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Homogeneous Epoxy-Acrylic Interpenetrating Polymer Networks: Preparation and Thermal Properties

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SUMMARY

The simultaneous interpenetration of two networks, one based on diglycidyl ether of bisphenol A crosslinked by an aliphatic diamine and the other one based on diglycidyl ether of bisphenol A dimethacrylate, leads to systems transparent to visible light. The measurement of glass transition temperature of these IPNs as a function of the composition and of the crosslinks density, gives relatively low and single values. This behavior is interpreted by the homogeneous structure of these systems.

INTRODUCTION

The simultaneous or successive formation of two polymer networks with different chemical structure, leads generally to heterogeneous systems (SPERLING 1977, LIPATOV and SERGEEVA 1976). The tendency to phase separation can be attenuated both by forming simultaneously the two networks (TOUHSAENT et al 1974) and by choicing prepolymers having a good mutual affinity (HUELCK et al 1972). We have studied the interpenetration by polymerization of prepolymers each possessing the bisphenol A group, but having reactive functions that can lead, for the first one, to chain reaction (acrylic function) and for the other one to polycondensation (epoxy function). For such a system, we searched the conditions for simultaneous formation of the two networks and we studied the variation of the glass transition temperature as a function of the system composition and of the density of the

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networks. Indeed, this property is strongly dependent on the nature (homogeneous or heterogeneous) of the system formed.

EXPERIMENTAL

1 - Synthesis and purification of monomers :

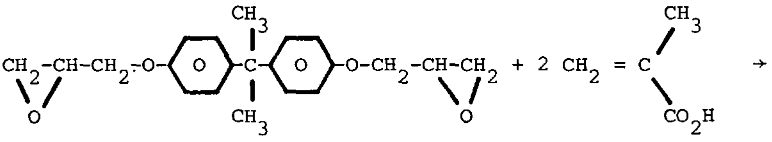
In order to allow a good knowledge of the structure of the systems studied, we proceeded to a thorough purification of all the monomers used, followed by a checking of the purity.

The diepoxy monomer, diglycidyl ether of bisphenol A (DGEBA), was obtained from the resin Araldite GY 250 (CIBA) by preparative HPLC (apparatus chromatospac 100. Jobin-Yvon). The eluent used was a mixture toluene/ethyl acetate (90/10). The purity of the DGEBA was checked by ^{1}H NMR and by titration of epoxy groups ($\bar{f}$ = average functionality = 1.98).

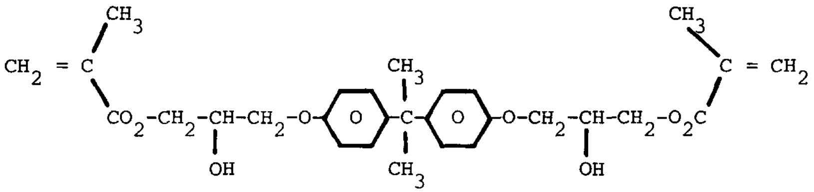
The phenyl glycidyl ether (PGE) (Shell) was purified by distillation under reduced pressure (Teb = 118°C/8 mm Hg). The purity of this monomer was checked like for that of DGEBA.

Epoxy monomers were crosslinked by using 4,9-dioxa dodecane 1,12-diamine (BASF) purified by distillation under reduced pressure (Teb = 167°C/10 mm Hg) and the purity checked by ^{1}H NMR.

Methacrylic derivatives were synthetised by reacting methacrylic acid with epoxy monomers (DGEBA and PGE). For example, with DGEBA :



DGEBA



DGEBAMA

The experimental conditions for the synthesis were previously described (ADES and FONTANILLE 1979). Methacrylic derivatives were purified by using preparative HPLC (eluent : hexane/ethyl acetate 60/40). The purity of PGEMA was checked by VPC and mass spectrometry. For DGEBAMA we used ^{1}H NMR and mass spectrometry.

The purity of all monomers used was higher than 98 percent.

2 - Preparation of networks :

Preliminary experiments revealed the existence of a gradient of concentration for the two networks interpenetrated in certain conditions of preparation. We searched the necessary conditions in order to be allowed to neglect this gradient of concentration and we found the following process : DGEBA, PGE, DGEBAMA, PGEMA were mixed at room temperature with N,N-dimethyl p-toluidine, benzoyl peroxide and the diamine. After homogeneization by pouring, the mixture was degassed under vacuum for two hours, in order to remove the oxygen dissolved. (Oxygen inhibates the radical polymerization of acrylic monomers). After that, the mixture was keeped at 100°C for 1 hour.

To check the lack of a gradient of concentration in the systems studied, we determined the concentration of each network at different level of the samples. For that, we prepared, with convenient conditions, the IPN in a tube and we titrated by I.R. spectrophotometric analysis, thin sheets cut off from the so formed cylinder. This method of titration is very sensitive and allows us to reveal gradients of concentration of about 2 percent. The frequency used for titrate is that of the c = o stretching vibration at 1720 cm^{-1}.

3 - Glass transition temperature measurements :

Tg were determined by DTA with a Du Pont 990 analyser. The rate of heating was 5°C per minute.

RESULTS AND DISCUSSION

All IPNs prepared from monomers above cited are transparent to visible light. This property is not a sufficient proof for a monophasic structure.

It is the reason why we have carried out the measurement of Tg. Indeed, when a single Tg is observed for polyblends at a value different from those of the pure components, the homogeneity of the system is very probable (FRISCH et al 1975).

In a first stage, we studied the interpenetration of 2 networks formed :

- the first one from DGEBA crosslinked by dioxa-4,9 dodecanediamine-1,12
- the other one from DGEBA dimethacrylate.

