EPOXY POLYMERS: EFFECT OF THE ELASTOMER IN THE KINETICS OF POLYMERIZATION

E. PEZZATI[1], P. BALDINI[2] and A. SCHIRALDI[3]

[1] C.S.T.E.- CNR, Viale Taramelli 16, 27100 PAVIA (Italy)
[2] Dipartimento di Chimica Fisica, Università di Pavia
[3] DISTAM - Chimica Fisica, Università di Milano, Via Celoria 2,
20133 MILANO (Italy)

SUMMARY

The polymerization kinetics of three epoxy adhesives HX-205, HX-206 and F-185 was defined by means of thermal analysis techniques (DSC and TMA).

It was found that the liquid carboxy-terminated butadiene acrylonitriles (CTBN) and the solid rubber elastomer present in HX-206 and F-185 do not affect the phenomenological kinetics of the isothermal cure process by comparison with HX-205, which contains the same epoxy but no elastomer.

It was also found that the isothermal (373 K) cure of these adhesives follows a two-range behaviour, i.e., the phenomelogical order of the cure kinetics is close to zero before and close to one after a "critical" time of cure.

The trend of the glass transition temperature T_g vs the cure degree α for HX-206 and F-185 was always below that for HX-205.

T_g did not approach the temperature of cure T_c for $\alpha = 1$ for elastomer-added adhesives, whereas HX-205 displayed an almost liear trend, with e.g. $T_g = 87°$ C for $\alpha = 85\%$.

INTRODUCTION

Elastomeric modifiers are commonly added to epoxy adhesives to enhance their toughness.

Liquid carboxy-terminated butadiene acrylonitriles (CTBN) are one group that have recently been the subject of closer attention (refs. 1, 2).

Before gelation, CTBN copolymerizes with the epoxy component to form particles (diameter of few microns) that are dispersed throughout the epoxy matrix.

The mechanical properties of epoxy adhesives can be further improved by adding both liquid CTBN and solid rubber chemically coated with an epoxy layer (1) so to obtain two kinds of segregated particles.

This paper investigates the effect of elastomeric modifiers on the cure kinetics.

Three adhesives, HX-205, F-185 and HX-206, with the same epoxy component, but different amounts of liquid CTBN and rubber or none (HX-205), were examined by means of two thermal analysis techniques (DSC and TMA).

EXPERIMENTAL

The content of the epoxy resin was (in weight %) 73% Diglycidyl ether of

Bisphenol A (DGEBA), 20% Bisphenol A, and 7% Dicyandiamide (DICY) (ref.2).

Table i reports the weight % composition of the three adhesives according to ref. 2 .

TABLE 1

component	HX-205	F-185	HX-206
Epoxy resin	100	86.5	91.9
Liquid CTBN	0	8.1	8.1
Solid Rubber	0	5.4	0

30 mg samples were precured at 373 K for different periods to attain different cure degree, α , values.

The samples were then DSC checked at 10°/min heating rate to evaluate the heat delivered in exhausting polymerization.

Other precured samples were checked with TMA to detect their glass transition temperature, T_g. Typical T_g signals, however, were also observed in some DSC traces: as a rule, T_g(TMA) and T_g(DSC) values from samples with the same α were in close agreement with each other.

To investigate the effect of aging, the experiment was repeated after one-year storage at 273 K in a common refrigerator with no special measure to avoid the moisture other than a simple polyvinyl lid.

RESULTS AND DISCUSSION

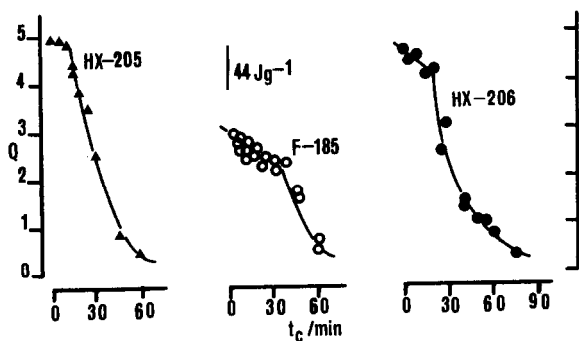The Q values were plotted vs the cure time t_c (see Fig. 1) (for procedure, see ref. 3).

