Polymer Bulletin 17, 97–102 (1987)

Polymer Bulletin

Existence of an introduced elastomer interphase in a glass beads-filled epoxy thermoset

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SUMMARY

A rubbery (CTBN based) thin layer is added onto the surface of glass beads embeded in a DGEBA - DDA matrix. The chemical and the coating processes are described.

The existence of a specific relaxation of the interphase is evidenced using viscoelastic measurements. The presence of an other α' relaxation is discussed.

INTRODUCTION

Different ways have been investigated in order to enhance the fracture toughness of reinforced thermosets. The most widely used methods concerned the improvment of the network itself or/and increase of the filler-matrix adhesion.

In the first case, the use of a second elastomeric phase was first described by Sultan and Mac Garry (1) since then numerous works have been done on rubber-modified thermosets (2) and on hybrid particulate composites (3).

In the second case, the use of coupling agents increased the filler-matrix adhesion (4) and provided higher modulus and strength but generally no significant improvment for impact toughness and fatigue are noticed.

A mixed way is the encapsulation of fillers with a thin layer of low modulus elastomer which is able to give a tougher composite with a modulus in a same order of magnitude. This method has been suggested with rigid spherical inclusions (5) and further calculations have been done on particulate or fibers composites (6)(7). Only few experiments have been conducted on glass beads (8), glass (9) or carbon fibers (10 and ref. cited) which confirm the conclusions of the theorical assignments.

We have recently reported the increase in toughness of epoxy matrix into which thin rubber-coated glass beads were introduced (11). For the coating, we used the concept of block copolymers proposed previously by Riess et al (12) but based on carboxyl terminated butadiene acrylonitrile copolymer (CTBN) and epoxy reactions.

This publication describes the chemical and the coating process and the viscoelastic behavior of this interphase.

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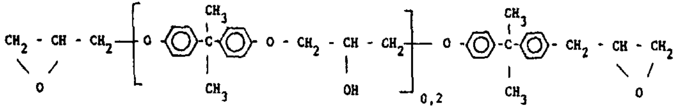
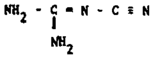
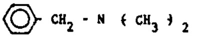
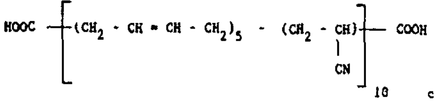
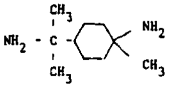
EXPERIMENTAL

Materials : The chemical products used in this study are listed on table 1.

Table 1

Chemical products

Materials	Chemical formula	Trade mark
Epoxy Prepolymer $\overline{M_n}$ = 380 g/mol	 diglycidyl-ether of bisphenol A	DGEBA 0164 Bakelite
Hardener DDA or Dicy	 $NH_2-\underset{NH_2}{\underset{\vert}{C}}=N-C\equiv N$ dicyan-diamine	VE 2560 Bakelite
Catalyst BDMA	 benzyl dimethyl amine	Fluka
Rubber CTBN $\overline{M_n}$ = 3500 g/mol	 $HOOC-\left[(CH_2-CH=CH-CH_2)_5-(CH_2-\underset{CN}{\underset{\vert}{CH}})\right]_{10}-COOH$ carboxyl terminated butadiene acrylonitrile	Hycar CTBN 1300 x 8 Goodrich
Liquid diamine (MNDA)	 1-8 p.menthane diamine	Aldrich

Instrumental : The chemical and physical analysis using Size Exclusion Chromatography (SEC), FTIR and Differential Scanning Calorimetry (DSC) were performed with the apparatus already described (13). The viscoelastic measurements (real part of modulus E' or G' and loss factor tg δ) were reported both with an inverted forced oscillation pendulum (14) and a dynamic mechanical thermal analyser DMTA from Polymer Laboratories. The spectra were recorded in the temperature range - 150 / + 170°C in the frequency range 10^{-2} - 10 Hz.

RESULTS

Synthesis of the elastomeric adduct : The prepolymer DGEBA and CTBN (1300 x 8) are miscible at T > 60°C (13) and are mixed with a carboxyl-to-epoxy ratio a/e = 0.5. The mechanism of this reaction has been already discussed (13)(15). The reaction is carried out at 85°C under mechanical stirring and a nitrogen flow using 0.15 % by weight of triphenylphosphine as activator and no etherification occurs. At this temperature the SEC analysis shows that the number average molecular weight of the CTBN-DGEBA mixture increases linearly with time at 85°C up to 17 h. After 19 h., the reaction is ended (Fig. 1b) and the liquid menthane diamine (MNDA) is added.