The networks so obtained have a strong density of crosslinks and one can preview that a part of reactive functions (oxiranne and acrylic double-bonds) are not able to react, due to steric hindrance. The measurement of the equilibrium swelling ratio and of the tensile strength (ADES 1978) suggests that several percent of pending chains, resulting from the partial transformation of reactive functions, are present.

On such systems we have carried out measurements of Tg against the composition of the IPN. The corresponding results are represented in the figure 1.

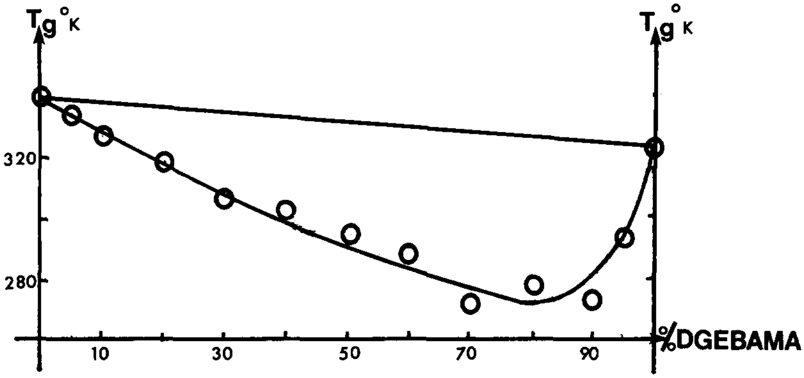


Fig. 1 : Variation of Tg vs composition, for IPN prepared from DGEBA and DGEBAMA.

As shown by Fig. 1, whatever the composition of the IPN, one observes a single value of Tg, lower than the weighted average of Tg of the component networks. This result is very consistent with the homogeneity of the system.

In order to lower the crosslink density of the networks and to allow, as a consequence, the complete transformation of reactive functions (oxiranne or acrylic), we diluted the two main prepolymers by adding two monomers each bearing only one reactive function per molecule. These two monomers present a structure which can be considered as a model of the two main prepolymers :

- the phenyl glycidyl ether (model molecule of DGEBA)
- the phenyl glycidyl ether methacrylate (model molecule of DGEBAMA)

We first studied the variation of Tg with the crosslink density for each network. The curves drawn on figure 2 show that Tg varies only slightly for the acrylic system up to 50 percent of monofunctionnal monomer. The epoxy system behaves differently. Indeed, for the latter, we note a continuons decrease with increasing the

PGE ratio.

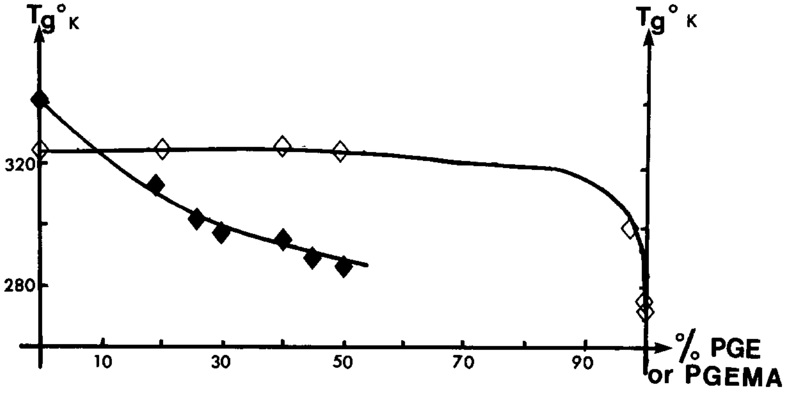


Fig. 2 : Influence of the functionality of prepolymers on Tg of single networks
◆ epoxy network
◇ acrylic network

We have carried out preliminary experiments, in order to determine the optimal composition leading to networks with a well-defined structure : then we choosed to study the systems resulting from the polymerization of 20 percent of monofunctionnal monomer and 80 percent of bifunctionnal monomer ($\bar{f}_{\text{acrylic}}$ = 3.30 and $\bar{f}_{\text{epoxy}}$ = 2.30).

Figure 3 reports the values of Tg for these systems as a function of the composition. As for highly crosslinked networks, we observe again for each composition a single value for Tg. This value was also found to be lower than the weighted average of Tg of the pure corresponding interpenetrating networks.

Such a behavior can be explained only by the miscibility of the two networks. This unusual phenomenon necessitates a relatively high cohesive energy density. This energy must be brougth by the bisphenol A group which is strongly cohesive, and also by the

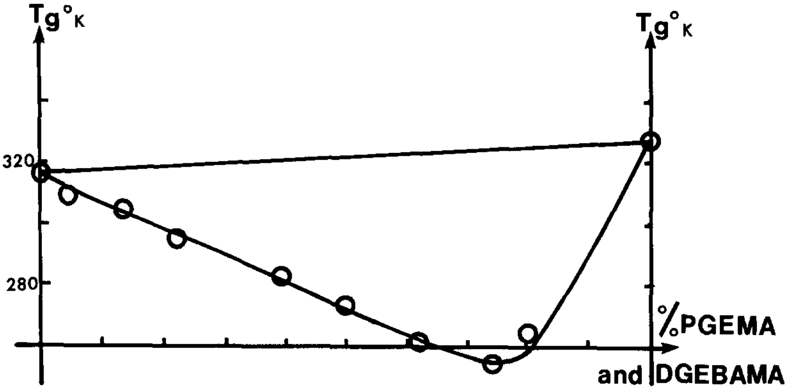


Fig. 3 : Variation of Tg with the composition of epoxy/acrylic IPNs.

existence of hydrogen bonds between the two networks.
The study of the mechanical properties of such systems are in progress.

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