ATLAC A-382, before and after exposure to MCB, are shown in Figure 1(a,b) for the loss factor, tan δ , and the storage modulus, E', respectively. The untreated resin showed only one α relaxation peak that appeared at a temperature, T_{α} , a function of the frequency, of 137°C at 1 Hz. After the resin was exposed to MCB, although the T_{α} was approximately that for the untreated compound, a broad shoulder appeared in the low-temperature region of the α relaxation. Besides, the height of the α relaxation clearly decreased with respect to that for the untreated resin independently of the test frequency. The storage modulus, E', showed a sharp drop in the α relaxation region, thereafter steadying as the resin went into the rubberlike region. For the resin kept in touch with MCB, E' slowly decreased in the zone where the shoulder appeared. Nowadays,^{8–11} it is well known that three types of processes are implied in unsaturated polyester curing: polyester vinylene group polymerization, polyester and styrene C=C bond copolymerization, and styrene homopolymerization. The high styrene content in the initial formulation along with the constancy of the main α relaxation temperature and the lowering of its height after immersion in MCB for 6 h seem to indicate that the shoulder possibly corresponded mainly to solventplasticized polystyrene-containing regions. Nevertheless, the overall crosslink density of the network did not present remarkable variations after solvent exposure as the rubber modulus remained nearly constant, as shown in Figure 1(b). The existence of both α relaxations could also indicate that there was an unswollen matrix in the inside of the specimen while there was swollen matrix on the outside because the specimen was not fully saturated with the solvent after immersion in MCB for 3 h.

On the other hand, as shown in Figure 2(a,b), for the unsaturated polyester SYNOLITE 593, the α peak changes after MCB solvent soaking were less pronounced as the height decrease was lower than for ATLAC A-382, and the shoulder was almost not evident. Again, these variations could correspond mainly to the dissolution of polystyrene (PS), which would be in a lower amount in the cured resin as its initial content was lower than that for the ATLAC 382 resin. Thus, the slight decrease of the T_{α} after MCB exposure could be attributed to PS removal from the cured resin as the T_{α} of pure PS at 1 Hz is around 120–125°C. It is worth noting that for longer exposure times, such as 1 day, the specimens disintegrated because an important amount was dissolved in MCB.

As has been previously shown for a vinyl ester resin containing a lower amount of styrene,⁷ the dynamic mechanical behavior of the resin remained close to that for the original sample, even for an uncompleted cure schedule, after MCB exposure. This fact, along with those above shown, seems to indicate that the viscoelastic observations observed for these materials are related to

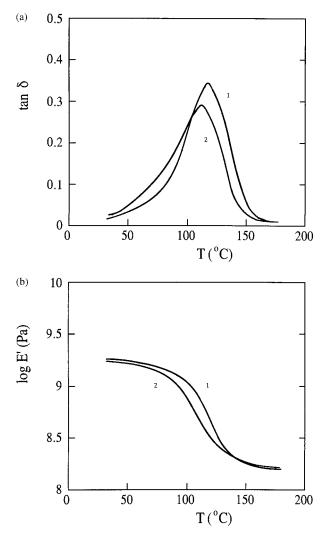


Figure 2 Dynamic mechanical behavior after exposure to MCB for SYNOLITE 593: (a) loss factor; (b) storage modulus; (1) original sample; (2) after 6 h in MCB.

the styrene content in the overall material but they could also correspond to differences in the chemical composition of the resins.

