Amorphous Copolyesters Based on 1,3/1,4-Cyclohexanedimethanol: Synthesis, Characterization and Properties

Yuhsin Tsai,[1,2] Cheng-Hsing Fan,[1] Chi-Yuan Hung,[1] Fuu-Jen Tsai[2,3,4]

[1]Nano-Powder and Thin Film Technology Center, Industrial Technology Research Institute, Tainan, Taiwan
[2]Graduate Institute of Chinese Medical Science, China Medical University, Taichung, Taiwan
[3]Department of Medical Genetics, Pediatrics and Medical Research, China Medical University Hospital, Taichung, Taiwan
[4]Department of Biotechnology and Bioinformatics, Asia University, Taichung, Taiwan

ABSTRACT: Two series of amorphous copolyesters, PETGN and PETGS, were synthesized by the copolymerization of 2,6-naphthalene dicarboxylic acid (NDA) (0–40%), succinic acid (SA) (0–40%), 1,3/1,4-cyclohexanedimethanol (1,3/1,4-CHDM) (10–50%), ethylene glycol (EG), and terephthalic acid (TPA). The compositions and molecular weights of the copolyesters were determined by ^{1}H NMR spectroscopy and viscometry, respectively. The thermal behaviors were studied over the entire range of copolymer compositions, using DSC and TGA. The optical characteristics, heat-shrinkable effects and tensile properties of these polymers were also determined. Experimental results indicated that the thermal, optical, ten-sile, and shrinkage properties of PETGN and PETGS were functions of NDA or SA content. DSC and X-ray analysis demonstrated that both PETGN and PETGS series were amorphous. Incorporating NDA and SA influenced the T_g values of those polymers, from about 37°C for $PETG_{30}S_{40}$ to 89°C for $PETG_{30}N_{40}$. Furthermore, the shrinkage of these amorphous copolyesters was more than 40% when the heating temperature was higher than the corresponding T_g. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2598–2604, 2008

Key words: polyester; copolymerization; films; amorphous; transparency

INTRODUCTION

The favorable basic properties of poly(ethylene terephthalate) (PET) make this polymer attractive for an increasing variety of domestic and technical applications. However, the tendency of PET to crystallize severely limits the increase in the range of uses of this polymer to some fields,[1,2] in which both transparent and heat-shrinkable properties are required.

Glycol-modified PET copolyester (PETG), generally poly(ethylene terephthalate-co-1,4-cyclohexylene-dimethylene terephthalate), is an amorphous thermoplastic of the commercial PET family. The presence of the bulky 1,4-CHDM group in the main chain unit makes PETG highly amorphous and without a melting temperature (T_m).[3–7] Owing to its highly amorphous nature, PETG exhibits very high transparency and excellent clarity. One of the major PETG applications is used as the transparently shrinkable film which shows the shrinkage behavior upon heating. Shrinkable polyester films are particularly advantageous for use on polyester containers, as they facilitate the recycling process by allowing polyester containers to be reclaimed along with their polyester labels without introducing incompatible resins into the recycling stream.[8]

We recently synthesized a PET copolymer by copolymerizing 1,3/1,4-CHDM, EG, 5-tert-butyli-sophthalic acid, and TPA.[9] This polyester is amorphous and has the optical transmission about 88%. To obtain 1,3/1,4-CHDM-based amorphous copolyesters with various values of T_g for different shrinkable film applications, this work reports the preparation and properties of several series of new polyesters PETGN and PETGS, which are the derivatives of 1,3/1,4-CHDM-based PETG. PETGN is prepared from EG, TPA, 1,3/1,4-CHDM, and NDA; PETGS is prepared from EG, TPA, 1,3/1,4-CHDM and SA. The thermal, optical, mechanical, and heat-shrinkable properties polymers are studied.

