Acetophenone-assisted Main-chain Photocrosslinking of Poly(ethylene terephthalate)

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ABSTRACT: Maximum gel fraction of 99.1% was obtained under continuous UV irradiation of a UV energy of 200 J cm^{-2} on poly(ethylene terephthalate) (PET) containing only in presence of 2.9%(w/w) acetophenone (AP). The fragmented AP radicals abstract the hydrogen atoms of methylene units in PET, producing secondary methine radicals which couples to main-chain cross-links. The crystal structure of the crosslinked PET became disordered remarkably. The glass transition temperature disappeared and the peak thermal decomposition temperature was significantly retarded as much as 85°C. The crosslinking density and molecular weight between crosslinks reaches up to 0.129 mol g^{-1} and 7.7 g mol^{-1}, respectively. Also tensile modulus and strength increased by 200 and 72% compared with those of the pristine PET respectively, resulting in more toughened PET. The solid-state photocrosslinking may extend high-temperature applications of PET with enhanced thermal and mechanical properties. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39802.

INTRODUCTION

While uncrosslinked thermoplastic materials soften and eventually melt at elevated temperatures, chemically crosslinked polymer networks retard the molecular movement severely during deformation and hence are more stable against heat and mechanical stresses.[1,2] Chemical crosslinking of linear polymers can alter and improve several physicochemical properties including higher tensile strength, impact strength, shape-memory, and the resistances to solvents, heat, abrasion, and scratch, often changing a thermoplastic polymer into a thermoset.

Poly(ethylene terephthalate) (PET) is a thermoplastic and the third-most-produced polymer after PE and PP in the world.[3] It has been widely used in textile fibers, packaging bottles and materials due to its good tensile and impact strength, chemical resistance, and good barrier property. While the thermoplasticity enable the PET to be melt-processed and recycled into various articles, the fabricated PET articles require better thermal stability for some high temperature applications such as tire cords and insulation cables because the good strength and modulus of PET decrease dramatically above the glass transition temperature. Generally thermosetting polymers are considered to have the characteristics of low shrinkage, high modulus and excellent thermal resistance.

Chemical crosslinking of PET has been attempted by two main methods of thermal crosslinking and radiation crosslinking including photochemical crosslinking. The thermal methods involve the copolymerization with the crosslinkable comonomers of polyfunctional alcohols or acids in a standard PET synthesis of ethylene glycol and terephthalic acid or dimethyl terephthalate. The copolymerization of 5,5-bis(hydroxymethyl)-2-phenyl-1,3-dioxane and trans-esterification produced a thermoset polyesters.[4] The copolymerization of dimethyl 2,6-anthracenedicarboxylate and successive Diels–Alder cycloaddition with bis(maleimide) can form a thermally reversible crosslinked polyester.[5] Melt-state crosslinking was also possible by the trans-esterification of multifunctional crosslinkers or inorganic fillers added into the melt before PET fabrication. Simple incorporation of small amounts of pentaerythritol, trimellitate, or glucose into PET melts lead to a branched or crosslinked copolyesters.[6,7] Because surface hydroxyl groups of silica may react with the carboxy end-groups of the macromolecule, the blending of inorganic nanoparticles such as silica and polyhedral oligomeric silsesquioxanes also yielded the crosslinked structures depending on the formulation and processing conditions.[8,9]

Compared to melt-state crosslinking, solid-state processing via the diffusion of multifunctional reagents can be more

convenient for facile production of various shaped articles and a controlled functionalization at low degradation and deformation levels. Partially crosslinked polyester fibers were obtained by incorporating a solution of disulfonyl azide in the solid state and thermal decomposition of the azide under 230°C.[10] Thermal crosslinking of PET in melt and solid states was achieved by the diffusion of alkoxy silane derivatives and subsequent hydrolysis-condensation reactions of the alkoxysilane end groups and PET.[11,12] The thermal crosslinking of polymers may have some limitations such as the synthesis and copolymerization of crosslinkable copolymer derivatives before molding or extrusion, heat stability and miscibility of the crosslinkers, process modification of the PET fabrication, and the removal of unreacted impurities such as crosslinker or byproducts.

While PET retains relatively good resistance to radiation due to the aromatic groups that are effective at dissipating the radiation energy, severe molecular weight reduction was observed under high energy irradiation such as gamma and electron beam indicating dominant main chain scission of the macromolecule.[13–15] Because PET undergoes dominant main-chain scission and degradation during *in vacuo* electron beam irradiation, exceptionally high radiation is required to obtain a crosslinked PET network. Acetylene-impregnation of polyesters reduced chain scission and increased degree of crosslinking.[16] The combined use of crystallinity reduction and acetylene impregnation in the polyester improved the ratio of crosslinking to scission by the increased acetylene penetration and reduced β-bond scission.[17] Although only a small improvement in the gel fractions of PET was achieved by impregnating the acetylene, high irradiation dose under controlled atmosphere is still required.

