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S0032-3861(96)00333-3

Polymer Vol. 37 No. 20, pp. 4657–4659, 1996

0032-3861/96/$15.00+0.00

Note

Improved interfacial adhesion via chemical coupling of *cis*-polybenzobisoxazole fibre–polymer systems

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(Received 29 November 1994; revised 27 November 1995)

cis-Polybenzobisoxazole (PBO) fibres exhibit outstanding mechanical, thermal and electrical properties but poor interfacial adhesion to a variety of resin systems. In order to improve the interfacial adhesion between PBO fibres and a model resin system, a PBO end-capped benzocyclobutene–PBO dope blend was prepared to chemically couple the fibre to the matrix resin. It was demonstrated that a 75% increase in interfacial adhesion was achieved as measured using the microbond test method without sacrificing any of the other desired properties of the fibre. The process of dope preparation, fibre spinning and sample testing are described in detail. Copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: fibres; interfacial adhesion; *cis*-polybenzobisoxazole; benzocyclobutene)

Introduction

cis-poly[benzo(1,2-*d*:5,4-d′)bisoxazole-2,6-diyl-1,4-phenylene] (PBO) can be manufactured into an organic fibre exhibiting high tensile strength and stiffness with a low density (1.58 g cm^{-3}), which results in exceptionally high specific mechanical properties[1∇4]. PBO fibres have been used in research and development laboratories to manufacture prototype advanced composites using a number of processes, including autoclaving, filament winding and resin transfer moulding. Initial data collected on various mechanical properties and fracture surfaces of composite materials manufactured at The Dow Chemical Company have indicated that resins reinforced with PBO show failure modes typical of poor fibre–matrix adhesion. This may be due in part to the lack of polar functional groups in the polymer repeat unit. As a result, chemical interaction between PBO and matrix resins is limited to weak secondary atomic interactions such as van der Waals and dipole-induced dipole interactions. Efficient stress transfer from the fibre to the matrix material was less than desirable; therefore, the full potential of the mechanical properties of the fibre could not be translated to the composite material. Early studies indicated that low interfacial shear strengths could also yield matrix cracking, especially in angle ply laminates, and splitting in unidirectional composites.

Initial attempts[5] by the Dow Chemical Company researchers to improve the interfacial shear strength between the PBO fibre and various matrix resins concentrated on activating the fibre surface through treatment with a reactive plasma. It was reported[6] that approximately a two-fold increase in interfacial shear strength (from 19.4 to 33.2 MPa) could be attained using the oxygen plasma. A second method employed by the same group to improve interfacial shear strength focused on the formation of a chemical bond between the fibre and the matrix material. This could be achieved by either using a PBO copolymer which included a functional group in the backbone so that the functional group can react with the matrix molecule or by the addition of small quantities of a functionalized PBO molecule, such as benzocyclobutene diketone (BCB) end-capped PBO, into the PBO fibre dope.

The copolymer method has the disadvantage in that the spun fibre exhibited significantly lower overall mechanical properties at all compositions than the PBO fibre. This can be partially attributed to the lower molecular weight of the copolymer molecule compared to that of the PBO molecule. The copolymer fibre may not lead to the highly oriented rigid rod structure which the PBO fibre enjoys. Furthermore, most of the functional groups in the backbone are not on the fibre surface and would not be available to react with the matrix resin. Only a very small fraction of all the functional groups in the bulk of the fibre is utilized to improve the interfacial shear strength.

The latter procedure, the additive method, is more effective since the load carrying the PBO backbone chemistry is not altered by using copolymers. Fibres spun from blends of BCB end-capped PBO molecules in PBO dope should yield mechanical properties similar to PBO itself.

The purpose of this article is to report data on the chemically improved interfacial shear strength between the PBO fibre and a model matrix resin system. It should be noted that the same technique can be used with other matrix systems by end-capping PBO fibre with a suitable reactive group.

