Processing of bulk (*p*-phenylene benzobisthiazole)/nylon-6,6 molecular composites

C. S. Wang
University of Dayton Research Institute, Dayton, OH 45469-0001, USA

and I. J. Goldfarb and T. E. Helminiak
Materials Laboratory, Wright-Patterson Air Force Base, OH 45433-6533, USA
(*Received 2 October 1987; accepted 25 October 1987*)

A novel process for the fabrication of rigid-rod polymer reinforced thermoplastic molecular composites into bulk articles is presented. The as-processed poly(*p*-phenylene benzobisthiazole) (PBT)/nylon-6,6 molecular composites, depending on their PBT content, showed significantly higher tensile properties than nylon-6,6 and maintained an excellent bulk integrity even above the melting temperature of nylon. The Young's moduli of these molecular composites were compared to those predicted from the rule of mixtures for three-dimensionally isotropic fibre composites. By assuming PBT/nylon-6,6 molecular composites to be stiff fibre composites, the reinforcement efficiency of PBT was estimated to achieve 50–70% that of the maximum.

(Keywords: rigid-rod polymer; poly(*p*-phenylene benzobisthiazole); molecular composite; thermoplastic; nylon-6,6; consolidation)

INTRODUCTION

The concept of a rigid-rod molecular composite involves the molecular reinforcement of a ductile, flexible-coil polymer with a stiff, strong rodlike polymer analogous to a fibre-filled composite. While most, if not all, rigid-rod and flexible-coil polymers are incompatible in nature, the molecular dispersion of rigid-rod molecules in a host polymer has been achieved by rapid coagulation of a ternary solution. Therefore, fibres and films were naturally the first to be prepared as molecular composites. Among those, molecular composite fibres with poly(*p*-phenylene benzobisthiazole) (PBT) in poly(2,5(6)-benzimidazole) (ABPBI) and poly(2,6-benzothiazole) (ABPBT), respectively, were reported to show nearly perfect orientation of molecularly dispersed PBT judging from the rule of mixtures for uniaxially aligned fibre composites[1]. However, a major drawback of these aromatic heterocyclic polymer systems is that they are not melt-processable.

Recently, thermally mouldable molecular composites using thermoplastic polymers as matrices have drawn researchers' attention in an attempt to fabricate molecular composites into large structural components[2,3]. These thermoplastic molecular composites were first fabricated into films and then laminated into thick pieces by compression moulding. Unfortunately, the laminated articles had very weak bonding at the interfaces between adjacent films and delaminated easily under stress or at elevated temperatures. To overcome this, Nishihara *et al.* found that it is necessary to adhere the composite films together with a layer of matrix material coated on the surfaces of each individual film prior to lamination.

The present paper reports a new process for the production of bulk thermoplastic molecular composites. This process consolidates the coagulated wet molecular composites into bulk form by utilizing (1) the increased surface energy resulting from a large surface area of wet composites and (2) the plastic flow of wet molecular composites with residual solvent and coagulant acting as a plasticizer. Preliminary experimental studies have been conducted on the fabrication of PBT/nylon molecular composites. The objective is to fabricate bulk molecular composites with three-dimensional properties for structural applications.

EXPERIMENTAL

Materials

The solvent used was 98% anhydrous methanesulphonic acid (MSA) from Aldrich Chemical Company. Rodlike PBT with an intrinsic viscosity of 21.4 dl g^{-1} in MSA was obtained from Dr James Wolfe of SRI International. Its weight-average molecular weight (M_w) and aspect ratio of polymer molecule length to diameter (L/D) were calculated[4] to be 33 400 g mol^{-1} and 330, respectively. The nylon-6,6 was Zytel 42 from E. I. DuPont Chemical Company. Zytel 42 is a semicrystalline nylon, which has a nominal M_w of 30 000 g mol^{-1} and a melting temperature (T_m) of 255°C. In this study, MSA was used as received, while PBT and nylon were vacuum dried at 60°C overnight before use.

Processing scheme

The entire processing procedure may be divided into five steps: (1) solution preparation; (2) coagulation; (3) wet state consolidation; (4) residual solvent and coagulant removal; and (5) thermal annealing and moulding. Initially, PBT and nylon-6,6 were codissolved in MSA to prepare a solution below the critical

0032–3861/88/050825–04$03.00

concentration (C_{cr}) at which an isotropic-to-anisotropic phase transition occurs. This is a necessary condition for attaining a molecularly dispersed composite. The exact concentration prepared for each PBT/nylon solution is given in *Table 1*. Such a concentration would allow the solution to flow continually at a flow rate of about 1 ml min^{-1}. In coagulation, the solution flowed slowly from a separatory funnel into a large quantity of stirred distilled water. The molecular composites ended up as continuous thin filaments, which were entangled. Immediate coagulation of these very fine filaments, presumably, would minimize the degree of phase separation. The composites were thoroughly washed with free-running distilled water for at least two days and, thereafter, kept wet at all times.

