Influence of Cure Schedule and Solvent Exposure on the Dynamic Mechanical Behavior of a Vinyl Ester Resin Containing Glass Fibers

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ABSTRACT: This study deals with the dynamic mechanical properties of a glass-reinforced vinyl ester resin. The viscoelastic parameters of the loss factor and the storage modulus as a function of the cure temperature were used as a criterion to determine the optimum cure conditions to be employed. It is shown that the cure temperature usually used to cure these resins is not enough to reach the maximum glass transition temperature, and, therefore, an additional postcure should be used. The influence of several solvents on the dynamic mechanical behavior of these resins cured following the cure pathway proposed by the supplier was also analyzed. This behavior was compared with the solvent uptake at various exposure times, and the changes observed were related to the crosslink density as well as to the chemical structure of both the resin and the solvent. Finally, the effects of varying the exposure temperature were also investigated for the resin exposed to a liquid which simulates petroleum fluid. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2595–2602, 1998

Key words: vinyl ester resin; cure conditions; chemical resistance; dynamic mechanical behavior

INTRODUCTION

The vinyl ester resin family includes different kinds of materials which have as a common feature a bisphenol-A epoxy group and/or an urethane group in their structure.¹ Differences in the chemical structures lead to variations in the mechanical and thermal properties.¹ As has been shown for other thermoset resins,^{2,3} variations in the cure conditions can lead to cured materials with a wide variation in their ultimate properties, mainly as a consequence of differences in the extent of curing due to a not adequate choice of the cure schedule employed. At present, it is well known for thermoset resins that a postcure temperature higher than the maximum glass transition temperature, $T_{g^{\infty}}$, will result in a complete cure of the system studied. Lee and Lee⁴ showed for vinyl ester resins that the reaction mechanism does not vary with changing the isothermal cure conditions, and, thereby, the choice of a cure temperature higher than the $T_{g^{\infty}}$ should be necessary to obtain completely cured materials. Nevertheless, temperatures lower than the $T_{g^{\infty}}$ are often used in curing these materials. In the present study, the importance of the cure schedule, including changes of cure temperature, in the dynamic mechanical behavior of vinyl ester resins was analyzed.

On the other hand, vinyl ester resins are often used in applications where solvents are in touch with these materials. There is much information

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in the literature survey arising from the influence of water⁵⁻⁸ and other solvents⁹⁻¹¹ in the physical behavior of thermoset resins. Solvent absorption depends greatly on the chemical structures and the morphology as well as on the extent of curing of the exposed materials.⁶ However, despite its technological importance, the influence of using different solvents in the ultimate properties of uncompletely cured thermoset resins, and particularly of vinyl ester resins, is not well known, although the amount of solvent absorbed, and so the use-life behavior, possibly can be different. Therefore, another objective of this investigation was to study the effect of solvents with different chemical structures on the dynamic mechanical behavior of vinyl ester resins not completely cured. Thus, the influence of exposure time to several solvents at different temperatures was also analyzed.

EXPERIMENTAL

A commercial vinyl ester resin, based on methacrylate ester of a phenolic-novolac epoxy resin containing 36 wt % styrene, Derakane 470-36 purchased from the Dow Chemical Co. (Quimidroga, Barcelona, Spain) with an acid index of 8.9, designed for solvent resistance and high-servicetemperature fiber reinforced plastics applications, was used. A 1.5 wt % of a 50 wt % phthalate solution of methyl ethyl ketone peroxide (MEKP), manufactured by Peróxidos Orgánicos (La Zaida, Zarogoza, Spain), and used as an initiator, was dissolved in the commercial resin. A 6 wt % solution of cobalt octoate was used as an accelerator at percentages ranging from 0.2 to 0.6 wt %. All were mixed by mechanical stirring at 20°C for 5 min, and after impregnating a 350-g/m² Vetrotex glass fiber mat (10 wt % of the sample) previously placed in the mold, a vacuum was applied for 30 s.