EXPERIMENTAL

Materials

TPA (98%), EG (99+%), NDA (99%), SA (99%), trifluoroacetic acid (TFA), phenol, tetrachloroethane,
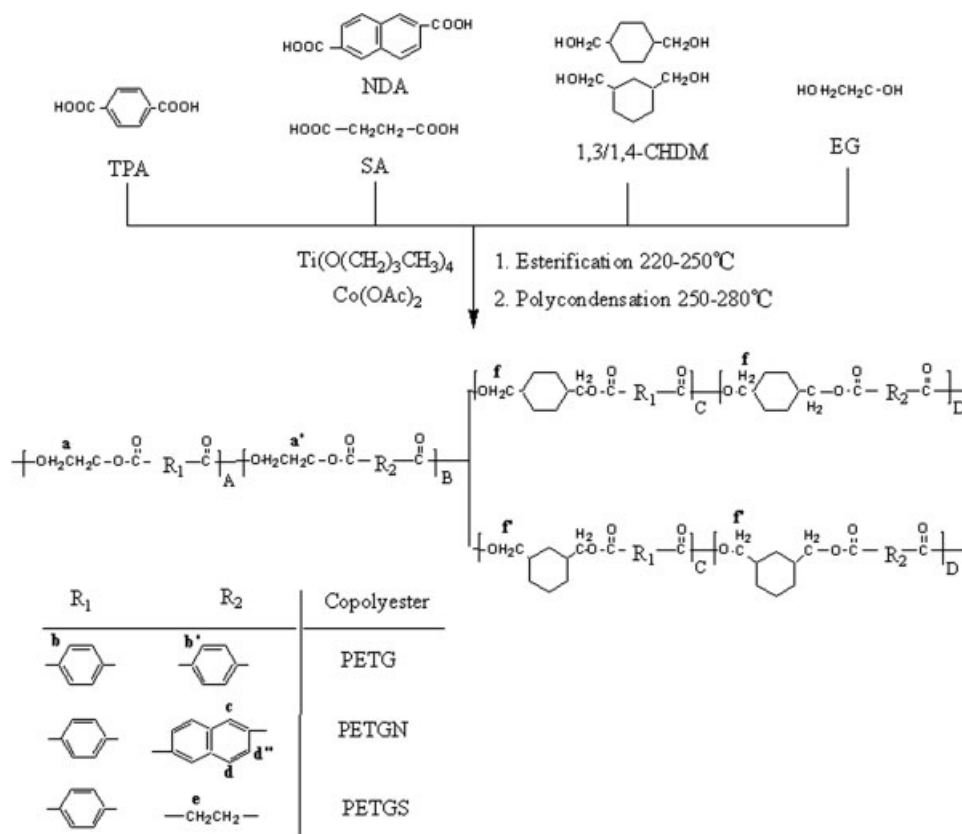
Figure 1 Outline of synthetic route followed for the preparation of PETG, PETGN and PETGS copolyesters. NMR assignments are indicated on the chemical formula of the copolymer.

cobalt acetate catalyst (Co(Ac)$_2$), and tetrabutyl titanate catalyst (Ti(O(CH$_2$)$_3$CH$_3$)$_4$) (99.99%) were purchased from Aldrich (USA). The 1,3/1,4-CHDM, which was an equilibrium mixture of 1,4-trans/1,4-cis/1,3-trans/1,3-cis 29.1/13.3/30.9/26.7, was purchased from Dow Chemical Company, USA. All the chemicals were used as received without further purification.

Synthesis

All of the copolymers were prepared by two-stage melt polycondensation (esterification and polycondensation) in an autoclave reactor. The details of the synthesis can be found elsewhere.[9–11] In each preparation, the reaction mixture comprised excess EG, various amounts of diol and diacid (molar ratio of diol/diacid = 1.4), 350 ppm Ti(O(CH$_2$)$_3$CH$_3$)$_4$ and 90 ppm Co(OAc)$_2$ by weight. The reaction mixture was heated to the final temperature (220–250°C) in an atmosphere of nitrogen, and was stirred at a constant speed (500 rpm). This first step was considered to be completed after 4 h, when the theoretical amount of water was collected.