Because high energy radiation was too energetic to induce crosslinking of some polymers rather than main-chain scission, photo-crosslinking has been considered as a better choice due to low energy level of the UV radiation. UV irradiation alone on PET did show chain scissions rather than crosslinking under oxidative conditions.[18] Some copolyesters such as poly(alkylene terephthalate-*co*-1,4-phenylene bisacrylate)[19] and poly(ethyleneterephthalate-*co*-2,6-anthracenedicarboxylate)[20] can be crosslinked through the photo-cycloaddition of the unsaturated ethylene linkages. PET copolymers containing benzophenone dicarboxylate chromophores can be photocrosslinked in the solid state, most probably by the hydrogen abstraction of the benzophenone segments in the backbone upon UV irradiation.[21] Photoactive comonomers for the crosslinking of polyesters must withstand the high-temperature polymerization and subsequent processing steps. In particular, the comonomers should resist thermally-induced crosslinking reactions during the polymerization and should be incorporated in low concentrations such that the physical properties of PET are not modified and maintain the economy of polyester production.

While high temperature trans-esterification of PET blends containing multifunctional monomers and particles usually produces the chain-extended (Y-type) crosslinking between terminal end groups of main PET chains, the radiation cross-linking of PET and its copolymers formed in the form of main-chain (H-type) crosslinks between adjacent backbone chains. Recently depth-gradient photocrosslinking of solid poly (ethylene oxide) film without photoinitiator can be to form H-type crosslinks, even though low crosslinking level can be achieved due to competing main-chain scission.[22] And poly (lactic acid) containing benzophenone as a photoinitiator was photocrosslinked in solid state by both amorpous and crystall crosslinking.[23] However there has been no main-chain photocrosslinking of solid-state PET without using copolymers and photo-reactive comonomers.

For the first time, PET containing acetophenone as a radical photogenerator was crosslinked via methine-methine coupling under UV irradiation after the sublimation of the aceotophenone. The molecular and crystal structures of the crosslinked polymer network were investigated by NMR and XRD analyses. Also the enhanced thermal stability and mechanical strength were assessed by solvent resistance, DSC, TGA, DMA, and tensile strength analyses.

EXPERIMENTAL

Materials and Chemicals

Granules of a regular grade poly (ethylene terephthalate) of a number-average molecular weight of 16,000 were supplied from Woongjin Chemicals. Acetophenone was used as a photoinitiator for generating free radicals. Phenol and deuterated phenol-d_6 were used as an extraction solvent and an NMR solvent for the PET respectively. All the chemicals, provided from Aldrich Chemicals, were used as received without further purification.

Preparation of PET Films and UV Irradiation

PET powders containing certain amounts of acetophenone were pressed between two heated brass plates at 280°C for 20 min under a pressure of 50 MPa, which was subsequently quenched with cold water. The thickness of the films was about 300 μm. And the acetophenone in the film was sublimated at 205°C for 10 min using a tenter in order to distribute the photoinitiator evenly within the PET films. For the annealed samples, the sublimated film was further heat-set for different time periods at 210°C. No appreciable changes in the phenol solubility during the film preparation processes described above, and the degradation of PET during the film preparation, if any, would decrease the level of crosslinking due to lower molecular weight of the degraded PET. UV irradiation was carried out at the room temperature on both sides of films by a continuous UV irradiator containing a UV bulb of a power of 80 W cm^{-1}. A Fe-doped mercury lamp was chosen to maximize the photocrosslinking of PET rather main chain scission because the maximum emission wavelength of the bulb located above 350 nm. Total UV energy was adjusted by controlling conveyor speed and irradiation passes.

Gel Fraction Measurement

Before the measurement, unreacted photoinitiator and its fragments in the irradiated PET films were removed by the high temperature treatment at 280°C for 1 h. The PET samples were weighed and then extracted with distilled phenol at 60°C for 2 h. The remaining undissolved gel was weighed to calculate a

gel fraction after vacuum drying. The gel fraction (%GF) was calculated using the following equation:

$$\%GF = \left(\frac{W_g}{W_0}\right) \times 100 \qquad (1)$$

where W_0 and W_g are the vacuum-dried weights of the UV-irradiated PET films before and after solvent extraction, respectively.

NMR Analysis

The pristine and crosslinked PET samples were dissolved in phenol and the insoluble gels were removed by filtration. The filtered polymer solutions were dried under vacuum and subsequently dissolved again in phenol-d_6. ^{1}H NMR spectra of the 0.1% (w/w) solution of PET samples were acquired by a 400 MHz NMR spectrometer (Avance Digital 400, Bruker). The qualitative and quantitative analyses were fulfilled to find out the croslnking mechanism and degree of crosslinking (DX) of the soluble fraction by the following peak area calculation:

$$\%DX = \left(\frac{2H_{b'}}{H_b + 2H_{b'}}\right) \times 100 \qquad (2)$$

where H_b and $H_{b'}$ are the peak areas of methylene and methine protons in the ^{1}H NMR spectra of the PET samples respectively.

Solid-state ^{13}C NMR spectra of the pristine and crosslinked films were also obtained to verify the photocrosslinking mechanism of PET using a 600MHz solid-state NMR spectrometer (Unityl NOVA600, Varian).