Viscoelastic changes as a function of the cure schedule used have been studied in the case of the bisphenol-A-based vinyl ester PALATAL A-430. Results are shown in Figure 3(a,b) for samples cured at 70°C for 24 h, 130°C for 3 h, and 180°C for 3 h, respectively. Curing at 70°C was clearly not able to completely cure the resin as two α relaxations, one centered at 112°C and the other at 80°C at 1 Hz, appeared. The elastic modulus decreased for each one of these relaxations, thereafter steadying in the rubberlike region at high

temperatures. The lower α relaxation surely corresponded to uncompleted curing because a nonazeotropic polymerization can occur for resins cured at low temperatures with monomers such as styrene.^{8–11} When curing was made at higher temperatures as 130 and 180°C, solely, one α relaxation was evident, so indicating that polymerization was practically completed after curing at 130°C. However, the slight increase in T_{α} after curing at 180°C (from 120°C for 130°C curing to 124°C for 180°C curing) and the decrease on the height of the α relaxation, independently of the accelerator amount used, seems to indicate that some ulterior reactions take place at cure temperatures higher than 130°C. As shown in Figure

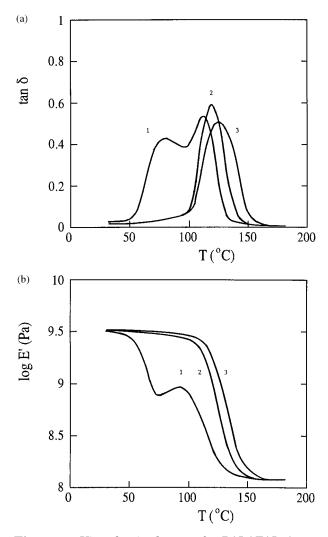


Figure 3 Viscoelastic changes for PALATAL A-430 as a function of cure conditions used: (a) loss factor; (b) storage modulus; (1) 70°C (24 h); (2) 130°C (3 h); (3) 180°C (3 h).

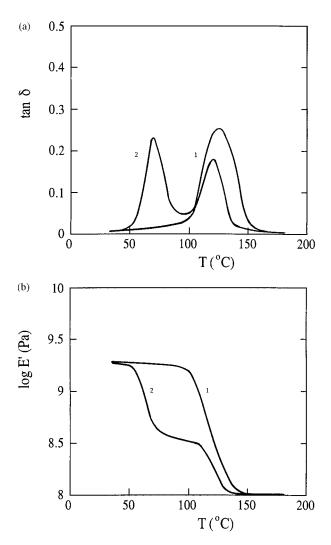


Figure 4 Dynamic mechanical behavior after exposure to TLSP for PALATAL A-430: (a) loss factor; (b) storage modulus; (1) original sample; (2) after TLSP exposure.

3(b), the similarity of the rubber modulus values for all curing conditions indicates that the crosslink densities of the formed networks were very close, although for the sample cured at 70°C, the value of the rubber modulus corresponds to the increase of the crosslink density during the scan, as E' increased after the cure temperature used was overcome, ulteriorly again decreasing.

Furthermore, the PALATAL A-430 resin postcured at 180°C was immersed at 50°C for 10 h in TLSP liquid, and the dynamic mechanical variations were again registered. As shown in Figure 4(a,b) for the resin cured with a 0.50 wt % accelerator, the main α relaxation temperature decreased around 5°C for all frequencies after solvent soaking, and the height of this transition clearly decreased. In addition, a second α relaxation at lower temperatures, centered at 70°C at 1 Hz, was also evident, so indicating that an important amount of the cured resin interacted with TLSP during solvent soaking, in the same way previously seen for another vinyl ester resin, DERAKANE 470-36.⁷ Indeed, on the one hand, the TLSP could slightly plastify the polymer chains more related to polyester molecules, and on the other hand, TLSP would clearly act as a diluent for the styrene-derivated polymeric chains.

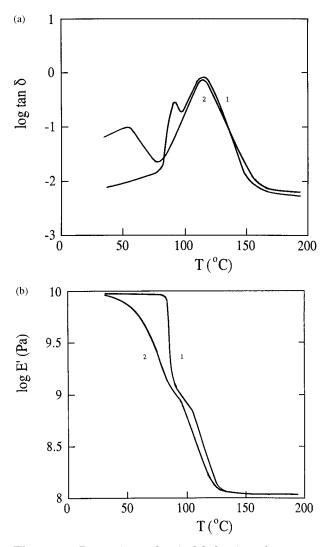


Figure 5 Dynamic mechanical behavior after exposure to sulfuric acid for ATLAC A-580 cured at 85°C: (a) loss factor; (b) storage modulus; (1) original sample; (2) after 30-days exposure.