In the second step, a vacuum (5 Torr) was applied slowly over a period (of about 30 min) to avoid excessive foaming and to minimize oligomer sublimation, which was a potential problem during melt polycondensation. The temperature was increased with the strength of the vacuum. The polycondensation was continued for about 2.5 h until the agitator speed decreased to 350 rpm, because the viscosity of the melt increased. After the polycondensation reaction was completed, the product was obtained from the autoclave reactor. All polyester samples were ground in a mill, sieved, washed with methanol, and dried at 60°C for 24 h at reduced pressure.

The copolyesters described in this work are indicated in Figure 1 and Table I. Figures 2 and 3 present the ^{1}H NMR spectra of the PETG$_{30}$N$_{10}$ and PETG$_{30}$S$_{20}$ copolymers, respectively.

Characterization

The intrinsic viscosities of the polymers were measured using an Ubbelohde viscometer at 25°C in a mixture of phenol and tetrachloroethane (60 : 40, w : w). ^{1}H NMR spectra were obtained on a Bruker DRX-400 spectrometer at 25°C and 400 MHz. Duterated trifluoroacetic acid (TFA) was used as solvent.

Thermal characterization was performed in an atmosphere of dry nitrogen using a differential scan-

TABLE I
Compositions, Viscosities, and Thermal Properties of Polyesters

Polyester	Composition[a] TPA/NDA (or SA)/EG/CHDM (mol %)	Composition[b] TPA/NDA (or SA)/EG/CHDM (mol %)	Viscosity[c] IV (dL/g)	Thermal properties (°C)			
				T_g[d]	T_m[e]	T_{cc}[e]	T_d[f]
PETG$_{10}$	100/0/90/10	100/0/90.4/9.6	0.67	76	221	–	404
PETG$_{20}$	100/0/80/20	100/0/80.6/19.4	0.65	76	196	–	399
PETG$_{30}$	100/0/70/30	100/0/71.0/29.0	0.73	77	–	–	398
PETG$_{40}$	100/0/60/40	100/0/61.4/38.6	0.73	77	–	–	398
PETG$_{50}$	100/0/50/50	100/0/51.6/48.4	0.73	78	–	–	396
PETG$_{30}$N$_{10}$	90/10/70/30	90.3/9.7/70.9/29.1	0.71	80	–	–	406
PETG$_{30}$N$_{20}$	80/20/70/30	80.5/19.5/70.9/29.1	0.73	83	–	–	410
PETG$_{30}$N$_{30}$	70/30/70/30	70.9/29.1/70.8/29.2	0.73	85	–	–	413
PETG$_{30}$N$_{40}$	60/40/70/30	61.1/38.9/70.8/29.2	0.65	89	–	–	416
PETG$_{30}$S$_{10}$	90/10/70/30	90.3/9.7/71.0/29.0	0.65	65	–	–	396
PETG$_{30}$S$_{20}$	80/20/70/30	80.6/19.4/70.8/29.2	0.67	52	–	–	393
PETG$_{30}$S$_{30}$	70/30/70/30	70.8/29.2/70.8/29.2	0.65	44	–	–	390
PETG$_{30}$S$_{40}$	60/40/70/30	61.3/38.7/70.9/29.1	0.73	37	–	–	388

[a] Theoretical composition.
[b] Determined from ^{1}H NMR spectra.
[c] Intrinsic viscosity (dL/g) measured at 25°C in a phenol/tetrachloroethane mixture 60/40 w/w.
[d] T_g was obtained as the inflection point of the heating DSC traces of the melt-quenched samples recorded at 20°C/min.
[e] The T_m and T_c temperatures of the pristine samples were measured by DSC at heating/cooling rates of 20°C/min.
[f] Temperature at which a 10% weight loss was observed in the TGA traces recorded at 20°C/min.

ning calorimeter (DSC) (Seiko SSC-5200). Both temperature and heat flow were calibrated using indium and tin standards. In the DSC measurement, a polymer sample (3.0–5.0 mg) was preheated at 300°C for 10 min to remove its thermal history, and then cooled to 0°C at a rate of 20°C/min. Then, the cooled sample was heated to 300°C at a rate of 20°C/min. T_m and T_c (crystallization temperature) were the temperatures of the peak maximum transition measured in the heating run and the cooling run, respectively. T_g was the temperature of the middle point of the glass transition in the heating run. Thermogravimetric analysis (TGA) was performed using a Seiko Exstar 6000 thermobalance at a heating rate of 20°C/min in an atmosphere of nitrogen.