Chemistry

Compound **A** was prepared* by the reaction of 4-benzocyclobutenecarboxylic acid with 1,3-diaminores-

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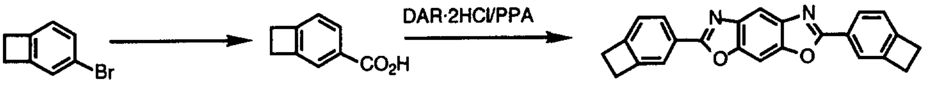
* For synthesis procedures of compound **A**, analysis and curing of **A** in PBO fibre, and details on spinning conditions and properties of PBO–BCB blend fibres, see So *et al.*[7]



(A)

Scheme 1

orcinol (DAR) dihydrogen chloride in polyphosphoric acid (PPA) (*Scheme 1*). 4-Benzocyclobutenecarboxylic acid was made using a procedure described in the literature[8].

Thermal stability of A in PPA. Compound A was shown to be stable in 83.5% PPA at 150°C for 6h. No detectable degradation was observed in the ^{13}C n.m.r. spectra of these samples with a detection limit of about 5% of the sample. The sample, however, did turn dark at elevated temperatures (150°C).

Fibre spinning

PBO fibre with 9 wt% of A. A twin-piston[7] was loaded with 500 g of PBO dope which contained 14 wt% polymer, and 6.5 g of A. The blend was mixed at 150°C for 2 h. The fibres were extruded at 165°C out of a 180 μm spinneret with 42 holes vertically downwards into a coagulation bath, using the dry-jet wet spinning technique. A glass shroud was placed in the air gap, between the spinneret face and the surface of the coagulation funnel.

Fibres described in this paper were produced using a shear rate of about 1100–2000 s^{-1} at the spinneret hole wall. Spin/draw ratios utilized were 20–45 with fibre take-up speeds of 50–200 m min^{-1}. The fibre diameter was maintained at 11.5 μm under all conditions. The coagulation was initially carried out with a continuous flow of deionized water through the extraction/coagulation funnel, and subsequently replaced with PPA solution (5–25 wt%). The PBO fibre samples were washed 'off-line' in water (immersion of spun yarn bobbins in water buckets) at 23°C for 48 h. The fibre was then dried at room temperature under a continuous flow of nitrogen. No heat treatment was performed on the fibre.

PBO fibre with 18 wt% of A. Five hundred grams of PBO dope were mixed with 115 g of PPA solution containing 18 wt% of A in a piston reactor at 160°C for 3 h. Spinning was carried out as described earlier.

Copolymer fibre with 50% BCB. Fibres with 50% BCB functionalized PBO in their backbone[†] were used for this part of the study.

Interfacial shear strength measurements

The tensile properties of the as-spun fibres used in this study are presented in *Table 1*. The data in *Table 1* were obtained on fibres which were spun at a shear rate of 1165 s^{-1} with a spin/draw ratio of 25, and at a line speed of 60 m min^{-1}. The coagulation was performed in a 20 wt% PPA–water solution.The tensile strengths of the BCB–PBO blend fibres were similar to the control PBO fibre, while the tensile modulus increased 34 and 38%, respectively, for the 9 and 18% blend fibres. The 50% copolymer fibre, however, exhibited a tensile strength considerably lower than the PBO control, about 47% at 2.6 GPa, while there was no change in the modulus.

The adhesion of BCB to PBO fibres was measured using the microbond method[9∇11]. The microbond method is a pull-out technique which involves the measurement of the force required to shear a microdroplet of resin deposited on a single fibre. The working principle of the microbond pull-out is shown in *Figure 1*. The microdrop specimen is attached to a load cell and the jaws of a microvice are brought into light contact with the fibre. The jaws move along the length of the fibre until they contact the microdroplet, causing it to debond and slide along the fibre. The interfacial shear strength can be calculated by

$$\tau = \frac{\text{force}}{\text{area}} = \frac{F}{\pi dl}$$

where F is the debond force, d is the fibre diameter and l is the embedded length of the droplet.