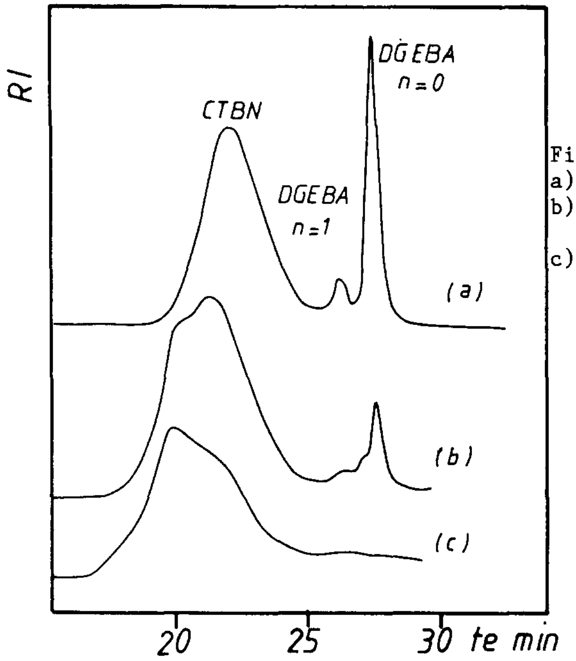


Fig.1. SEC chromatograms
a) CTBN + DGEBA initial mixture
b) CTBN + DGEBA after 19 h at 85°C
c) CTBN + DGEBA + MNDA after 4 days at 25°C

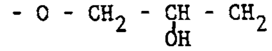
The selection of MNDA-epoxy reaction was not arbitrary. The primary amine hydrogen atoms react slowly at room temperature. Hence, the secondary amine hydrogens are less reactive due to the steric hindrance of the nearly methyl groups and they reacts at higher temperature (16). A ratio amine-to-epoxy a/e = 2 is chosen, assuming that half of epoxy groups has already reacted in the previous stage, so we have an excess of amine. This mixture is kept at 25°C during 4 days ; the SEC analysis (Fig. 1c) of the final product shows that all the residual DGEBA molecules have disappeared and that a further increase in number average molecular weight has taken place. Even DGEBA molecules have disappeared, epoxy groups are still present as shown by FTIR analysis (peak at 910 cm^{-1}). We observe only one glass transition Tg rather constant around - 55°C.

.*Coating process* : 100 g of glass beads are mixed with 3.5 g of the CTBN-DGEBA-MNDA adduct dissolved in 350 ml of methyl-ethyl-ketone (MEK) at 25°C for to 10 min. The solvent is then evaporated under vacuum. Then the beads are dried at 120°C during 12 h. At this temperature, some of the secondary amine hydrogen atoms react with the residual epoxy groups and the coating becomes insoluble in MEK or DGEBA.

It's essential that the rubbery coating becomes crosslinked at this stage to prevent its dissolution during the preparation of the composites. We have to notice that after this curing amine hydrogen atoms are still present and are able to react with new DGEBA molecules and thus insure a good interfacial adhesion.

The thickness of the coating is estimated at 3 % of the glass beads radius as determined by a gravimetric method. The treated glass beads were screened and introduced in a DGEBA-DDA matrix. We use an amine-to-epoxy ratio a/e = 0.6 with 1 phr of BDMA as accelerator. The glass beads are added according to different volume fractions (10, 20 and 30 %). The materials are mixed by mechanical stirring under vacuum at 60°C for 1 h. Then the mixture is casted into a PTFE coated mould and cured at 160°C for 1 h followed by 1 h at 180°C. With these conditions we obtain a fully cured material with a glass transition temperature Tg = 127°C independent of the filler content and coating.

Viscoelastic properties of the model system : The amount of adduct (0.6, 1.2 and 1.6 % in composites filled respectively with 10, 20 and 30 % of glass beads) is very small, so it cannot be displayed by DSC measurements. Such an interphase can be revealed by dynamical measurements (17).