Fig. 1. Heat delivered in the DSC scan vs the time of isothermal (373 K) pre-cure for the three adhesives investigated.

The (Q, t_c) data showed an apparent two-range behaviour, viz., before and after an intermediate t_c value: 10 - 15 min, 15 - 20 min, and 30 - 35 min for HX-205, HX-206 and F-185, respectively.

The experimental trend beyond the intermediate t_c can be described with a phenomenological first-order kinetics.

When the Q data are scaled with respect to the pure epoxy content, they can be satisfactorily fitted with the same expression for all the adhesives (see Fig. 2), viz.,

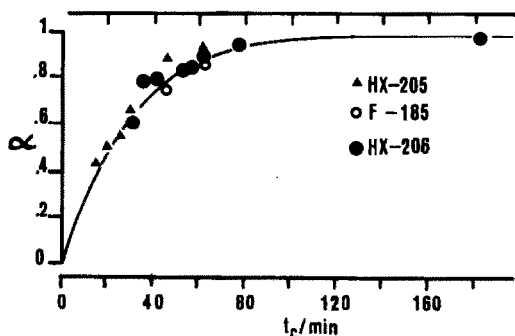$$\alpha = 1 - \exp(35 \ 10^{-2} \ t_c/min) \tag{1}$$

Fig. 2. Cure degree vs the time of the isothermal cure: data refer to the pure epoxy content of the three adhesives investigated.

In this t_c range, therefore, the cure process seems to involve only the epoxy component. The elastomer has no significant effect on either the kinetic constant or the reaction order.

The trend for shorter t_c's, however, cannot be solely attributed to the presence of the modifiers, since one can observe a non-exponential decrease of Q also for the pure epoxy adhesive.

It is indeed well known (ref. 4) that a number of phenomena take place in the first part of the isothermal cure: e.g., segregation of the elastomeric particles, cross-linking between the epoxy coating of the rubber and the epoxy matrix, formation of oligomeric molecules, and, eventually, the beginning of the gelation process, viz., the extension of the cross-links throughout the low-viscosity liquid-like system.

The experimental evidence suggests that these processes would actually follow

distinct kinetic pathways with respect to the subsequent reticulation of the epoxy matrix, and that the overall progress of the system occurs with a nearly zero-order kinetics.

What is actually observed in this work is the heat delivered by the system after a given t_c at 373 K, which corresponds to the area underlying the exothermic peak in the non-isothermal DSC trace.

After a short t_c, the area of the peak decreases (see Fig. 1), suggesting that some epoxy groups also react in the preliminary steps preceding gelation.

No significant thermal effect, however, seems attributable to segregation of the rubber and to rubber-epoxy interaction.

These early cure events nonetheless impose some constraints on the subsequent steps (ref. 4), viz., when only epoxy and dicyandiamide reacting groups are involved.

The time required to start gelation is indeed very crucial. It decreases with the increase of T (ref. 4): its importance is mainly technical, since it is correlated with the time available for casting a thin film of the adhesive between the bodies to be joined together.

Samples stored for one year clearly show analogous behaviour after a short t_c, although with a significant downward shift: Fig. 3 reproduces the case of HX-206.
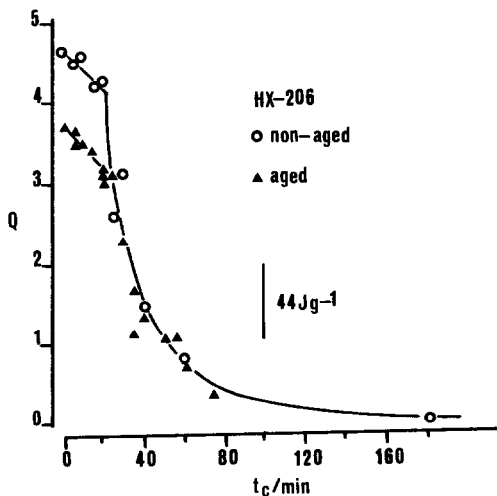

Fig. 3. Heat delivered in DSC scan vs the time of the isothermal precure for aged (one year at 273 K) and non-aged HX-206 samples.

