Crosslinking Studies on Poly(ethylene terephthalate-*co*-1,4-phenylene bisacrylate)

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ABSTRACT: Several compositionally different poly(ethylene terephthalate-*co*-1,4-phenylene bisacrylate) (PETPBA) copolymers were melt spun into fibers. The resulting fibers were subjected to UV irradiation to induce crosslinking. Evidence of crosslinking was obtained from FTIR, solid-state ^{13}C-NMR, thermal analysis, and solubility. Irradiation of the fiber results in an increased glass-transition temperature, reduced thermal shrinkage, and enhanced modulus retention at elevated temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1698–1702, 2004

Key words: fibers; crosslinking; photochemistry; irradiation; glass transition

INTRODUCTION

The photochemistry of α,β-unsaturated carbonyl compounds is well understood. An example of such photochemistry is that of *trans*-cinnamic acid derivatives, which undergo [2+2] cycloaddition in the solid state and isomerize to the *cis* compound in solution.[1] Since the discovery of the dimerization of *trans*-cinnamic acid upon UV irradiation in 1895, photocrosslinkable polymers containing cinnamic acid derivatives have been developed mainly for printing, lithographic, and resist applications.[1] It is of interest to investigate the effect of photocrosslinking on the thermal and mechanical properties of a thermoplastic polymer, where the reactive chromophores form part of the main chain. Poly(ethylene terephthalate) (PET) is a commercially important polymer that finds applications in textiles, and as reinforcement fiber in tires, as well as in food and beverage packaging.[2,3] Opportunities for extending the range of PET applications include enhancing its gas barrier properties, as well as maintaining its mechanical properties at elevated temperatures. Crosslinking is potentially one of the most effective ways to improve these properties.[4] In the case of thermoplastics, where melt processing of the polymer is an important consideration, a postprocessing UV crosslinking step is an attractive approach by which to improve thermomechanical properties without sacrificing melt processability. Random copolymers of PET and the photochemically active comonomer, *p*-phenylene bisacrylate (PBA), have been synthesized by melt polymerization.[5] PBA was chosen because it is difunctional and thermally stable under PET polymerization conditions; PBA can be successfully incorporated into PET using the typical melt polymerization process.[5]

There are few examples[5,6] in the literature of successful incorporation of such reactive comonomers in condensation polymers where polymerization is carried out at high temperatures. The resulting copolyesters undergo photochemical [2+2]-cycloadditions upon UV irradiation. Although the photochemistry of PBA monomer has been thoroughly elucidated,[7–12] the steric requirements of the cycloaddition reaction were thought to be too stringent for cycloaddition to occur between cinnamoyl units in an amorphous polymer.[1,11] Although this view was supported by early research, subsequent research has shown that compounds containing cinnamoyl units do react in the amorphous regions. The effect of solid matrix on the efficiency of the cycloaddition process has been demonstrated by Egerton et al.[12] Ethyl cinnamate undergoes cyclodimerization in high yields in the glassy state.[13] Evidence for cyclodimer in irradiated polymer films has been reported for poly(vinyl cinnamate) and copolymers,[14–16] poly[1,4-bis(2-hydroxyethoxy)cyclohexane-(phenylene bisacrylate)], poly[1,4-bis(2-hydroxyethoxy)cyclohexane-(cinnamate)],[12] liquid crystalline main chain copolyesters,[17,18] and poly(ester imide).[19,20] Gas chromatographic analysis of some these irradiated films (after hydrolysis) show that photocy-

TABLE I
Thermal Properties of Fibers[a]

Sample	IV (g/dL)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PET	0.64	253 (253)[†]	44 (45)[†]	199 (199)[†]	37 (36)[†]
PETPBA 3.4	0.60	246 (245)	46 (46)	197 (170)	35 (19)
PETPBA 4.4	0.61	247 (247)	39 (37)	195 (159)	32 (7)
PETPBA 15	0.57	228 (220)	37 (39)	172 (—)	27 (—)
		(185)[†]	(34)[†]	(—)	(—)

[a] Data in brackets are for fibers irradiated for 1 h and the data in brackets with [†] are for fibers irradiated for 5 h.

cloaddition is the principal method of crosslinking. In this article we present evidence of PBA crosslinking in a PET matrix and discuss the effects of the resulting crosslinking upon the thermal and mechanical properties of PETPBA copolyester fibers.