In the composites with uncoated glass beads (Fig.2), two main relaxations have been identified : a high temperature α process, associated with the glass transition process and at lower temperature, a secondary relaxation β (- 125 to - 25°C) associated with the motions of glyceryl units  $-O-CH_2-\underset{OH}{CH}-CH_2-$ and diphenylpropane units (18).

In the composites with coated glass beads, the presence of the elastomeric adduct is displayed by viscoelastic measurements. Beside the relaxation peak (maximum at - 90°C) of the epoxy matrix (Fig. 3), relaxation peak (at - 56°C) corresponding to the glass transition of elastomeric interphase takes place. Discremination of peaks is only possible at low frequencies (10^{-2} to 10^{-1} Hz) due to the large difference in apparent activation energies between the α relaxation of the adduct and the β relaxation of the matrix. With measurements performed on PL/DTMA, activation energies of DGEBA-DDA matrix β relaxation have been estimated to be 58 kJ.mole-1 and 220-230 kJ/mole^{-1} for the relaxation α of the adduct.

It has been reported however that the cured epoxy networks have another mechanical relaxation α' (observed both in heating and cooling measurement process) in the range 50°C to 90°C ; Pogany (19) and Arridge (20) interpreted this relaxation as arising from the motion of the loosely crosslinked network embedded in the cure epoxide network. The α' relaxation is evidenced in the case of glass beads covered with the elastomeric adduct, and, in agreement with the litterature, this relaxation could be explained by a loosely crosslinked DGEBA-MNDA network at the interphase. New experiments have to be performed to confirm this hypothesis.

