Polymer Bulletin 12, 399-405 (1984)

Polymer Bulletin

Mechanical Characterization of Structural Evolution in Modified Unsaturated Polyester Resins

G. Coulon, J. M. Lefebvre, and B. Escaig

Laboratoire de Structure et Propriétés de l'Etat Solide C.N.R.S. (LA 234)
Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex - France

SUMMARY

The aim of this paper is to report on structural characterization of unsaturated polyester resins modified by grafting elastomer. D.S.C. tests, dynamic mechanical tests and work-hardening rate measurements have been performed. The latter can be regarded as a very sensitive micro mechanical probe of thermoset structure : the work-hardening rate K exhibits appreciable variations with the elastomer wt %.

INTRODUCTION

Structural characterization of highly cross-linked thermoset resins is a problem of great importance in view of their use as matrix of various composite materials. It has been recognized for long that matrix properties may strongly influence the behaviour of manufacturated composite elements.

In particular several attempts are made to achieve chemical modification of the thermoset networks which are aimed at improving elastic properties, fracture toughness and, or better impact strength. A typical illustration is given by the grafting of elastomers on unsaturated polyester networks. These resins are commonly used as matrix of short glass fiber composites and the addition of elastomer leads to better mechanical properties of the finished products, more especially better impact strength.

It is the purpose of this paper to report on some structural characterization of such modified unsaturated polyester resins including differential scanning calorimetry (D.S.C.), dynamic mechanical test and work-hardening rate measurement, a new method to characterize the non-elastic behaviour of polymeric materials we have developed recently. The latter was first applied to study the physical ageing of atactic PMMA (1) and further proved to be a very sensitive tool to follow the evolution of cross-linking with the curing-time as illustrated in the case of polyimide resins (2) for which usual methods like swelling or I.R. spectroscopy were quite inefficient. We shall see in this paper how much the work-hardening rate is influenced by the elastomer content in a grafted unsaturated polyester resin. This method consists in measuring the non-elastic work-hardening rate K defined as (3) : $K = \left(\frac{\partial\sigma}{\partial\varepsilon_p}\right)_{\varepsilon_t,T}$ where σ is the flow stress corresponding to the total strain $\varepsilon_t = \varepsilon_h + \varepsilon_p$; ε_h is the Hookean elastic part of the strain and ε_p the non elastic one.

K expresses the resistance of the material to non-elastic strain ; it is quite sensitive to local microstructure changes since it can be easily shown (3) that it is the inverse of the net number of defects produced by unit stress. A purely elastic behaviour means K infinite while at yield K equals zero. Fhurthermore, K is quite easily accessible to experiment in a much reliable way (4).

MATERIAL

1) The unsaturated polyester

The unsaturated polyester is of isophtalic type, it was synthesized by standard techniques from 1,2 propylene glycol, isophtalic acid and maleic anhydride. The acid value was about 19 and about 80 % of the maleic groups had isomerized to the trans form.

2) The modified unsaturated polyester by grafting elastomers

Chlorinated elastomer particles with number average molecular weight 1700 were introduced during the polyesterification by simply mixing. Three different concentrations of particles have been chosen : 3 %, 5 % and 8 % weight.

3) The resins

At this stage, 36 wt. % styrene was added to both the unmodified and modified polyester solutions. The resins were polymerized in sheet-shaped moulds by the following curing procedure : gelled at room temperature for 24 hr, then cured at 80°C for 2 hr followed by a postcure at 120°C for 1 hr. The shrinkage in volume was about 8 %.

PRELIMINARY INVESTIGATIONS

In order to characterize the network structure and the different phases of the final thermoset state, conventionnal physicochemical tests have been performed on the polyester resins grafted with 0 %, 3 %, 5 % and 8 % wt elastomer.

1) Differential Scanning Calorimetry

Thermal analysis was carried out on a Perkin-Elmer DSC-2 differential calorimeter. The instrument was used at 80°C/min at sensitivity 10 mcal/s. The analysis was made with a steady flow of nitrogen and the Perkin-Elmer DSC 2 was calibrated with Indium both in temperature and energy. The mass of the samples extracted from the resin sheets was in the range of 20-30 mg.