The wet molecular composites were ready to be consolidated into desired experimental specimens under pressure and temperature. This was conducted in a closed mould with the temperature and pressure applied by a microprocessor-controlled hot press (Wabash 30-1515-2TMX). The forming was carried out first at room temperature with a pressure ramp from 0 to 45 MPa in 30 min, followed by a temperature ramp to 175°C in 30 min, and then held at that condition for another 30 min. After consolidation, the specimen was dried further under vacuum at 100°C for 24 h and subsequently at 175°C for 24 h to remove solvent and coagulant residues.

Figure 1 presents a dynamic torsion measurement of consolidated and dried 40/60 PBT/nylon molecular composite from 20°C to 300°C and then back to 50°C using a Rheometrics Dynamic Spectrometer (RDS 7700). The specimen showed a dramatic decrease in both the storage modulus (G') and loss modulus (G'') upon heating at about 120°C and resumed the properties at about 200°C. The minimum properties were at about 175°C, which is the consolidation and drying temperature, indicating that the residual stress remaining in the consolidated specimen was significant. In addition, numerous voids were expected within the specimen after the drying step. Therefore, the specimen was thermally annealed under 45 MPa by gradually increasing the temperature to the melting point of nylon.

Mechanical testing

An Instron Universal Test Machine (model 1122) was used to measure the mechanical properties of PBT/nylon molecular composites. The experimental specimens were in a dogbone shape with the centre portion about 28 mm long, 4.5 mm wide and 1.0 mm thick. The elongation of the specimens was monitored by a half-inch gauge length extensometer. A crosshead speed of 0.05 cm min^{-1} was used in all measurements. For each PBT/nylon composition, the tensile properties were determined from measurements of 4–6 specimens.

RESULTS AND DISCUSSION

The solution concentration, PBT volume fraction and tensile properties of various composition PBT/nylon molecular composites are listed in *Table 1*. The PBT volume fraction V_f was estimated from its weight percentage w by the equation

$$V_f = (w/d_f)/[w/d_f + (100 - w)/d_m]$$

where the densities of PBT (d_f) and nylon (d_m) are 1.56 and 1.14 g cm^{-3}, respectively. As shown in the table, the tensile strength (*TS*) and Young's modulus (*E*) of these molecular composites increase significantly with PBT content to about 50 wt% and then decrease slightly to 60 wt%. The decrease of tensile properties at higher PBT content is believed to be due to insufficient matrix material fusing the molecular composite filaments together. If this is true, then the composites prepared from broken particles should have lower properties than those

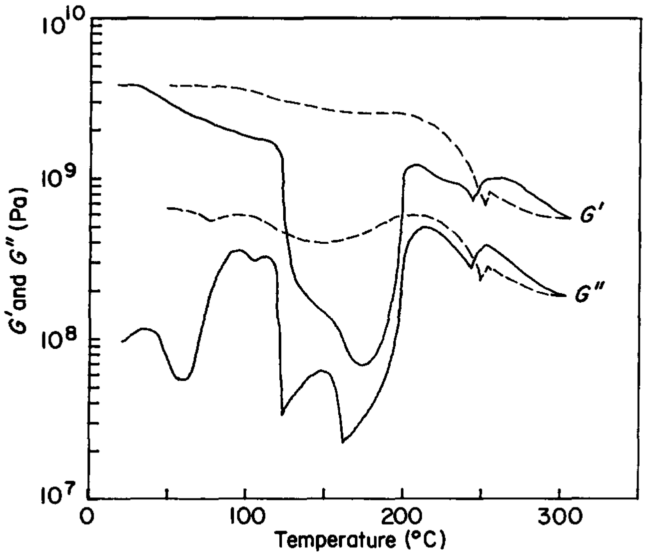

Figure 1 Dynamic torsion properties of a consolidated and dried 40/60 PBT/nylon-6,6 molecular composite: (———) heating; (– – –) cooling