The samples for X-ray analyses and the UV ray transmittance test were prepared from the glassy, unoriented, and amorphous film, which was obtained by melt compression followed by immersion in ice-cold water. X-ray analyses were performed using a Siemens D-500 diffractometer with Kα Cu radiation at a wavelength of 1.5418 Å. The UV ray transmittance of the polyesters was measured on a UV1000F ultraviolet spectrophotometer to characterize the UV radiation transmittance of the polyesters. All polymers were injection-molded into unheated molds in an injection-molding machine to yield specimens for tensile tests. The tensile mechanical properties were measured according to the ASTM D 638 standard on injection-molded specimens. The drawing speed used in the tests was 20 mm/min. The presented mechanical properties are averages of five tests.

The monoaxial shrinkage effect of copolyesters was performed on rectangular specimens (50 × 10 mm) cut from amorphous, isotropic films with a thickness of about 1-mm. The tests were conducted on a Zwick BZ2.5/TN1S universal tensile testing apparatus equipped with a temperature-controlled thermal cabinet. The specimen was stretched to an extension ratio of about 200% for 5 min at a temperature which was 20°C higher than the corresponding T_g. Then, it was fixed under this strain and cooled to 25°C for 10 min to measure the original length (L_o). Finally, the specimen was placed into the thermal cabinet again at a specific temperature for 5 min without any stress and the final length (L_f) was
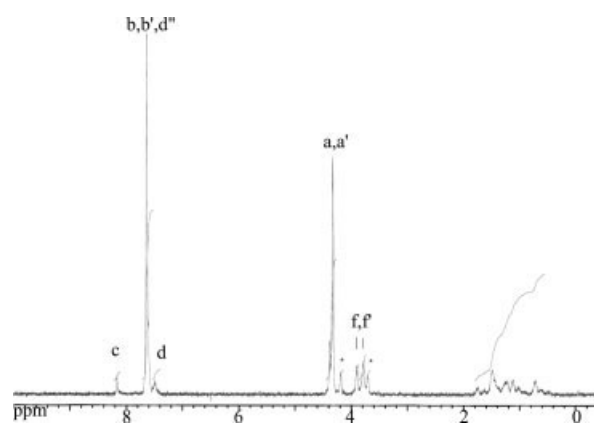

Figure 2 400 MHz ^{1}H NMR spectra of PETG$_{30}$N$_{10}$ recorded in deuterated trifluoroacetic acid (TFA). Peaks that arise from diethylene glycol units, present in small amounts in the polyesters, are labeled (*).
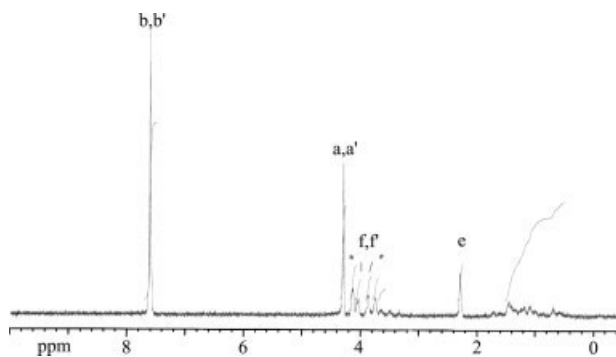
Figure 3 400 MHz ^{1}H NMR spectra of PETG$_{30}$S$_{20}$ recorded in deuterated trifluoroacetic acid (TFA). Peaks that arise from diethylene glycol units, present in small amounts in the polyesters, are labeled (*).