The results obtained for both unmodified and modified polyester resins don't exhibit significant differences :

. in each case, there exist a slight variation of specific heat C_p in about the same temperature region $120°C < T < 180°C$. By analogy with glassy polymers it can be regarded as the "glass transition" of the whole network formed by styrene and unsaturated polyester (5,6).

. no secondary peak, characteristic of the elastomer glass-transition ($T_g \simeq -25°C$), was observed in the modified resins.

2) Dynamic mechanical tests

A Metravib viscoelasticimeter was used to measure the variations of the dynamic modulus E', the loss modulus E" and the loss tangent tan δ of each resin with temperature (from - 100°C to + 200°C) at different frequencies from 7.8 Hz to 1 KHz. It is a non resonance forced vibration instrument (7).

Parallelipipedic samples (3 x 3 x 40 mm), extracted from the four types of polyester resins were subjected to a sinusoidal tensile strain of constant amplitude (2 µm). The phase angle δ between strain and stress in the sample and the complex dynamic stiffness were measured by direct-reading.

The variations of dynamic modulus E' and of tan δ with temperature for unmodified, 5 % and 8 % modified polyester resins are given at 7.8 Hz in figures 1, 2, 3.

No appreciable differences are seen for unmodified or modified resins. In each case, the skewed nature of tan δ curves suggests the existence of two relaxations characteristic of the unmodified unsaturated resin. The major or α relaxation occurs in the temperature range 150°C-130°C, while the shoulder in the curve around 70°C indicates the presence of secondary or β relaxation. At such a styrene concentration of 36 wt %, these results are consistent with the observations of Cook and al. (8). Their study concluded to the assignment of α relaxation to the glass transition of the whole network, while β relaxation was associated with the motion of polyester segments between cross-link points.

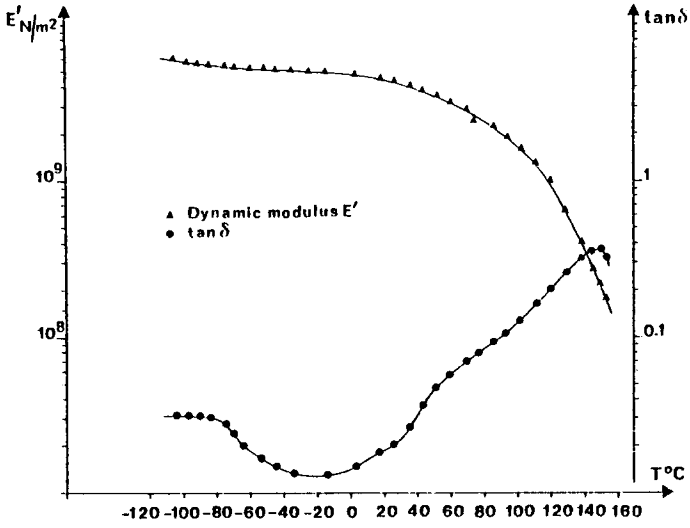

Figure 1 : Temperature dependencies of E' and tan δ for unmodidified unsaturated polyester resin (ν = 7,8 Hz).