Table 1 Tensile properties of bulk PBT/nylon-6,6 molecular composites

PBT/nylon composition (wt/wt)	Solution conc. (wt%)	V_f	*TS* (MPa)	*E* (GPa)	Elongation at break (%)	K_f
0/100[a]	–	0.00	85	2.82	90	–
10/90	2.00	0.075	85±7	5.4±0.3	1.77–2.35	0.58
20/80	1.43	0.15	106±13	7.4±0.1	1.90–4.00	0.49
30/70	1.00	0.24	130±23	11.4±1.0	1.05–2.45	0.60
40/60	0.80	0.33	146±12	14.9±1.0	1.10–1.47	0.61
40/60[b]	0.80	0.33	146±10	14.7±1.0	1.10–1.20	0.60
50/50	0.67	0.42	183±10	20.8±1.9	0.81–1.13	0.70
60/40	0.59	0.52	172±6	20.5±2.1	0.82–1.12	0.50
60/40[b]	0.59	0.52	93±3	13.4±1.2	0.65–0.81	–

[a] Nominal tensile properties of Zytel 42

[b] Specimens prepared from a blended slurry

prepared from continuous filaments, because the former requires more fusion than the latter. For this comparison, specimens at 40/60 and 60/40 compositions were also prepared from the wet molecular composites which had been blended into a slurry from continuous filaments before consolidation. As reported in *Table 1*, the 60/40 composition specimens prepared from the slurry, indeed, exhibit substantially lower properties than those prepared from continuous filaments. As to the 40/60 composition specimens, those prepared from the slurry and continuous filaments had essentially identical tensile properties, indicating that the fusion of the fine particles provides a bond almost as strong as continuous filaments at this composition. The fusion between 40/60 composition molecular composites was excellent even at elevated temperatures. This has been shown in the dynamic torsion measurements.

Theoretical correlations that predict the Young's modulus of randomly oriented fibre-filled composites (E_{3D}) from the material properties and compositions of their constituents have been derived in a variety of forms. Christensen predicted E_{3D} by averaging the Young's modulus along the fibre direction over all geometrical directions[5]. For simplicity, a composite system was assumed to be incompressible if both constituents were incompressible. For such a system, a Poisson's ratio of 0.5 was used for both constituents, and E_{3D} may be expressed as:

$$E_{3D}=\tfrac{1}{5}V_fE_f+\tfrac{1}{5}\left(\frac{(5+2V_f+V_f^2)E_f+(5+V_f)(1-V_f)E_m}{(1-V_f)E_f+(1-V_f)E_m}\right)E_m \tag{1}$$

where V is volume fraction, E is Young's modulus, and subscripts f and m indicate the fibre and matrix, respectively. Another composite system was termed a stiff fibre composite, in which the fibre had a much higher modulus than the matrix. For this system, a Poisson's ratio of 0.25 was used for both constituents, and E_{3D} becomes:

$$E_{3D}=\tfrac{1}{6}V_fE_f+\left(\frac{1+V_f/4+V_f^2/6}{1-V_f}\right)E_m+O(\ldots) \tag{2}$$

Nielsen derived the correlation by approaching the Young's modulus transverse to the fibre direction (lower bound) towards the Young's modulus along the fibre direction (upper bound) upon increasing fibre content and he predicted E_{3D} to be[6]:

$$\log E_{3D}=V_f\log E_f+(1-V_f)\log E_m \tag{3}$$

However, the relative merits of these correlations have not been adequately tested experimentally because the three-dimensionally isotropic fibre-filled composites are nearly impossible to prepare unless the fibre is very short or the fibre content is very low.

The maximum volume fraction attainable for randomly oriented fibres, $V_f(\max)$, was found to depend on the fibre aspect ratio (L/D), and if the aspect ratio is large enough (e.g. larger than 10), the two may be correlated by a simple equation as

$$V_f(\max)=kD/L$$

where L is the fibre length, D is the fibre diameter and k is a constant. The constant k has been experimentally and theoretically determined to be 5.3 and 4, respectively, by randomly packing rods into empty space[7]. Rodlike polymers have the same characteristic[4,8] that in a solution rodlike molecules are isotropically dispersed only when their concentration is below C_{cr}. For the same reason, there must exist a critical composition for rodlike molecules to be randomly dispersed in a molecular composite. The critical concentration and critical composition, like $V_f(\max)$, are only a few per cent if the aspect ratio of rodlike polymer is above 100.