Their behaviour after a longer t_c, on the other hand, is superposable on that of the non-aged samples.

This suggests that ageing only affects the earliest steps of the cure process and does not significantly modify the kinetics of the final reticulation.

HX-206 was investigated in greater detail, because larger amounts were available.

The T_g(TMA) and T_g(DSC) values detected on samples with long t_c can be correlated with the cure degree α computed according to eq. (1).

$$T_g = T_g(\alpha, t_c) = 2 + 3.0 \ 10^{-3} \ \alpha^2 + 4.6 \ 10^{-5} \ \alpha^3 \qquad (2)$$

For the short-t_c range (t_c = 20 min), T_g(TMA) data were found to obey this fitting law when they are matched with the α values computed according to eq.(1)

This means that, in the early steps of the process, the actual α drawn from Q data (which remains below 0.2) does not adequately represent the progress of the cure.

Phenomena which do not involve significant heat delivery are indeed responsible of significant T_g changes.

The correlation found between these T_g values at low t_c and the corresponding fictitious α computed according to eq. (1) could be only fortuitous; it however allows a direct comparison with the elastomer-free adhesive.
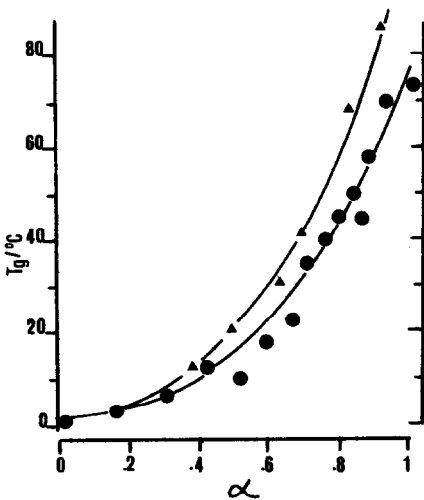

Fig. 4. Glass transition temperature T_g vs cure degree α for HX-206 (full circles) and HX-205 (triangles).

The T_g vs α trend of HX-206 (Fig. 4) systematically remains below that observed for the pure epoxy adhesive HX-205 and does not approach the temperature of cure for $\alpha = 1$.

This again suggests that the earliest steps of the cure process condition the structure and the mechanical properties of the final polymer, this being the product of a reaction forced to progress in a peculiar way as a consequence of the phenomena occurring before reticulation.

Reactions between epoxy and primary amine groups, which account for the lengthening of the polymer chains before reticulation, are faster than those between epoxy and secondary amine groups, which are responsible of the cross-linking.

The former will therefore occur in the earliest steps of the cure. Any pro - cess which may enhance or inhibit the lengthening of the polymer chains will affect the subsequent reticulation: the shorter the chains, the easier the cross-linking and the harder the final polymer (ref. 3).

Further information about these systems can be gained from the Time-Temperature-Transformation (TTT) diagrams usually obtained from thermomechanical analysis.

Another work will seek to define the TTT diagram of one of these adhesives by means of isothermal and non-isothermal DSC investigations (ref. 5).

CONCLUSIONS

The phenomenological interpretations reported above are quite crude, but reasonably simple. They suffice to support the main conclusions of this work: (i) the elastomeric modifier only affects the cure kinetics of the epoxy matrix in the first stages of the process; (ii) this action, however, conditions the subsequent reticulation, so that the properties of the final polymer depend on the presence of the elastomer; (iii) precoated rubber and liquid CTBN play similar roles and, presumably, do not significantly interact with each other.

REFERENCES

1 T.T. Wang and H.M. Zupko, J.Appl.Polym.Sci., 26 (1981) 2391-2401

2 W.D. Bascom, R.Y. Ting, R.J. Moulton, C.K. Riew and A.R. Siebert,
  J.Mat.Sci., 16 (1981) 2657-2664
3 A. Schiraldi, Termochim. Acta, 96 (1985) 283-297, with other references to the
  same author
4 X. Peng and J.K. Gilham, J. Appl. Polym. Sci., 30 (1985) 4685-4696
5 A. Schiraldi, E. Pezzati and P. Baldini, Thermochim. Acta, in press