X-ray Diffraction (XRD) Analysis

The crystal structures of the photocrosslinked PET films were investigated by X-ray diffraction method. The diffraction patterns were recorded in the reflection mode with a Rigaku X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV and 150 mA) at a scanning rate of 2° min^{-1}. The spacing between the planes in the atomic lattice (d) and the thickness of crystallites (L) can be analyzed using Bragg's and Scherrer's equation:

$$d = \frac{\lambda}{2\sin\theta} \qquad (3)$$

$$L = \frac{\kappa \cdot \lambda}{\beta \cdot \cos\theta} \qquad (4)$$

where λ is the X-ray wavelength ($\lambda = 1.54$ Å), β is the full-width at half-maximum, κ is the shape factor ($\kappa = 0.9$), d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

Thermal Behavior and Thermal Stability

Thermal behavior of PET samples was recorded with a Perkin–Elmer Diamond DSC under nitrogen atmosphere. The melting point (T_m), glass-transition temperature (T_g) and enthalpy of melting (ΔH_m) of each sample were searched over 50–300°C at a heating rate of 10°C min^{-1}. The crystallinity (χ) was determined as the ratio of the experimental melting enthalpy to the theoretical melting enthalpy of a 100% crystalline polymer

($\Delta H_m^o = 140.1$ J g^{-1}). Also the effect photocrosslinking on the pyrolysis of the crosslinked PET films were assessed using a thermogravimetric analyzer (TGA Q500) over 50–600°C at a heating rate of 20°C min^{-1} under nitrogen gas atmosphere.

Tensile and Dynamic Mechanical Analyses

Tensile properties of the crosslinked films were measured at room temperature using a universal tensile tester (Instron 4467) using 100N load cell with a crosshead speed of 0.5 mm min^{-1} and grip length of 5 cm. The mean values were obtained from testing of ten samples or more. Dynamic mechanical measurement was made using a dynamic mechanical analyzer (DMA-Q800). Samples in the form of strips (25 mm × 3 mm × 0.2 mm) were measured in tensile mode at a constant frequency of 1.0 Hz as a function of temperature from 0 to 300°C at a heating rate of 1°C min^{-1} under nitrogen atmosphere. The storage modulus is assumed to be proportional to the crosslinking density of crosslinked polymers. The molecular weight between crosslinks (M_C, g mol^{-1}) and crosslinking density (X_c, mol g^{-1}) can be derived from the storage modulus measurement of the irradiated films, which are calculated by the following equations[22]:

$$M_c = \frac{3\rho RT}{E} \qquad X_c = \frac{1}{M_c} \qquad (5)$$

where ρ is the density of PET at 534.15 K, R is the gas constant (8.3145 MPa cm^{-3} K^{-1} mol^{-1}) and T is fixed at 534.15 K to evaluate M_c from the rubbery modulus values of the crosslinked polymers.

RESULTS AND DISCUSSION

Crosslinking Conditions and Gel Fractions

Acetophenone (AP) was the most efficient photoinitiator for the PET in obtaining high degree of gel formation compared with other Norrish type II photoinitiators such as benzophenones even though they have been a successful photoinitiator for the photocrosslinking of other thermoplastic polymers such as poly (ethylene), poly (ethylene oxide) and poly (lactic acid).[23] The efficiency of acetophenone (AP) over benzophenone (BP) in the photocrosslinking of PET may be influenced by more facile sublimation of AP withinin the film before UV irradiation and smaller molecular sizes of the photofragmented products of the AP such as methyl and benzoyl radicals after UV irradiation, which can encourage the uniform penetration and distribution of AP within the PET film coupled with effective hydrogen abstraction capability of the two photofragmented radicals of AP compared with BP. Also the AP may have higher miscibility to PET during film preparation due to similar chemical structure to the molecular structure of PET.

The effect of UV energy and AP concentration on the gel fraction (GF) of the irradiated PET films were shown in Table I and Figure 1. Without the photoinitiator, UV irradiation alone did not produce appreciable gel formation of the PET irrespective of sublimation or annealing treatments. Without the sublimation treatment, the PET films containing acetophenone gave marginal gel fraction only. The high-temperature sublimation treatment of the melt-cast PET film containing AP was

Table I. Gel Fractions of the UV-Irradiated PET

AP concn[a] (w/w %)	UV energy (J cm^{-2})	GF (%)	GF[b] (%)
0	0	–[c]	–[c]
	200	–[c]	–[c]
	0[d]	–[c]	–[c]
	200[d]	–[c]	–[c]
2.9	0	–[c]	–[c]
	200	17.1 ± 0.7	2.4 ± 0.5
	0[d]	–[c]	–[c]
	200[d]	99.1 ± 0.6	56.4 ± 0.8

[a] Determined after sublimation.
[b] Annealed for 10 min before irradiation.
[c] No gels are formed.
[d] Sublimated before annealing or irradiation.

indispensible to produce a substantial degree of gel formation. The highly crosslinked PET networks can be formed only when the AP particles are evenly distributed throughout the PET film by the sublimation treatment. Additional annealing treatment after the sublimation did decrease the gel fraction because the excessive heat treatment increases the crystallinity of the PET and decreased the AP content in the film, both of which are detrimental to the photocrosslinking.