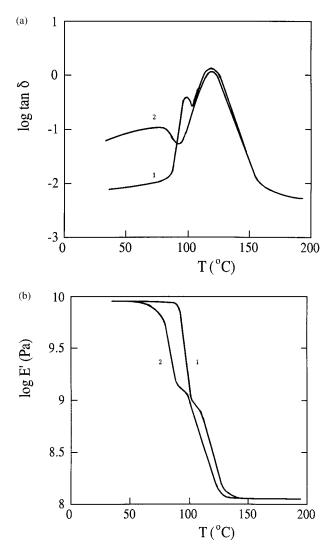


Figure 6 Dynamic mechanical behavior after exposure to sulfuric acid for ATLAC A-580 cured at 130°C: (a) loss factor; (b) storage modulus; (1) original sample; (2) after 30-days exposure.

Finally, some resins cured at different temperatures were subjected to sulfuric acid for different times. Thus, the urethane vinyl ester ATLAC A-580 cured at 85, 130, and 180°C was immersed in sulfuric acid. As Figures 5–7 show, independently of the cure temperature used, the maximum of the α relaxation practically occurred in the same temperature range after exposure to sulfuric acid. For whatever cure condition used, no observable change occurred before 30 days of solvent soaking despite that curing at temperatures higher than 85°C slightly increased the glass transition temperature of the cured material. This behavior seems to indicate the usefulness of this vinyl ester resin for sulfuric acidcontaining containers or pipes, in the same way shown for another vinyl ester resin.⁷ Table II shows the evolution of the temperature maximum values of both peaks as a function of exposure time to sulfuric acid. The existence of a very sharp peak in the region of 90°C, with a tendency to disappear at long soaking times, seems to indicate that for the specimens not cured at 180°C, although some additional curing could occur during the DMTA run, the final network consisted of segments with different structures, possibly because of competitive reactions during curing. Thus, for the specimens not fully cured, some

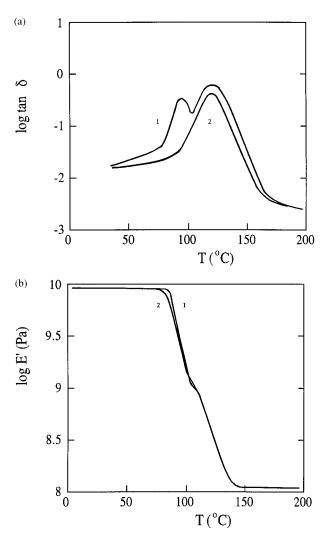


Figure 7 Dynamic mechanical behavior after exposure to sulfuric acid for ATLAC A-580 cured at 180°C: (a) loss factor; (b) storage modulus; (1) original sample; (2) after 30-days exposure.

		t Solvent (days)			
Grade	$T_{\rm cure}~(^{\rm o}{\rm C})$	0	15	30	50
ATLAC A-580	85	116 (97)	115 (98)	116 (92)	113 (54)
	130	121 (95)	122(82)	119 (97)	119 (78)
	180	120 (95)	120 (94)	120 (97)	120 ()
PALATAL A-420	180	143.5	142	142.5	142

Table II T_g's of ATLAC A-580 and PALATAL A-420 Resins After Exposure to Sulfuric Acid

Temperature for the maximum of the lower α relaxation.

partial sulfuric acid degradation of the sample would lead to broad α relaxation at low temperatures.