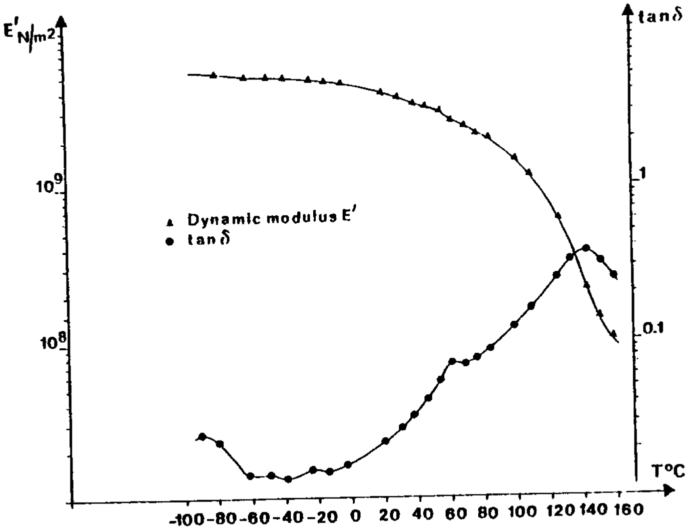

Figure 2 : Temperature dependencies of E' and tan δ for elastomer 5 wt. % modified unsaturated polyester resin (ν = 7,8 Hz).

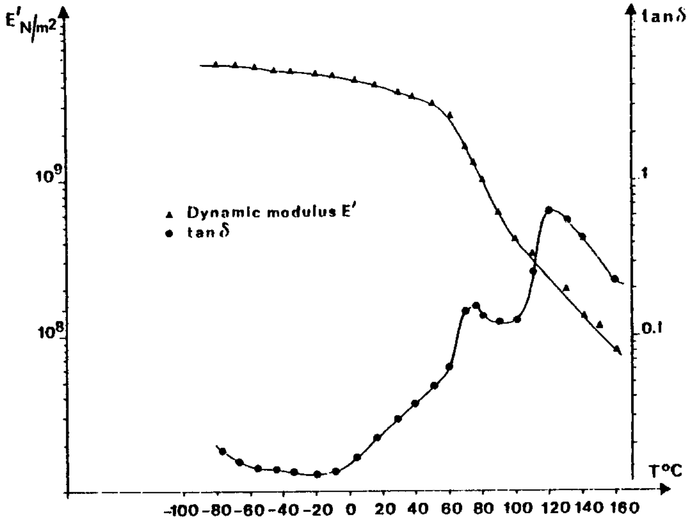

Figure 3 : Temperature dependencies of E' and tan δ for elastomer 8 wt. % modified unsaturated polyester resin (ν = 7,8 Hz).

Only in the case of the 8 % modified resin, the grafting of elastomer seems to have some influence on dynamic properties. There is a shift of the α transition to lower temperatures, from 150°C to 130°C and the β peak appears to be more pronounced. This would suggest that elastomer grafts facilitate the relaxation of polyester segments and make local movements easier in the resin. As already discussed in the litterature (9, 10) this increase in the β damping may be correlated to the improved impact strength observed in the elaborated compound (modified polyester resin + glass fibers). Although dynamic tests reveal that in the elastomer 8 wt. % resin the network appears to be more flexible, the tests were not accurate enough to follow quantitatively this evolution versus the elastomer wt. %.

So, it appeared worthwile to investigate the variations of static mechanical properties with elastomer wt. % by measuring the work-hardening rate K in the pre-yield stage. As we mentioned it above, K is very sensitive to any slight change in microstructure, since its value gives an insight into the nucleation rate of defects in the chain arrangement. More specifically, it should be able to detect presumable changes in the jump frequencies of polyester chains (1, 2).

K MEASUREMENTS

Method

The method has been already explained in detail in previous papers (1, 2), so we mention here only the main features.

During compression tests at constant strain rate $\dot{\varepsilon}_t$ and constant temperature K is measured by stress relaxation from some stress value σ_o. In the experiments, K is a function of both the non-elastic strain ε_p and the elastomer wt. % ; so, in order to investigate the only influence of elastomer wt. %, all the K measurements have to be performed at the same value of ε_p. As we noticed in previous papers, the method is optimized for an ε_p value which corresponds to a stress σ_o somewhere between the yield stress σ_y and $\sigma_y/2$.

For each type of resin, the evaluation of K needs two samples be tested at the same ε_p : a single relaxation test which leads to the value of experimental activation volume V_{exp} and a 8 to 10 successive relaxations test which yields the quantity $\frac{V_o K}{M}$ where M is the Young modulus and V_o the apparent activation volume (1, 2).

By measuring M at the beginning of stress-strain curve and by using the relation $V_{exp} = V_o + \frac{V_o K}{M}$ the value ok K can be determined (1, 2).