Significant amount of UV energy is required to excite enough AP molecules to triplet state and to withstand the oxygen inhibition of the free radicals generated from the AP photoinitiator. With increasing UV energy up to 200 J cm^{-2}, the gel fractions of the crosslinked PET increased proportionally but the gel fraction decreased above the UV energy even with higher amounts of AP in the films, indicating that the photo-scission of the already-formed crosslinks became more dominant over new crosslink formation under the excessive UV irradiation. Nevertheless, the UV irradiation is expected to induce much lower polymer degradation compared with high energy irradiations such as electron beam or gamma rays.
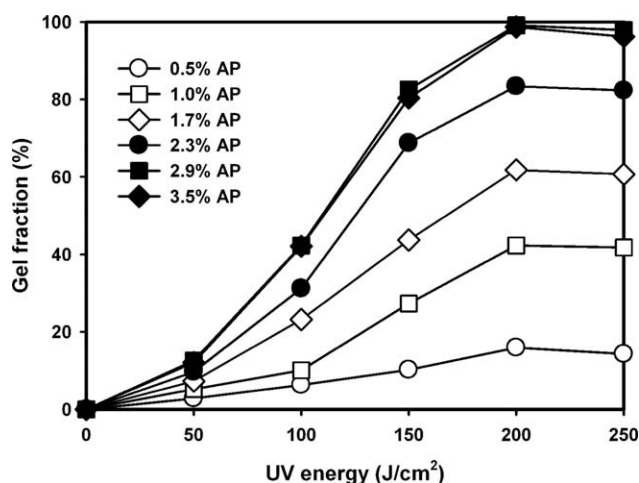
Figure 1. Gel fractions of PET depending on UV energy and AP concentration.

With increasing AP concentration in the PET after sublimation, the gel fraction increased up to 2.9%(w/w) AP and leveled off above the concentration. The excess APs in the surface can block the UV absorption of the APs within the film necessary for bulk crosslink formation, implying that AP concentration should be adjusted considering optical density distribution in relation with the film thickness of PET.

Molecular and Crystal Structures of the Photocrosslinked PET

Upon UV irradiation, the fragmentation of the excited acetophenone generates benzoyl and methyl radicals,[24] which can subsequently abstract hydrogen atoms from adjacent PET chains. The recombination of the polymer radicals forms a three-dimensional network imparting phenol insolubility to PET. To clarify the crosslinking mechanism of PET, ^{1}H NMR analysis was carried out using phenol-soluble fractions of the crosslinked PET as shown in Figure 2. The pristine PET showed well-defined spectrum where four benzene protons (a) appeared as doublet at 8.15 and 8.06 ppm and the methylene (b) in ethylene glycol unit as triplet peaks centered at 4.81 ppm. A sharp peak of methine protons (b') at 5.14 ppm newly appeared and strengthened as increasing gel content in the case of the photocrosslinked PET. The soluble fraction of the highest crosslinked sample (GF 99.1%) showed dominant methine protons over the methylene ones, suggesting that the crosslinks were formed by the recombination of methine radicals between the polymer main chains. The peak area ratio of methine to methylene protons in the ^{1}H NMR spectra corresponds to a degree of crosslinking of the soluble portion in the polyester. The degrees of crosslinking of the PET with gel fractions of 82.6 and 99.1% were determined to be 53.2 and 74.6% respectively, suggesting that approximately two or four adjacent ethyleneglycol units are interconnected by the methine-methine coupling as depicted in Figure 2. However no appreciable crosslinking between phenyl rings was observed, even though it has been reported that poly(butylene terephthalate), poly(neopentyl isophthalate), and poly(phenylene sulfide) can be photocrosslinked to form diphenyl linkages via phenyl–phenyl coupling under UV irradiation.[25,26]