The dynamic mechanical behavior of PALA-TAL A-420, a terephthalic acid-based unsaturated polyester resin, especially designed for solvent-in-touch applications, was also analyzed after curing at 180°C for 3 h. Although not shown, for the resin not exposed to sulfuric acid, accelerator contents ranging from 0.20 to 0.50 wt % did not influence the viscoelastic properties of the cured resin. In other ways, as reported in Figure 8(a,b) and Table II, solvent soaking of the resin in sulfuric acid for several exposure times did not lead to any significant variations either of the temperature corresponding to the α relaxation or to the height of this transition. These trends clearly indicate the adequacy of that resin to exposure for long times to sulfuric acid, since besides the nearly nil variations on the dynamic mechanical properties upon solvent soaking, neither ping-holing nor swelling defects were observed once sulfuric acid exposure was concluded.

CONCLUSIONS

In this work, the influence of cure conditions and that for the exposure to different chemicals on the dynamic mechanical properties of several vinyl ester and unsaturated polyester resins containing a 10 wt % glass fiber was investigated. Results obtained outline the importance of the choice of an adequate resin and that of the completion of the cure process for each application to be made. The results can be summarized as follows:

For all the vinyl ester and unsaturated polyester resins studied, the amount of the acceler-

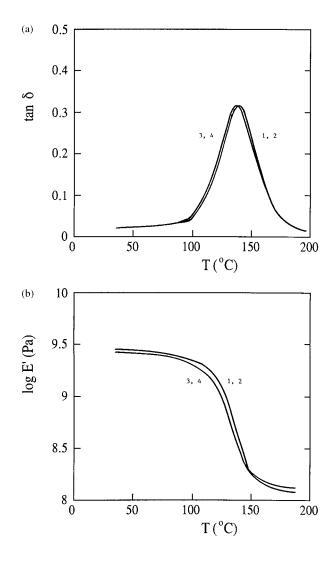


Figure 8 Dynamic mechanical behavior after exposure to sulfuric acid for PALATAL A-420: (a) loss factor; (b) storage modulus; (1) original sample; (2) after 15days exposure; (3) after 30-days exposure; (4) after 50-days exposure.

ator used had practically no influence on the dynamic mechanical response of the used systems. Exposure to aromatic compounds like monochlorobenzene (MCB) modifies the viscoelastic behavior of this class of materials. The variations obtained would be related to both the styrene content and chemical composition of the resin. Contact with liquids such as petroleum was simulated with a test liquid like TLSP. Interactions between the resin and this kind of liquid become evident, and those possibly occur through intermolecular bonding between the nonpolar chains of both the cured resin and solvent. Both especially designed resins for applications, in which sulfuric acid is kept in contact with the resin, showed an excellent resistance to acid exposure because only very small variations were observed for the urethane vinyl ester resin when it was not fully cured, and no changes happened in the case of the terephthalic acid-based unsaturated polyester resin after long-term exposure.

REFERENCES

- Launikitis M. B. in Handbook of Composites Vol. 3, G. Lubin, Ed., Van Nostrand Reinhold, New York, 1982, pp. 38-49.
- 2. Ghorbel I.; Valentin D. Polym. Compos. 1994, 14, 324.
- Verdu J. in Paris Vieillissement des Plastiques, Afnor Techniques, 1984.
- Springer G. S.; Sanders B. A.; Tung R. W. Environmental Effects on Composite Materials Vols. 1 and 2, Technomic, Westport, CT, 1981.
- 5. Mijovic J. Polym. Compos. 1983, 4, 73.
- Benameur T.; Granger R.; Vergnaud J. M. Polym. Test. 1995, 14, 35.
- 7. Valea A.; Martinez I.; Gonzalez M.L.; Eceiza A.; Mondragon I. J. Appl. Polym. Sci. to appear it is the other paper that I am sending you.
- 8. Yang Y. S.; Lee L. J. Polymer 1988, 29, 1793.
- 9. Jacobs P. M.; Jones F. R. Polymer 1992, 33, 1418.
- Huang Y. J.; Chen C. J. J. Appl. Polym. Sci. 1992, 46, 1573.
- 11. de la Caba K.; Guerrero P.; Eceiza A.; Mondragon I. Eur. Polym. J. 1997, 33, 19.