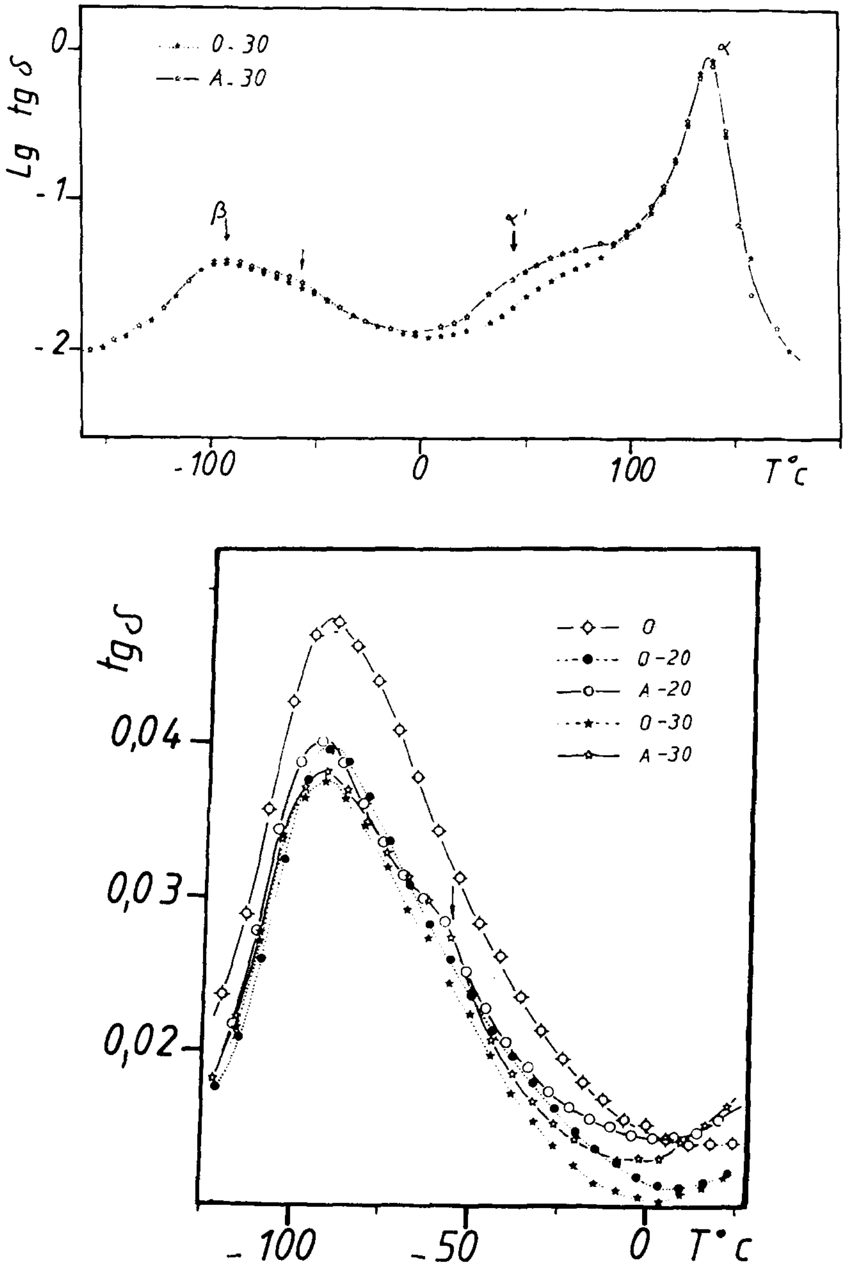


Fig. 2 and 3. Temperature dependences of mechanical loss factor tan δ /A : glass beads coated ; O : glass beads uncoated. The number(20) or (30) indicated the volume per cent of glass beads/(torsion pendulum at 0.01 Hz)

CONCLUSION

We have realised a coating process of glass beads based on elastomer - epoxy prepolymers blends. The temperature dependences of viscoelastic properties of a model system - epoxy resin - glass beads covered with CTBN-DGEBA-MNDA elastomer - allows the following conclusion to be drawn : the structure of the interphase region may be represented by a two phases system, a CTBN elastomeric phase and a loosely crosslinked DGEBA-MNDA network.

Similar coating process on fibers is now in progress.

References

1. J.N. Sultan, F.J. Mc Garry, Polym. Eng. Sci., 13 , 29 (1973)
2. C.K. Riew, J.K. Gillham, "Rubber Modified Thermoset Resins" ACS 208 (1984)
3. R.J. Young, D.L. Maxwell, A.J. Kinloch, J. Mat. Sci. 21 , 380 (1986)
4. H. Ishida, G. Kumar "Molecular Characterisation of Composite Interfaces", Plenum Press N.Y. (1983)
5. V.A. Matonis, N.C. Small, Polym. Eng. Sci. 9 , n° 2, 90 (1969)
6. L.J. Broutman, B.D. Agawal, Polym. Eng. Sci. 14 , n° 8, 581 (1974)
7. T. Ricco, A. Pavan, F. Danusso, Polym. Eng. Sci. 18 , n° 10, 774 (1978)
8. M.E.T. Dekkers, J.P.M. Dortmans, D Heikens, Polym. Comm. 26 , 145 (1985)
9. B. Schlund, M. Lambla, Polym. Comp. 6 , n° 4, 272 (1985)
10. J.H. Crammer, G.C. Tesoro, D.R. Uhlmann, Ind. Eng. Chem. Prod. Res. Dev. 21 , 185 (1982) and ref. cited)
11. Y.G. Lin, J.P. Pascault, H. Sautereau, "Polymer Composites" Walter de Gruyter, Berlin 373 (1986)
12. G. Riess, M. Bourdeaux, M. Brie, G. Joupuet, Proc 2nd Carbon fibers Conf. London 8 , 52 (1974)
13. P. Bartlet, J.P. Pascault, H. Sautereau, J. Appl. Polym. Sci. 30 , 2955 (1985)
14. S. Etienne, J.Y. Cavaillé, J. Perez, R. Point, M. Salvia, Rev. Sci. Instrum. 53 , 1261 (1982)
15. C.K. Riew, E.M. Rowe, A.R. Siebert, "Toughness and Brittleness of Plastics" R.D. Deanin and A.H. Guignola Ed. Adv. Chem. Series 154, 326 (1976)
16. S. Montarnal, J. Galy, H. Sautereau, J.P. Pascault, F. Michel-Dansac, JNC5, Ed. Pluralis, 443 (1986)
17. S. Yu, M. Lipatov, V.F. Rosovizky, V.V. Shifrin, J. Appl. Polym. Sci. 27 , 455 (1982)
18. J.G. Williams, J. Appl. Polym. Sci., 23 , 3433 (1979)
19. G.A. Pogany, Br. Polym. J., 1 , 177 (1969)
20. R.G.C. Arridge, J.H. Speak, Polymer 13 , 450 (1972)

Accepted December 9, 1986 C