The solid-state ^{13}C NMR analysis was also carried out to verify the crosslinked carbon structures as shown in Figure 3. The pristine PET showed the peaks of ester carbonyl carbons (a), quarternary carbons (b) and methine carbons (c) in benzene ring, and the methylene carbons (d) in ethylene glycol unit which appeared at 169.6, 134.7, 129.2, and 68.7 ppm, respectively. A new peak of the methine carbons (d') of the crosslinked PET appeared at 72.1 ppm, indicating the main-chain crosslinking by the coupling of adjacent methine radicals. Therefore benzoyl and methyl radicals are produced by the photochemical scission of excited triplet acetophenone under UV irradiation, which abstract the hydrogen atoms of methylene units in PET generating methine radicals as schematized in Figure 4. The methine radicals in the different polymer chains seemed to couple in zigzag pattern rather than complete ladder-like structures during the recombination of the carbon radicals to form covalent crosslinks.
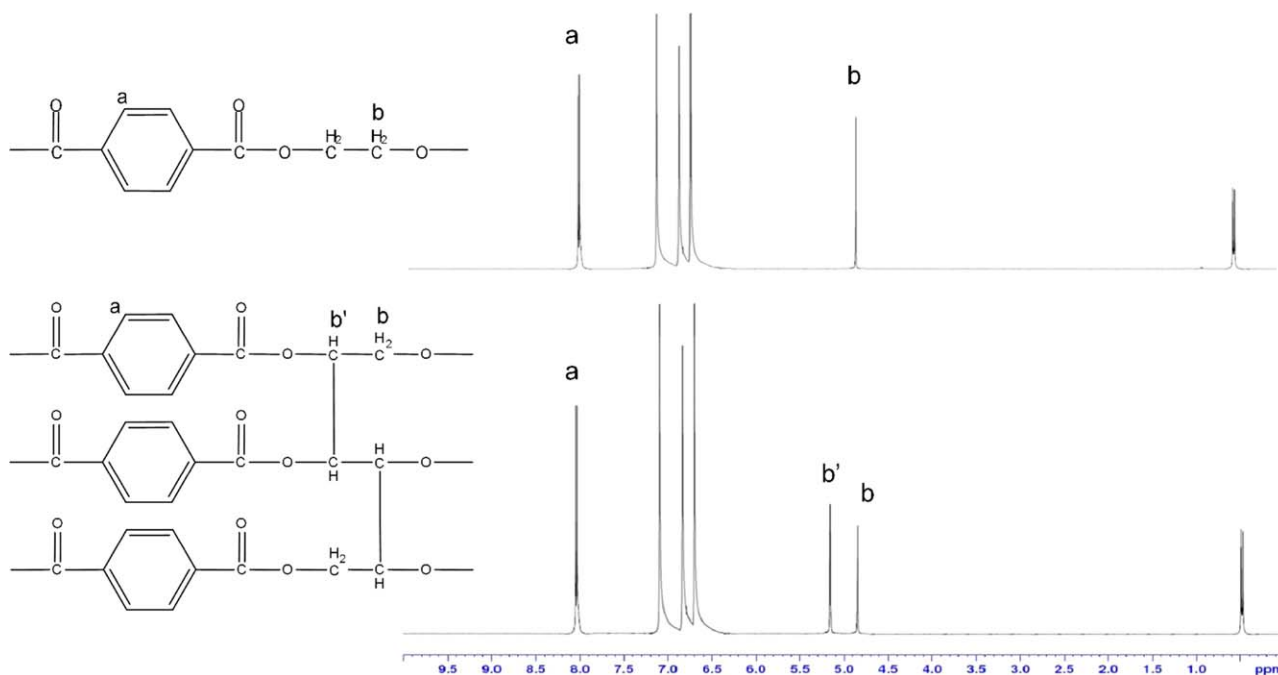
Figure 2. ^{1}H NMR spectra of pristine and crosslinked PET (GF 99.1%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The crystal structures of the crossliked PET films containing 2.9% AP, which was annealed at 210°C for 10 min after the sublimation and before the UV irradiation, were shown in Figure 5 and Table II. In case of untreated PET films, the main characteristic PET peak appeared 22.7°. Both diffraction angle, peak area, and crystallinity of the crosslinked PET
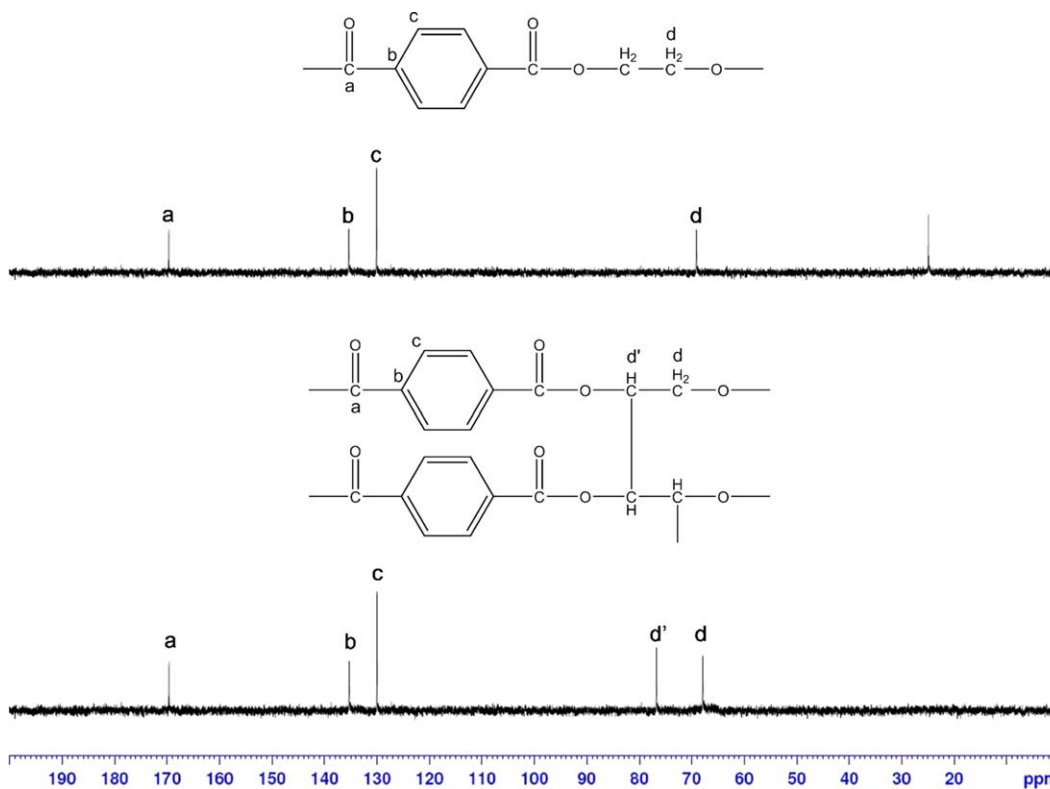

