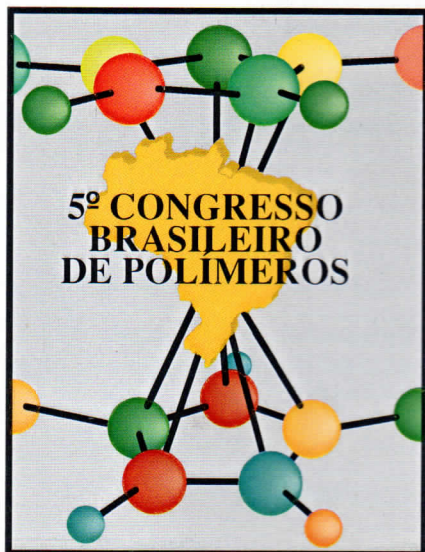


5º CONGRESSO BRASILEIRO DE POLÍMEROS

Águas de Lindóia, 7 a 10 de novembro de 1999



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STRUCTURAL RELAXATIONS DURING THE NETWORK FORMATION FOLLOWED BY ISOTHERMAL BRILLOUIN SCATTERING

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Abstract

The reaction of 1,4-butanediol diglycidyl ether (EP) with cis-1,2-cyclohexanedicarboxylic anhydride (CH) and triethylamine (TEA) has been studied by isothermal Brillouin spectroscopy. The curing process causes a physical state change (liquid-gel-glass solid) that consequently results to strong variation of the complex longitudinal modulus L^* . The real (L') and imaginary (L'') components of the longitudinal modulus were fitted by Cole plot and the evolution of the structural relaxation time (τ) during the reaction was observed.

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KEYWORDS: Structural relaxation, Brillouin spectroscopy, epoxy curing, complex longitudinal modulus.

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INTRODUCTION

From Brillouin Spectroscopy during the curing process it is known that the change of the physical states (liquid-gel-glass solid) properties can be observed at hypersonic frequencies^{1,2}. In this study we used the Brillouin Spectroscopy as a non destructive technique to characterize the curing process of 1,4-Butanediol diglycidyl ether (EP) and Cis-1,2-cyclohexanedicarboxylic anhydride (CH) and Triethylamine (TEA) as initiator.

According to the Brillouin Spectroscopy technique, the light is scattered by thermally activated acoustic waves of the sample. The spectra show a central quasi-elastic (Rayleigh) line and two anelastic (Brillouin) lines equally shifted from the central line. The frequency shift and linewidth of Brillouin lines give the sound velocity (U) and the attenuation (α) of the sample, respectively.

OBJECTIVE

During the curing process, the hypersonic velocity and the attenuation changed considerably. By the transformation of the U and α data into the real and imaginary components of the complex longitudinal modulus ($L^* = L' + iL''$)^{1,3}, it turns possible to estimate the characteristic time of the structural relaxation (τ) by $L^* = L_\infty + (L_\infty - L_0)N^*(\omega\tau)$, where N^* is an appropriate relaxation function¹. From this procedure, the pairs of calculated values of L' e L'' at each step of the curing process of the epoxy resin has been used to calculate the value of $\omega\tau$.

METHODOLOGY

Two kinds of samples were prepared, a stoichiometric one and a sample with an anhydride excess. The molar fraction ratios ($R = X_{CH}/X_{EP}$) are respectively $R=2.20$ and $R=5.00$. The samples with $R=2.20$ were studied at four different temperatures namely 115°C, 120°C, 130°C and 140°C. The samples with $R=5.00$ were measured at three temperatures namely 115°C, 130°C and 140°C.

Brillouin scattering measurements were performed by use of a Sandercock-type (3+3)-pass tandem interferometer. Light from a single mode 514.5nm Ar+ laser, polarized in the scattering plane, was focused onto epoxy samples and the backscattered light was then revealed⁴. The measurements were taken every three minutes and the accumulation time was 1 minute.

RESULTS

The figures 1(a and b) show the evolution of the hypersonic velocity until equilibrium was reached, while figures 1(c and d) show that the curing system attenuations presents a maximum value during the curing process.

The evolution of the structural relaxation times (τ) during the curing process obtained by using Cole plot¹ is demonstrated in figure 2. The τ values, in all samples, start to grow up after approximately 1000s and tend to reach a limited value. For samples relative to the same value of R , we note that the reaction starts at progressively lower times for increasing values of temperature. Moreover, at the end of the reaction, the samples with $R=5.00$ attain relaxation times which are lower than those of the samples at $R=2.20$.

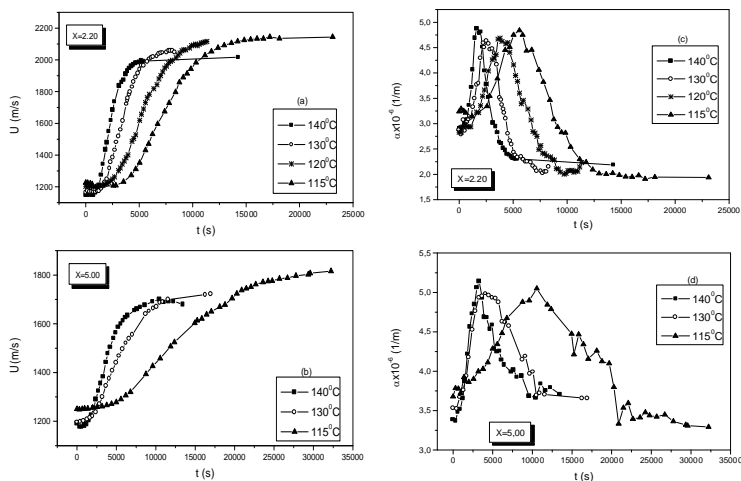


Figure 1 (a), (b), (c), (d): Brillouin spectroscopy data of $R=2.20$ and 5.00 samples.

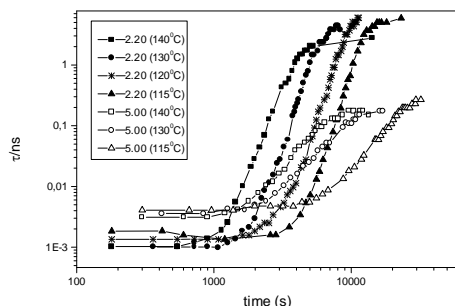


Figure 2: Evolution of the structural relaxation time for the $R=2.20$ and $R=5.00$ samples.

CONCLUSION

The data analysis of the curing of epoxy resins showed an irreversible increase in the structural relaxation time, which can be attributed to the segmental motions in the progress of the reaction.

Epoxy curing systems with different composition, $R=2.20$ (stoichiometric) and $R=5.00$ (CH excess), demonstrate similar structural relaxation time evolution during the curing process. The similarity of the behavior is due to the crosslink process, the quantitative differences being related to the composition of the system.

The Brillouin spectroscopy showed to be an adequate technique to observe the evolution of the structural relaxation time in the curing of the epoxy systems.

REFERENCES

1. I. Alig, K. Naeck, G. P. Johari, J. Polym. Sci.: Part B: Polym. Phys., **32**, 1465 (1994).
2. I. Alig, D. Lelliger, K. Naeck, A. Rizos, G. Fytas, J. Appl. Polym. Sci., **44**, 829 (1992).
3. J. Kieffer, Physica A **261**, 60 (1998).
4. D. Fioretto, L. Palmieri, G. Socino, L. Verdini, Phys. Rev. B, **50(1)**, 605 (1994).

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