EXPERIMENTAL

Sample preparation

Monomeric PBA and PET-*co*-PBA copolyesters were prepared using the published methods.[5] Polymers were produced from dimethyl 1,4-phenylenebisacrylate (Aldrich), dimethyl terephthalate (KoSa), and ethylene glycol (Celanese), using a manganese acetate (Sigma)/antimony oxide (Riedel de Haen) catalyst system, polymerizing in the melt at 285°C. Polymer samples used in this study are listed in Table I. The designation PETPBA*x* indicates the copolyester in which *x* mol % of aromatic diester structure units are 1,4-phenylene bisacrylates (PBA). Intrinsic viscosity (IV) measurements were made using 1% (w/w) solutions of polymer in dichloroacetic acid at 25°C.

Fiber processing

Before spinning, polymer samples were dried under vacuum at 80°C for 48 h. The spinning was carried out on a small-scale fiber extrusion unit manufactured by Bradford University Research Ltd. After spinning, the fibers were drawn on a hot plate at 105°C to a draw ratio of between 3 and 4, and then heat-treated at 150°C at constant length in an oven. Fibers were irradiated using a Rayonet photochemical reactor (Southern New England Ultraviolet Company, Branford, CT) equipped with medium-pressure Hg bulbs producing a maximum intensity at 300 nm.

Characterization

Infrared spectroscopy of fibers was carried out on a Perkin–Elmer Spectrum One FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) equipped with an Auto-IMAGE microscope. Solid-state NMR measurements were carried out on a Bruker DSX-300

spectrometer (Bruker Instruments, Billerica, MA) in a Bruker double-resonance magic angle spinning probe head. A standard cross-polarization pulse was used with ^{1}H and [13]C 90° pulses of 4.5 μs. Recycle delays of 5 s and sample spinning speeds of 5 kHz were used; 2K scans were accumulated for signal averaging. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 DSC (TA Instruments, New Castle, DE). Melting temperature (T_m) and enthalpy of melting (ΔH_m) were measured from the first heating cycle. Crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) were measured from the first cooling cycle. Heating and cooling rates were 20°C/min.

Fiber tensile properties were tested on an Instron tensile tester (model 5567; Instron, Canton, MA) at a gauge length of 2.54 cm and crosshead speed of 5 mm/min. Dynamic mechanical analysis (DMA) was carried out on Rheometric Scientific RSAIII (Amherst, MA); a static stress of about 10 MPa and dynamic strain of 0.1% were applied on 10-mm gauge length samples containing 20 filaments. Fiber shrinkage was measured on a TA Instruments thermomechanical analyzer (TMA-2940) at a stress of 50 kPa. Fiber solubility was tested in trifluoroacetic acid (TFA).

RESULTS AND DISCUSSION

The thermal properties and intrinsic viscosities of the polymers used in this study are presented in Table I. The fiber spinnability and postspinning drawability of the PETPBA copolymers are similar to those of PET for all copolymer compositions used in this study. Evidence of crosslinking upon irradiation was collected from changes in the FTIR and solid-state NMR spectra as well as from changes in solubility, thermal behavior, and mechanical properties of the fibers. Figure 1 shows the FTIR spectrum of the fibers irradiated at 300 nm for different times. Peaks are normalized with respect to the phenyl ring stretching vibration at 1580 cm^{-1}. The absorption attributed to the bisacrylate double-bond stretching mode at 1635 cm^{-1} is reduced with time, yet after 16 h of irradiation, a considerable number of the double bonds remain unreacted. With
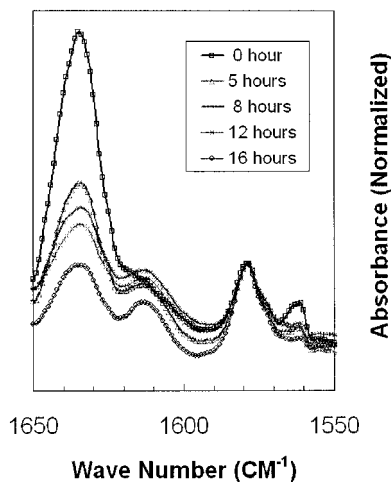
Figure 1 FTIR spectra of PETPBA15 irradiated for different times.

UV irradiation, as crosslinking occurs at the fiber surface, the resultant "bleaching" of the photoreactive moiety allows further radiation penetration, and

hence crosslinking occurs at greater depth with increased irradiation time.[21]

The chemical structures of the irradiated fibers were studied using ^{13}C solid-state NMR (Fig. 2). Upon UV irradiation, intensities of the 142 and 118 ppm peaks, corresponding to the olefinic carbon atoms of the PBA unit, decreased. Consistent with formation of the cyclobutane carbons of the photodimer, new low-intensity peaks appeared between 30 and 50 ppm.[21,22] The development of a shoulder on the carbonyl peak at 170 ppm indicates the generation of unconjugated carbonyl groups.