Plaques were prepared in glass molds by curing them to 70°C for 3 h. Further postcuring was done at several temperatures below that specified. Dynamic mechanical measurements were performed in bending in a Polymer Labs DMTA instrument 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 rubber modulus, E_r , was taken as the value of the elastic modulus at a temperature 30°C higher than the T_g . The samples were immersed in three solvents [70 wt % sulfuric acid at 50°C, monochlorobenzene (MCB) at room temperature, and at room temperature (RT) and 50°C for a test liquid for simulating petroleum (TLSP) that, according to AFNOR, contains in volume 50% toluene, 33% octane, 15% methanol, and 2% isobutanol]. The samples were weighed at several time intervals. For dynamic mechanical measurements, these samples were treated and conditioned according to an ISO 291 standard.

RESULTS AND DISCUSSION

Influence of Cure Conditions

To analyze the ultimate behavior of the thermoset resins, the study of the influence of the cure schedule used, and so the definition of the optimum cure schedule to use, becomes completely necessary, since when the cure temperature employed is lower than the $T_{g^{\infty}}$ of the resin, additional reactions will take place at higher cure temperatures. Besides, the crosslinking density reached for nonadequate cure conditions will stay far away from the maximum and so the thermal and other properties will be lower than those corresponding to the thermoset system cured to the optimum conditions.

Consequently, a series of experiments was conducted at various cure temperatures to determine the optimum cure conditions. These resins are often cured at temperatures lower than 100°C for commercial applications. Therefore, the first experiment was made by curing the mixture at 70°C for 3 h as recommended by the resin supplier. Accelerator concentrations ranging from 0.2 to 0.6 wt % was used. Figure 1 shows the variation of the loss factor, tan δ , and storage modulus, E', respectively, as a function of temperature for several accelerator percentages. Dynamic mechanical spectra were very similar independently of the amount of accelerator used. The α relaxation appeared centered around 150°C, showing a shoulder around 100°C. As has been shown by several authors,^{12,13} in thermoset resins, chemical reactions between reactive groups do practically stop when vitrification occurs due to that, after vitrification takes place, chemical reactions can occur solely by the physical diffusion inside the resin, and so chemical reactions are highly constrained. Therefore, despite some authors having identified the shoulder appearing at the beginning of the α



Figure 1 Variation of loss factor and storage modulus for mixtures cured at 70°C as a function of the accelerator amount used (%): (1) 0.2; (2) 0.3; (3) 0.4; (4) 0.5.

relaxation as a β relaxation,⁷ this shoulder, possibly as a consequence of a nonazeotropic polymerization in the same way shown for unsaturated polyesters in the literature survey,¹⁴ should correspond to the partial cure obtained by curing the mixture only with the 70°C step.¹⁵ Thereafter, during the DMTA run, the increased segmental mobility allows the sample to polymerize further, which shifts the relaxation maximum up to 150°C. The increasing damping in the shoulder of the α relaxation when the accelerator percent was higher is possibly related to the small morphological variations as a consequence of changes on the polymerization rate during curing of the resin. The storage modulus showed significant drops, especially at the α relaxation, as each above-cited relaxation was overcome, furtherly steading in the rubbery state.

As shown in Figure 2, curing at 90°C for 3 h practically did not change either the glass transition temperature or the height of the α relaxation region, although the shoulder at low temperature appeared now at a higher temperature and it was not so pronounced as that obtained for the resin cured at 70°C. Values of several characteristics of the α relaxation are shown in Table I. Similar trends were observed when curing was performed at 120°C for 3 h; in this case, the shoulder practically disappeared. Changes of the storage mod-

ulus upon temperature could be directly related to the variations shown for the loss factor. Indeed, the storage modulus in the rubberlike region appeared to be slightly higher for the resin cured at 120°C, in the same way that the height of the α relaxation was lower, which should correspond to some completion of the chemical reactions, possibly in the less crosslinked regions of the resin.