Figure 3. ^{13}C NMR spectra of pristine and crosslinked PET (GF 99.1%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
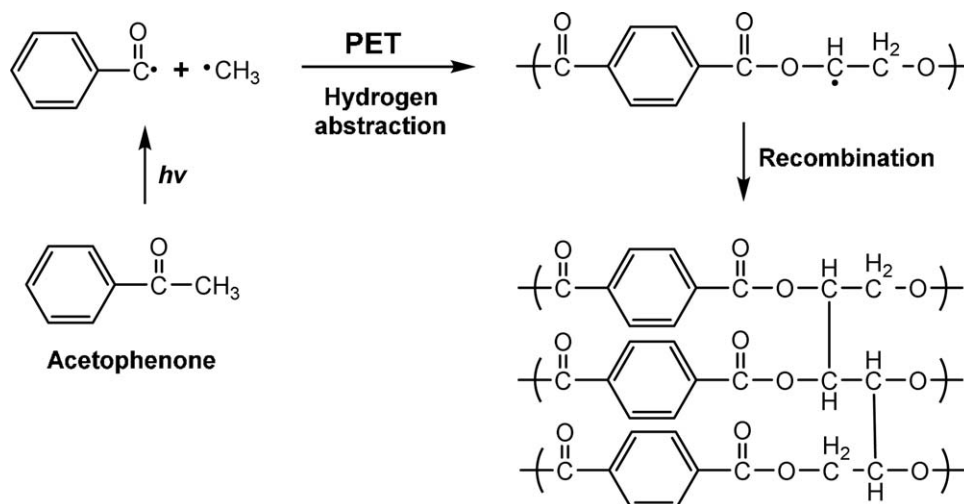
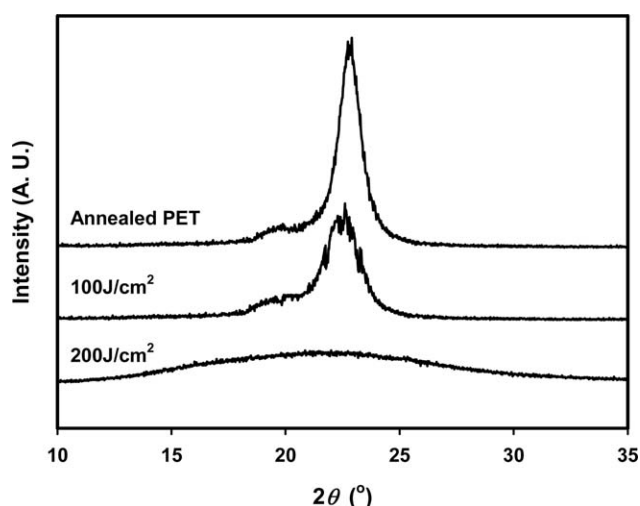**Figure 4.** Proposed photocrosslinking mechanism of PET containing AP.

Figure 5. XRD curves of the crosslinked PET.

films decreased as increase in UV energy, clearly indicating a structural transition from packed structure to disordered state with the increase in crosslinking. The inter-planar spacing of the atomic lattice increased and the thickness of crystallites decreased, resulting in significantly decreased crystallinity with the degree of crosslinking. Therefore the structure of the crosslinked network was formed in crystalline region as well as amorphous region as expected.[23] The crosslinked and disordered structures of the PET are expected to have significant influence on the thermal behavior and mechanical strength.

Table II. XRD Data of the Annealed PET Before UV Irradiation

UV energy (J cm^{-2})	GF (%)	2θ (°)	β (°)	d (Å)	L (Å)	Crystallinity
0	–	22.7	1.6	3.9	1.4	0.721
100	26.1	22.1	2.8	4.0	0.8	0.587
200	56.4	21.0	8.9	4.2	0.2	0.252

Thermal Behavior of the Photocrosslinked PET

The DSC curve and calorimetric data of the crosslinked PET were shown in Figure 6 and Table III. In case of pristine PET, glass transition temperature (T_g) appeared at 104.8°C, and melting point (T_m) and heat of fusion (ΔH_m) were 238.9°C and 48.3 J g^{-1}, respectively. However, the T_g of all the crosslinked PETs disappeared even at 42.3% GF and the T_m slightly increased together with decreased enthalpy. The crystallinity of PET also decreased with increasing gel fraction. The loss of T_g could be explained from the reduced mobility of the crosslinked macromolecules. The movements of macromolecular segments in the free volume are restricted due to the crosslinks which hold the polymer chains tight. However melting-free property cannot be achieved by the present photocrosslinking system.