Before irradiation, the fibers dissolved completely in TFA. After irradiation for 1 h, the PETPBAx fibers became insoluble, except for the PETPBA1, which was still soluble. By comparison, PET fibers dissolved rapidly in TFA, even after 5 h of irradiation. Irradiation also affects the thermal properties of PETPBA fibers, especially at higher PBA mole fractions. As shown in Table I, the melting temperature of PETPBA15 decreases by 8°C after 1 h of irradiation, and decreased by more than 40°C after 5 h of irradiation. The en-
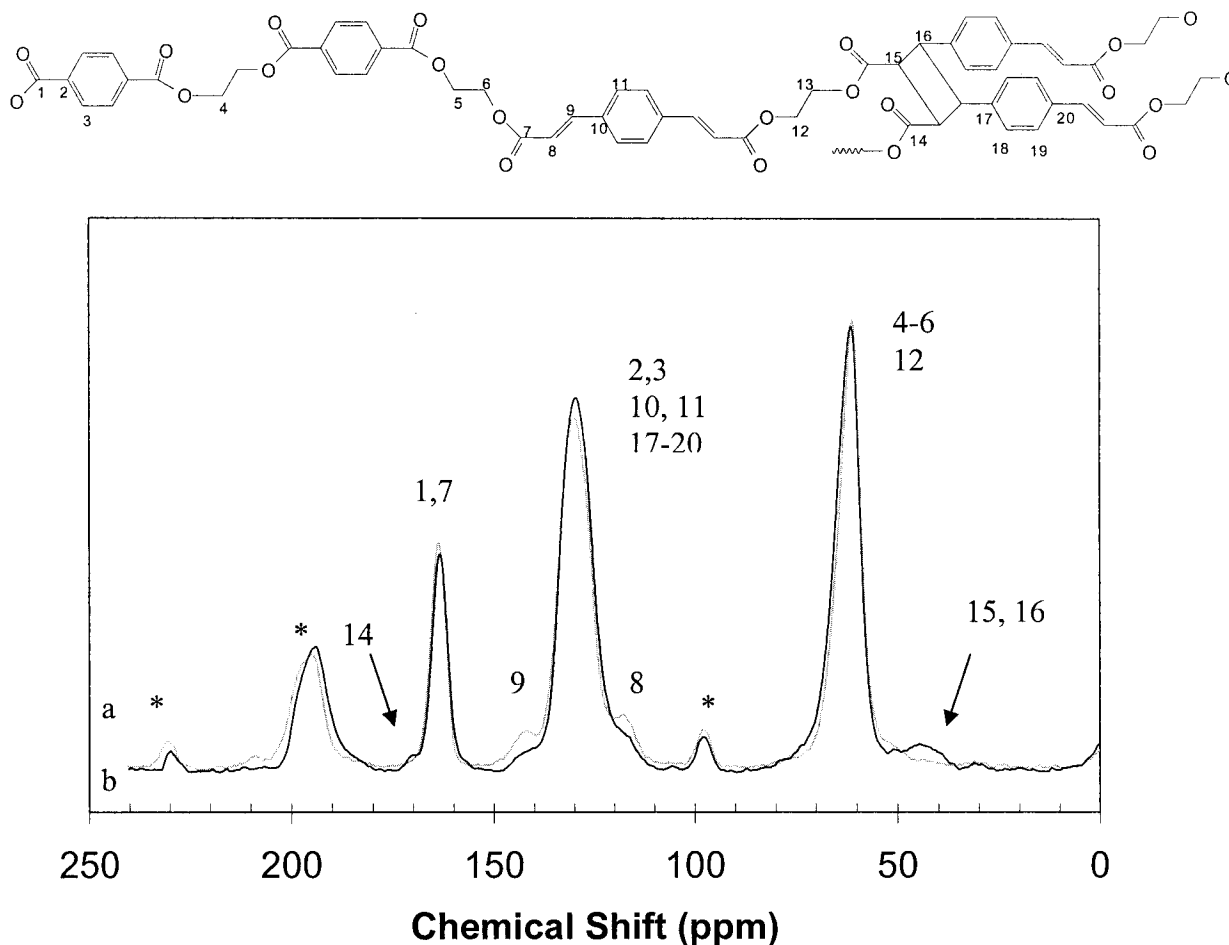

Figure 2 Solid-state NMR spectra of PETPBA15 fibers: (a) unirradiated; (b) irradiated for 15 h.