Further, postcuring was also applied at higher temperatures, 175 and 200°C, for 3 h. As shown in Figure 3, the significant increase of T_g with respect to those obtained for samples cured at lower temperatures clearly indicates the need of postcuring at high temperatures. This increase in T_{σ} should be a consequence of a significant increase of the extent of curing since the height of the α relaxation decreased and the elastic modulus in the rubber region became higher with respect to these values for curing at the lower temperatures used. Disappearance of the shoulder of the α relaxation when high cure temperatures were employed, along with the higher T_g of the main α relaxation and the near-constancy on rubber modulus values, could indicate that for curing at relatively low temperatures the less crosslinked regions could produce a plasticization effect in the overall matrix, so decreasing its glass transition temperature. The similarity of results obtained for 175 and 200°C postcure temperatures seems



Figure 2 Variation of loss factor and storage modulus for samples cured at different temperatures with a 0.2 wt % accelerator: (1) 70°C; (2) 90°C; (3) 120°C.

to indicate that by using the constituents described the 175°C postcure treatment, and even a lower one since the T_g appeared at 168°C, can be enough to obtain the optimum cured matrix.

Effects of Physical Aging

Liquid exposure of crosslinked thermosets may lead to dramatic variations in their thermomechanical and other properties. The amount of absorbed solvent depends greatly on the chemical structure of the resin and solvent as well as on the morphology⁷ and on the crosslink density of the exposed materials.⁶

In this study, the vinyl ester resin subjected to solvent absorption was crosslinked according to the cure conditions provided by the resin supplier, that is, for 3 h at 70°C. As shown above, no complete cure was reached at these conditions, and so the solvent uptake should be higher than for completely cured samples.

To investigate the physical aging due to solvent absorption, weight measurements of the samples and dynamic mechanical tests were carried out before and after exposure to solvent for different times. Variations of the loss factor and storage modulus of the so-cured resin were recorded as a function of the aging time.

Weight variations upon exposure times for the three solvents used are shown in Table II. In the case of MCB, the weight increase possibly corresponds to the filling of voids existing in the analyzed materials and no dissolution of any portion of the cured resin seems to occur. For sulfuric acid, a slightly higher sorption was observed

Table I Characteristics of the α Relaxation for the Several Cure Schedules Used

Parameter	$T_{ m cure}$ (°C)						
	70	90	120	175	200		
hα	0.45	0.43	0.42	0.38	0.37		
T_{g} (°C)	151	153	154	168	168		
$\log E_r$ (Pa)	7.6	7.6	7.7	7.8	7.8		



Figure 3 Dynamic mechanical behavior of postcured samples with a 0.2 wt % accelerator: (1) 70° C; (2) 175° C; (3) 200° C.

which decreased at longer times surely as a consequence of the dissolution of any unreacted molecules in the cured resin. For TLSP, a high increase of sample weight occurred from the beginning of the solvent exposure at 50°C, decreasing at long exposure times. This fact indicates that this solvent clearly interacts with the vinyl ester resin as a consequence of their similar polarity, further solving an important amount of the resin at high-temperature exposure, and so decreasing the sample weight at long exposure times.

On the other hand, Figure 4 shows the variation of the dynamic mechanical behavior of the cured resin after exposure to MCB at room tem-

Table IIWeight Variations in the Vinyl EsterResin as a Function of Exposure Time for theThree Solvents Used

	Δw (%)				
Solvent	7 Days	15 Days	30 Days	60 Days	
Sulfuric acid (70%)					
(50°C)	_	_	1.5	0.07	
MCB (RT)	0.50	_	_	0.70	
TLSP (50°C)	10.2	12.3	5.2	4.9	

perature for different times. No significant changes were apparent in the α relaxation peak although the height of the low-temperature shoulder increased and it moved slightly to higher temperatures independently of the exposure time. This behavior could be related to a low increase of the extent of curing of the less crosslinked regions of the resin or even to dissolution of some low molecular weight chains, as a consequence of the higher mobility of these chains as they were in



Figure 4 Dynamic mechanical behavior of samples after exposure to MCB for different times: (--) non-exposed; $(-\cdot -) 2$ days; (--) 10 days.