The thermal degradation behavior of the crosslinked PET was determined by thermogravimetric analysis under nitrogen atmosphere as shown in Figure 7 and Table III. Thermal decomposition of the crosslinked PET was severely hindered
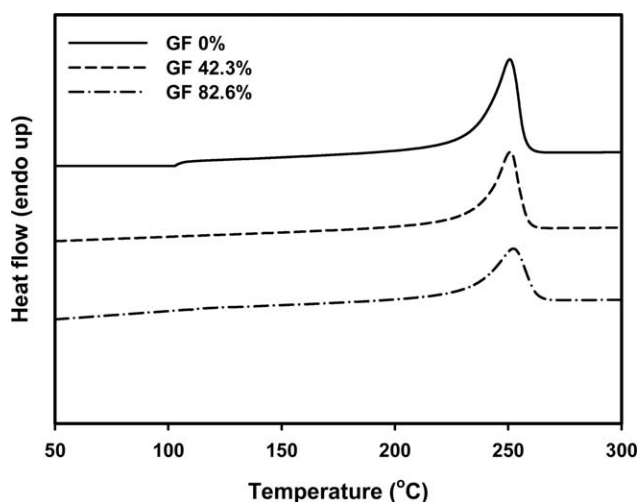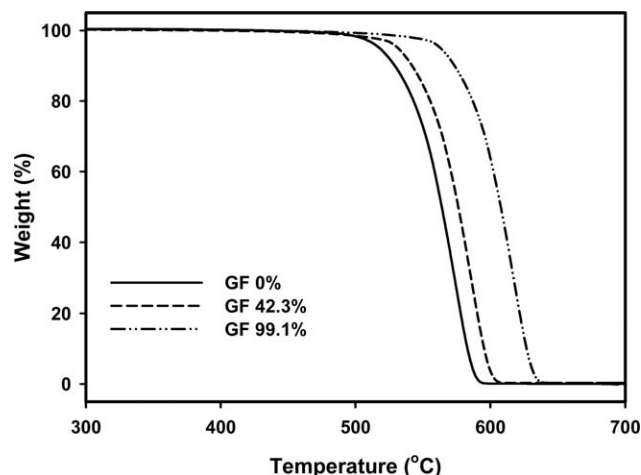

Figure 6. DSC curves of the crosslinked PET.

Table III. Calorimetric and TGA Data of the Crosslinked PET

GF (%)	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	DSC Xr[a]	XRD Xr[a]	T_{95} (°C)	T_{50} (°C)	T_5 (°C)	Peak[b] (°C)	ΔT[b]
0	104.8	238.9	48.3	0.345	0.312	346.2	392.3	414.6	402.8	–
42.3	–	242.2	40.9	0.292	0.256	360.7	406.9	429.1	417.3	+14.5
82.6	–	249.6	37.2	0.262	0.211	–	–	–	–	–
99.1	–	–	–	–	0.162	431.5	477.7	500.3	488.2	+85.4

[a] Degree of crystallinity.
[b] Maximum decomposition temperature in DTGA.

Figure 7. TGA curves of the crosslinked PET.

by the photocrosslinking. The decomposition temperatures of the crosslinked PET at the 5% weight loss (T_{95}) increased from 346.2°C for the pristine PET to 431.5°C as much as 85.3°C. Also the maximum peak of decomposition temperatures of the crosslinked PET increased by 85.4°C up to 488.2°C. The high thermal stability was attributed to the methine–methine crosslinks of the crosslinked PET network by retarding the pyrolysis of PET due to the presence of strong intermolecular covalent bonds between the polymer chains.

Dynamic Mechanical and Tensile Behaviors of the Photocrosslinked PET

The thermal viscoelasticity behavior of PET films is shown in Figure 8 and Table IV. The storage moduli at 0°C increased to

6.5 GPa from 5.2 GPa for the pristine PET because the crosslinked PET can store more energy elastically during deformation by the reduced chain mobility. The uncrosslinked PET film broke at 261°C just above the melting temperature because pristine PET chains considerably flow in molten conditions and totally loses its mechanical properties. The formation of a covalent network increases the elastic resistance of PET by hindering molecular motion in molten conditions. Because highly crosslinked polymer networks can effectively restrain the segmental mobility of PET during the heating, the crosslinked PET films did not break up at the temperature as expectedly, showing the permanent elastic modulus due to the chemical crosslinking. The crosslinked samples maintained the storage modulus as high as 2.0 GPa at the gel fraction of 99.1%. The molecular weight (M_c) between crosslinks of the crosslinked PET progressively decreased to 7.7 g mol^{-1} and the crosslinking density (X_c) increased up to 0.129 mol g^{-1} correspondingly. Such low molar mass between crosslinks suggested the abundant methine–methine coupling in most ethyleneglycol units indicating ubiquitous main-chain crosslinking of PET.