In the following table results are given for compression tests performed with an INSTRON machine at constant strain rate $\dot{\varepsilon}_t = 10^{-4} s^{-1}$ and constant temperature 293 K. The compression samples were parallelipipedic (8 x 3 x 3 mm). All the relaxation tests were made at $\varepsilon_p = 2{,}5.10^{-3}$, i.e. at a stress $\sigma_o \simeq \frac{3}{4}\ \sigma_y$.

Table 1 : Variation of K with the elastomer wt. %

	$\sigma_{o\,MPa}$	M_{MPa}	K/M	K_{MPa}	$\sigma_{y\,MPa}$
Pure Polyester resin	82	3400 ±100	0,58 ±0,05	1970 ±197	112
Polyester resin + 3 % elastomer	77	3300 ±100	0,50 ±0,05	1650 ±165	107
Polyester resin + 5 % elastomer	76	3300 ±100	0,40 ±0,04	1320 ±132	105
Polyester resin + 8 % elastomer	75	3100 ±100	0,30 ±0,03	930 ± 93	99

DISCUSSION

It can be seen that, whereas usual macroscopic mechanical quantities such as the Young modulus M or the yield stress σ_y don't vary noticeably (within about 10 %), K values exhibit appreciable variations due to the sole effect of the elastomer wt. %. K decreases by more than a factor 2 for an elastomer wt. % increasing from 0 to 8 with a uniform evolution for intermediate contents. So, K proves to be a quite sensitive probe for investigating microstructural evolutions due to the grafting of elastomer.

From the point of view of mechanical behaviour K varies as the inverse of the defect nucleation rate ; so, it appears that the resistance to plastic strain of the modified polyester resins is lower than the resistance of the unmodified one. This result reinforces the information given by dynamic tests in the case the 8 % polyester resin, namely the grafting of elastomer makes the network (more especially the polyester chains) more flexible so that defect nucleation becomes easier and easier. Furthermore, contrary to dynamic tests, K measurements detect this effect even in the case of lower elastomer wt. %.

The question still remains about the way in which elastomers modify the network flexibility. Do they affect the degree of cross-linking or the local interactions in the chains ? Solid state N.M.R. are in progress with the aim of bringing forth complementary informations on this point.

To conclude, up to now K measurements can be regarded as a very sensitive micromechanical probe of thermoset structure though the origin of its variation may not be definitively attribued to either chemical or physical evolution.

ACKNOWLEDGMENTS

We wish to thank Mr Blondeau and Mr Boinaut at CDF Chimie Drocourt, and Mr Morel at CDF Chimie Mazingarbe, for providing unsaturated polyester resins and for fruitful discussions during the course of this work.

REFERENCES

(1) C. Bultel, J.M. Lefebvre and B. Escaig, Polymer 24, 476, (1983)

(2) J.M. Lefebvre, C. Bultel and B. Escaig, J. Mater. Sci., accep. for publi. Oct. 83

(3) B. Escaig, "Plastic Deformation of amorphous and semi-crystalline materials", Ed. by B. Escaig and C. G'Sell, Les Editions de Physique, les Ulis, p. 187 (1982)

(4) C. Bultel, Thèse de 3e cycle, Université de Lille I (1982)

(5) W.D. Cook and O. Delatycki, J. Polym. Sci. : Polym. Phys. Ed. 12 1925, (1974)

(6) K. Tanaka, Bull. Chem. Soc. Japan, 33, 1702, (1960)

(7) J. Martinat, "Design engineering technical Conference", Cincinnati (Ohio), edited by ASME, (1973)

(8) W.D. Cook and O. Delatycki, J. Polym. Sci. : Polym. Phys. Ed. 12, 2111, (1974).

(9) L.E. Nielsen "Mechanical Properties of Polymers and Composites", Marcel Dekker, New York, (1974).

(10) J. Heijboer, J. of Polymer Sci. : part C 16, 3755, (1968)

Accepted September 13, 1984