Parameter		Solvent							
		MCB (RT)			Sulfuric Acid (50°C)		TLSP (50°C)		
		Time (Days)							
	2	5	10	7	15	30	4 ^a	7	30
hα	0.43	0.42	0.42	0.41	0.40	0.40	0.37	0.25	0.26
$T_g (^{\circ}C) \log E_r (Pa)$	$\begin{array}{c}151\\7.7\end{array}$	$\begin{array}{c}151\\7.7\end{array}$	$\begin{array}{c}151\\7.7\end{array}$	$\begin{array}{c} 150 \\ 7.6 \end{array}$	$92 \\ 7.4$	$79 \\ 7.3$			

Table III Glass Transition Temperatures, Height of the α Relaxation, h_{α} , and Rubber Modulus, E_r , Values as a Function of Exposure Time for the Three Solvents Used

^a Room temperature.

contact with the solvent. However, the constancy of the temperature corresponding to the α relaxation peak as well as the slight increase on the rubber modulus value as exposure time increased (see Table III) seem to indicate that this solvent practically did not affect the microstructure of the resin.

The variations of the dynamic mechanical properties upon exposure time to sulfuric acid at 50°C are recorded in Figure 5. Once again, low exposure times led to a magnitude increase of the low-temperature shoulder of the α relaxation, and, further, this shoulder did practically disappear, the α relaxation showing then a higher broadening in its low-temperature region. Besides, no significant shift in the location of the α transition peak upon exposure time was observed. In addition, a closely constant value of the rubber



Figure 5 Aging effects on the dynamic mechanical spectra after exposure to sulfuric acid at 50°C: (——) nonexposed; (— · —) 15 days; (– –) 30 days.

modulus was recorded through different exposure times. These trends show the adequacy of this kind of resin to sulfuric acid contact. The observed changes seem to indicate that, despite some hydrolysis reaction that may happen,⁷ sulfuric acid would act as a catalytic diluent which would improve the mobility of the less crosslinked regions of the resin, so leading to more crosslink reactions, to a low extent, inside the resin during the acid exposure.

As can be seen in Figure 6, for exposure to TLSP, the viscoelastic behavior after solvent sorption was completely different as a function of the temperature used. Thus, not very important variations were observed after 4 days of exposure at room temperature, but the relaxational behavior completely changed as exposure to the solvent was carried out at 50°C, a temperature closer to the 70°C cure temperature used. Indeed, after 7 days of exposure to TLSP, the main α relaxation disappeared because of the solvent sorption of the uncompletely reacted resin segments inside the sample. In addition, the low-temperature α relaxation decreased to lower temperatures possibly, as shown in Table III, because swelling and plasticization of the partially cured matrix occurred. The lower temperature in the α relaxation observed for longer exposure times should be a consequence of the simultaneous existence of partly and fully swollen regions of the matrix until the sample was completely swollen, surely around 15 days of exposure. After the sample was fully equilibrated in the solvent uptake, a higher resin dissolution could happen, and so the lower weight variation shown in Table II at long exposure times. Moreover, the rubber modulus, calculated from the dimensions after swelling, lowered when



Figure 6 Aging effects on the dynamic mechanical spectra after exposure to the test liquid: (----) nonexposed; (-----) 4 days at room temperature; (-----) 7 days at 50°C; (---) 30 days at 50°C.

the temperature for solvent exposure was increased. This fact is as a consequence of the crosslink density becoming lower because of the network dissolution. Hence, it seems to be clear that for some solvents a combination of temperature and solvent exposure can produce dramatic changes in these materials when they are cured at the conditions used in this study.

CONCLUSIONS

In this study, the dynamic mechanical properties of vinyl ester resins with glass fibers were investigated as a function of the cure schedule used as well as of exposure to different solvents. It has been shown that, despite the supplier recommendations, the need for using a complete cure schedule when working with vinyl ester resins becomes evident. Thus, the choice of an adequate postcure temperature becomes necessary to reach the optimum thermal and other properties of the socured materials. On the other hand, an incomplete cure schedule can lead to important variations when the cured materials have to be in contact with solvents. The chemical nature of the solvent, along with the thermal conditions for solvent exposure, are both important factors to be taken in account when this type of resin has to be in contact with solvents during its use life.

As has been shown for sulfuric acid and for a test liquid simulating petroleum, a combination of temperature and solvent exposure modifies the final properties of vinyl ester resins cured at 70°C. The observed changes are a function of the solvent used. Thus, for sulfuric acid, even an slight increase on cure extent can occur after exposure, while for the test liquid, dissolution of the resin can lead to an evident deterioration of the material upon exposure time.

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