The introduction of crosslink structure into PET increases tensile modulus and strength with decrease in the elongation at break at room temperature, resulting from that the crosslinks can make the polymer harder and more brittle with increasing crosslinking density. The mechanical properties of the untreated and crosslinked PET films were given in Figure 9 and Table IV. The photocrosslinking increased both tensile strength and modulus as much as 72% and 200% respectively, coupled with decreased elongation at break as little as 27%. Unexpectedly the toughness of the crosslinked PET remarkably increased by 20%. The presence of crosslinks turns PET chains uncoil and flow difficult and the stress of

Table IV. DMA and Tensile Data of the Crosslinked PET

GF (%)	$\dot{E}$[a] (GPa)	M_c[b] (g mol^{-1})	X_c[c] (mol g^{-1})	tan δ (°C)	Modulus (GPa)	Strength (MPa)	Strain (%)	Toughness (GPa)
0	–	–	0	112.8	2.3 ± 0.5	53.8 ± 1.9	23.1 ± 1.2	1.0 ± 0.3
42.3	1.2	13.1	0.076	113.4	3.1 ± 0.1	62.7 ± 1.2	20.7 ± 0.8	1.2 ± 0.1
82.6	1.5	10.3	0.097	113.9	5.1 ± 0.6	79.1 ± 1.7	18.3 ± 0.9	1.0 ± 0.4
99.1	2.0	7.7	0.129	115.3	6.9 ± 0.5	92.4 ± 1.4	16.9 ± 1.4	1.2 ± 0.1

[a] Storage modulus at 261°C.
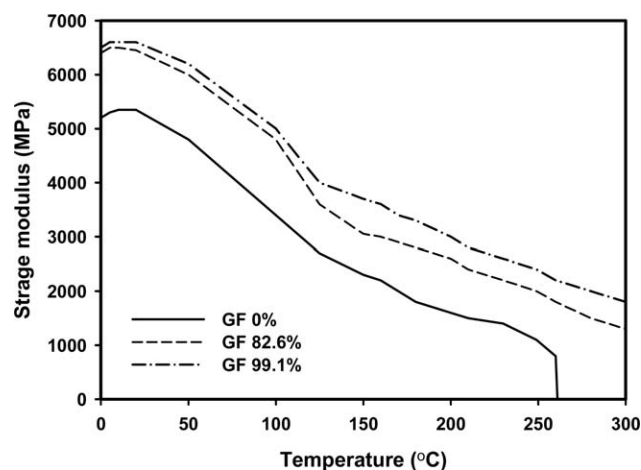[b] Molecular weight between crosslinks.
[c] Crosslinking density.

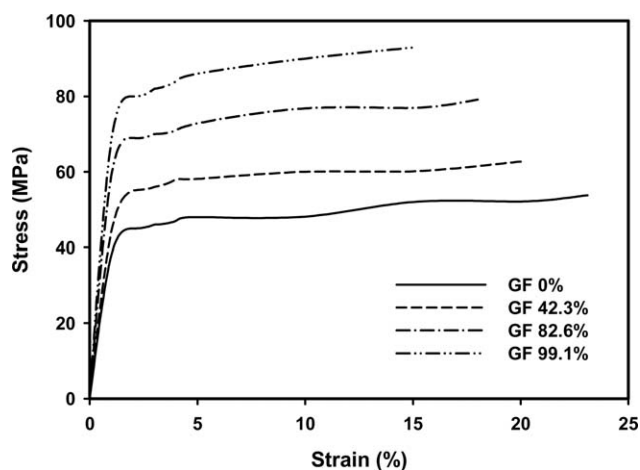**Figure 8.** DMA curves of the crosslinked PET.

Figure 9. Stress–strain curves of the crosslinked PET.

the crosslinked PET quickly increased so that the crosslinked samples become tougher and more brittle with an increase in crosslinking density. The mechanical properties depended on the distance between crosslink points as well as characteristics of the crosslinked polymer segments produced by the crosslinking treatment. The flexible ethane crosslinks between polymer chains introduced by the methine–methine coupling seem to be beneficial in imparting the improved tensile toughness and thermal stability to the PET. More thermally stable PET with better mechanical strength may find broader usage as structural adhesives, matrices for composites, protective coatings, foamed structures, binder resins with high char yield, and insulators for electronic packaging.

CONCLUSIONS

Crosslinked structures can be effectively introduced into PET film containing acetophenon as a photoinitiator by UV irradiation. The sublimation and subsequent UV irradiation of the PET containing 2.9% (w/w) AP can crosslink the PET up to the gel fraction of 99.1%. The benzoyl and methyl radicals, photofragmented from the excited acetophenones, abstracted the hydrogen atoms of the methylene units in PET, producing methine radicals which recombine to form main-chains crosslinks by methine–methine coupling. With the introduction of crosslinking structure, the elastic modulus of PET became higher and more resistant to high temperature deformation compared with that of pristine PET. The M_c and X_c of the crosslinked PET reached 7.7 g mol^{-1} and 0.129 mol g^{-1} respectively. Thermal stability of photo-crosslinked PET films improved as indicated by loss of T_g, lower heat of fusion and higher peak decomposition temperature as much as 85.4°C. Also tensile toughness substantially increased due to the harder and stronger polymer networks with slight reduced elongation at break as increase in crosslinking density. The thermally resistant PET can be made by the photocrosslinking after fabrication as films and fibers, which can widen the high temperature applications of PET due to high thermal stability and enhanced mechanical strength.

ACKNOWLEDGMENTS

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