TABLE II
Mechanical Properties of PETPBA15 fibers
Before/After UV Irradiation

Property	Before irradiation	After 5 h UV irradiation
Tensile strength, GPa	0.16 ± 0.02	0.21 ± 0.03
Tensile modulus, GPa	6.3 ± 0.6	7.0 ± 1.0
Extension at break, %	30	17

thalpy of fusion did not change significantly as a result of these UV irradiations. After 1 h of irradiation, copolymers containing low mole fraction bisacrylate exhibited lower crystallization temperatures and decreased enthalpy of crystallization, whereas PET-PBA15 did not further crystallize under the experimental conditions used herein.

Photocrosslinking of PETPBA15 fibers also was found to bring about small changes in their mechanical properties. These results, given in Table II, show that fiber tensile strength and tensile modulus increase moderately, whereas extension to break decreased as a result of irradiation. By comparison, 5 h of UV irradiation had no significant effect on the mechanical properties of the PET fiber. Dynamic mechanical properties of irradiated and unirradiated fibers are given in Figure 3. Irradiated fibers exhibit increased modulus retention above T_g. At 120°C, the storage modulus of the irradiated fiber is about two times that of the unirradiated fiber. However, at higher temperatures (>170°C), irradiated fibers show a sharper decrease in storage modulus; this decrease in modulus results from the low melting temperature of irradiated fibers. With irradiation, the tan δ peak temperature increased by more than 25°C and the magnitude of the tan δ peak decreased significantly, with the peak broadening toward higher temperature. These DMA results suggest both an increase in T_g and in the rubbery plateau modulus. Fiber shrinkage as a function of
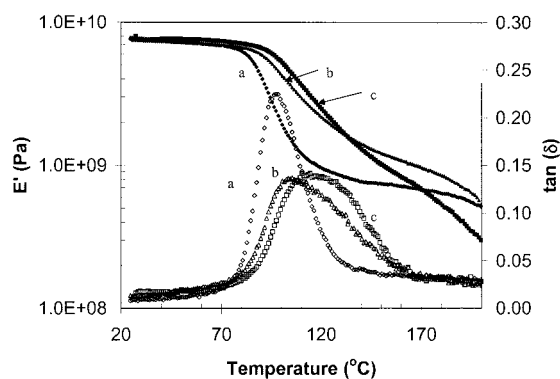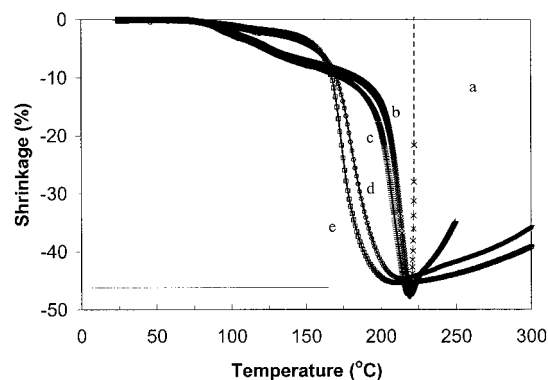

Figure 4 Effect of crosslinking on thermal shrinkage: (a) PET irradiated for h; (b) unirradiated PETPBA15; (c) PET-PBA15 irradiated for 1 h; (d) PETPBA15 irradiated for 5 h; (e) PETPBA15 irradiated for 10 h.

temperature is given in Figure 4. Fibers irradiated for over 5 h exhibit significantly reduced shrinkage up to about 150°C. Above this 150°C temperature these fibers show higher shrinkage because irradiated fibers exhibit significantly lower melting temperature. Upon melting, irradiated fibers do not break until they reach degradation temperature, whereas uncrosslinked [e.g., PET] fiber breaks immediately. All of the above thermal/mechanical results are consistent with crosslinking in the amorphous regions.

CONCLUSIONS

Fibers from PETPBA copolymer can be spun by conventional melt spinning and crosslinked by UV irradiation as shown by IR and NMR spectroscopic techniques as well as solubility test. The observed photochemical [2+2] cycloaddition reaction appears to occur in both the amorphous and the crystalline regions of the fibers, resulting in modest improvements in room-temperature mechanical properties. As would be expected, crosslinked fibers show increased T_g, increased rubbery plateau moduli, and reduced thermal shrinkage characteristics.

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Figure 3 DMA curves of PETPBA15 fibers: (a) unirradiated; (b) irradiated for 5 h; (c) irradiated for 10 h.

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