To prepare microbond specimens for interfacial shear strength measurements, single filaments of PBO fibres, selected at random, were mounted on metal tabs with a 0.7 × 2.5 cm perforation, and fastened in place with epoxy. A small amount of BCB resin was placed on a

Table 1 Tensile properties[a] of PBO–BCB fibres (standard deviation in parentheses)

Fibre	BCB content (%)	Denier	Tensile[a] strength (GPa)	Tensile modulus (GPa)	Elongation (%)
Control	0	498	5.50 (0.15)	160.0 (5.9)	3.40 (0.06)
Blend	9	72	5.00 (0.30)	213.7 (9.7)	2.80 (0.11)
Blend	18	61	5.30 (0.16)	221.6 (4.8)	2.80 (0.13)
Copolymer	50	28	2.62 (0.08)	157.4 (13.8)	1.90 (0.05)

[a] 10 inch (25.4 cm) gauge length, twist factor 6

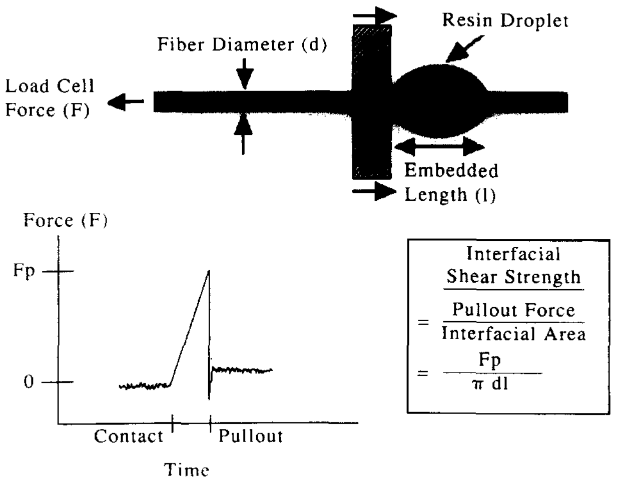


Figure 1 A schematic illustration of the microbond pull-out method

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[†] Experimental fibre obtained from Chau, C. C., The Dow Chemical Co.

Table 2 Microbond interfacial shear strengths: BCB diketone resin to PBO fibres

Fibre	BCB content (%)	Interfacial shear strength (MPa ± SD)	Change (%)
Control	0	18.8 ± 1.4	-
Blend	9	21.5 ± 2.4	14.4
Blend	18	32.6 ± 4.0	73.4
Copolymer	50	24.6 ± 2.5	32.4

glass slide and heated on a hot plate until fluid. An applicator was made using a single carbon fibre taped to a strip of cardboard. This was dipped into the BCB resin, and the droplets which formed on the fibre were transferred to the PBO test fibre on the tab under a 30X stereo microscope. Six droplets were applied to each fibre specimen. The specimens were cured under a nitrogen atmosphere using the following schedule: heat the sample rapidly from room temperature to 200°C; hold at 200°C for 60 min; continue heating from 200 to 210°C at a rate of $2.8^{\circ}\mathrm{C\,min^{-1}}$; hold at 210°C for 30 min; continue heating from 210 to 250°C at a rate of $2.8^{\circ}\mathrm{C\,min^{-1}}$; hold at 250°C for 30 min; continue heating from 250 to 260°C at a rate of $2.8^{\circ}\mathrm{C\,min^{-1}}$; hold at 260°C for 60 min; cool to room temperature with oven.

After curing, the embedded length of each droplet and the fibre diameter near each droplet were measured to the nearest $0.1\,\mu\mathrm{m}$ using a microscope fitted with a video micrometer at 200×. Each droplet was individually sheared at a test speed of $32.0\,\mu\mathrm{m\,s^{-1}}$. Typically, 20–25 droplets were sheared, and the average and standard deviation calculated. Statistical comparisons of the shear strengths of different fibres were conducted using JMP Statistical Software (SAS Institute, Inc.).

Results and discussion

The measured microbond interfacial shear strengths of the PBO fibres are given in *Table 2*. The results show that incorporation of BCB functionality into the PBO fibre significantly increases the interfacial shear strength. The copolymer fibre exhibited an interfacial shear strength 33% higher than the PBO control. This is a moderate increase considering the large amount of BCB incorporated into the fibre. In contrast, fibres prepared from the blend containing 18% BCB end-capped PBO exhibited a 74% increase in shear strength compared to the PBO control fibre. The higher shear strength observed with the blend fibre at a much lower BCB content supports the hypothesis that the lower molecular weight BCB molecule migrates to the surface of the fibre, where it can interact with the matrix resin.

Acknowledgements

The authors would like to acknowledge the contributions of Dr C. C. Chau for spinning the fibres and Ms J. Simon for her help in measuring the mechanical properties.

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