During the coagulation of PBT/nylon molecular composites, care has been taken to prevent significant shear-induced orientation of PBT molecules by slowly flowing the solution into the coagulant. But according to the argument of critical composition, PBT molecules must have oriented or aggregated to some degree after coagulation, since both the PBT content and aspect ratio are so high. However, the composites may still be considered to be globally isotropic even if PBT molecules are locally oriented or aggregated in the composites. This consideration is supported by the fact that the specimens prepared from the continuous filaments had tensile properties identical to those specifically prepared from the fine particles in a slurry. Therefore, equations (1) to (3) could be employed for mutual evaluation of the orientation and dispersion of PBT molecules in nylon molecular composites and the relative merits of these correlations if they are consistent. *Figure 2* shows that the Young's moduli of PBT/nylon molecular composites are higher than those predicted by equation (3), but lower than those by equations (1) and (2), if a PBT fibre modulus of 310 GPa and a nylon modulus of 2.82 GPa were used. Equation (3) underestimates the tensile properties of truly three-dimensionally isotropic composites. Since the modulus of PBT fibre is more than

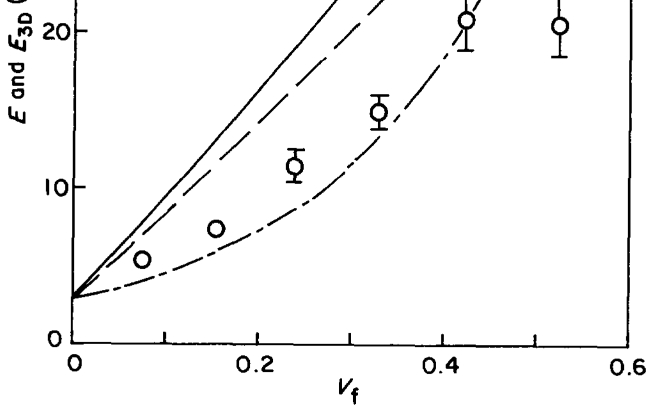

Figure 2 Comparison of the Young's moduli of bulk PBT/nylon-6,6 molecular composites to those predicted from the rule of mixtures for three-dimensionally isotropic composites: (———) equation (1); (– – –) equation (2); (— — —) equation (3)

100 times higher than nylon, the molecular composite is most likely to be a stiff fibre composite system. But, even so, the measured moduli failed to match those predicted by equation (2). Based on the previous discussion of critical composition, this mismatch is probably attributable to the aggregation of rodlike molecules as bundles or domains in the composite, which diminish the reinforcement efficiency. If a reinforcement efficiency factor (K_f) is taken into account in the reinforcing phase, then equation (2) may be rewritten as:

$$E_{3D} = \tfrac{1}{6} K_f V_f E_f + \left(\frac{1 + V_f/4 + V_f^2/6}{1 - V_f} \right) E_m + O(\ldots) \quad (4)$$

Also reported in *Table 1* are the calculated K_f values of bulk PBT/nylon molecular composites. These values are between 0.5 and 0.7 depending on the PBT content. In other words, these PBT/nylon molecular composites have achieved approximately 50–70% of the maximum reinforcement from their PBT molecules judging from the rule of mixtures for three-dimensionally isotropic stiff fibre composites. Although the present K_f values are only preliminary, they are already better than those calculated for the molecular composite fibres with PBT in an amorphous nylon ($K_f = 0.4$) and with PBT in poly(*p*-phenylene quinoxaline) (PPQ-412) ($K_f = 0.2$)[2]. This indicates that the present consolidation process is a feasible process to fabricate thermoplastic molecular composites into large structural components.

ACKNOWLEDGEMENT

This research was supported by US Air Force Contract No. F33615-84-C-5020.

REFERENCES

1 Hwang, W.-F., Wiff, D. R., Verschoore, C., Price, G. E., Helminiak, T. E. and Adams, W. W. *Polym. Eng. Sci.* 1983, **23**, 784
2 Hwang, W.-F., Wiff, D. R., Helminiak, T. E. and Adams, W. W. 'ACS Organic Coatings and Applied Polymer Science Proceedings', American Chemical Society, Washington DC, 1983, Vol. 48, p. 929
3 Nishihara, T., Mera, H. and Matsuda, K. 'ACS Polymeric Materials Science and Engineering Proceedings', American Chemical Society, Washington DC, 1986, vol. 55, p. 821
4 Hwang, W.-F., Wiff, D. R., Benner, C. L. and Helminiak, T. E. *J. Macromol. Sci.–Phys.* (*B*) 1983, **22**(2), 231
5 Christensen, R. M. 'Mechanics of Composite Materials', Wiley, New York, 1979
6 Nielsen, L. E. *Rheol. Acta* 1974, **13**, 86
7 Evans, K. E. and Gibson, A. G. *Compos. Sci. Technol.* 1986, **25**, 149
8 Flory, P. J. *Proc. R. Soc. Lond.* (*A*) 1956, **234**, 73