recorded. The shrinkage at this specific temperature was calculated by the following equation[8,12,13]

$$\text{Shrinkage} = (L_o - L_f)/L_o \times 100\%$$

RESULTS AND DISCUSSION

Synthesis

The copolyesters described in this work were prepared by a two-step melt-polycondensation, as indicated in Figure 1. TPA and NDA (or SA) with EG and 1,3/1,4-CHDM were esterified to form low-molecular-weight hydroxy-capped esters in the first stage. This process occurred at 220–250°C with the generation of water, which was continuously removed from the system to drive the reaction in the desired direction. The copolycondensation of these compounds, to yield PETG, PETGN, or PETGS copolyesters, occurred in the second step at 280°C under vacuum conditions to eliminate the excess EG, which was added at the beginning of synthesis. Table I presents the compositions, viscosities, and thermal properties in each case. The TPA/NDA (or SA)/EG/CHDM molar ratios covered a wide range of compositions. The determination of the intrinsic viscosity indicated that all polymers had relatively high molecular weights, given that their intrinsic viscosities were between 0.65 and 0.73 dL/g. The chemical structures of the polyesters were ascertained by ^{1}H NMR spectroscopy,[14–16] as shown in Figures 2 and 3. The NMR analysis clearly revealed that the composition of the resulting copolymer was essentially the same as that of the theoretical feed from which it was generated.

Thermal properties

The thermal behavior of all copolyesters was studied using TGA and DSC as shown in Table I. The DSC

results indicated that PETG copolyesters with < 20 mol % 1,3/1,4-CHDM, such as PETG$_{10}$, and PETG$_{20}$, were crystallizable, while those with > 20 mol% 1,3/1,4-CHDM, such as PETG$_{30}$, PETG$_{40}$ and PETG$_{50}$, were amorphous. These results indicated that introducing 1,3/1,4-CHDM into the PET homopolymer markedly affected both the melting temperature and the crystallinity of the copolyesters. Although studies have demonstrated that the incorporation of 1,4-CHDM into PET can increase the T_g of the resulting polymer,[3–5,17] incorporating different amounts of the 1,3/1,4-CHDM herein have different effects. All PETG samples in this work had similar T_g of about 76–78°C. Perhaps this observation was contributed by the 1,3-cis and 1,3-trans isomers of 1,3/1,4-CHDM monomer, which were similar to the effects of the isophthalic acid monomer in poly(ethylene terephthalate- co- ethylene isophthalate).[18,19] Various NDA or SA contents were introduced into the PETG$_{30}$ copolyester to form PETGN and PETGS series, respectively, which were characterized by DSC. T_m were not observed in neither PETGN nor PETGS series, like amorphous PETG$_{30}$, indicating that the incorporation of various amounts of NDA and SA into PETG$_{30}$ did not affect the crystallization behavior of PETG$_{30}$ macroscopically.

Table I also reveals that the T_g values of the PETGN series increase with the NDA content from 80°C for PETG$_{30}$N$_{10}$ to 89°C for PETG$_{30}$N$_{40}$. This trend was reversed in the PETGS series, in which the T_g values declined as the SA content increased, from 65°C for PETG$_{30}$S$_{10}$ to 37°C for PETG$_{30}$S$_{40}$. These results were consistent with the literature, which showed that naphthalene-substituted units increased the stiffness of the polymer chains and aliphatic substituted units increased the softness of the resulting copolyester.[20,21] Figure 4 plots DSC traces for polyesters PETG$_{10}$, PETG$_{30}$, PETG$_{50}$, PETG$_{30}$N$_{30}$ and PETG$_{30}$S$_{30}$, during both heating and cooling at a rate of 20°C/min.

The theoretical glass transition temperatures of the copolyesters were calculated by using the Flory-Fox equation and plotted along with the experimental data,[6,7] as shown in Figure 5.

$$1/T_g = W_1/T_{g_1} + W_2/T_{g_2} \quad (\text{Flory} - \text{Fox equation})$$

where W_1 and W_2 are the mole fractions of relative NDA(SA) amounts in the copolyesters and T_g, T_{g1}, and T_{g2} are the glass transition temperatures of copolyesters, PETG$_{30}$, and PETG$_{30}$N$_{40}$(PETG$_{30}$S$_{40}$), respectively.

TGA measurements were made in an atmosphere of nitrogen, in the 30–800°C temperature range, to evaluate the thermal stability of the polyesters. Table I compares the decomposition temperatures, measured at 10% weight loss, of all of the polyesters. The
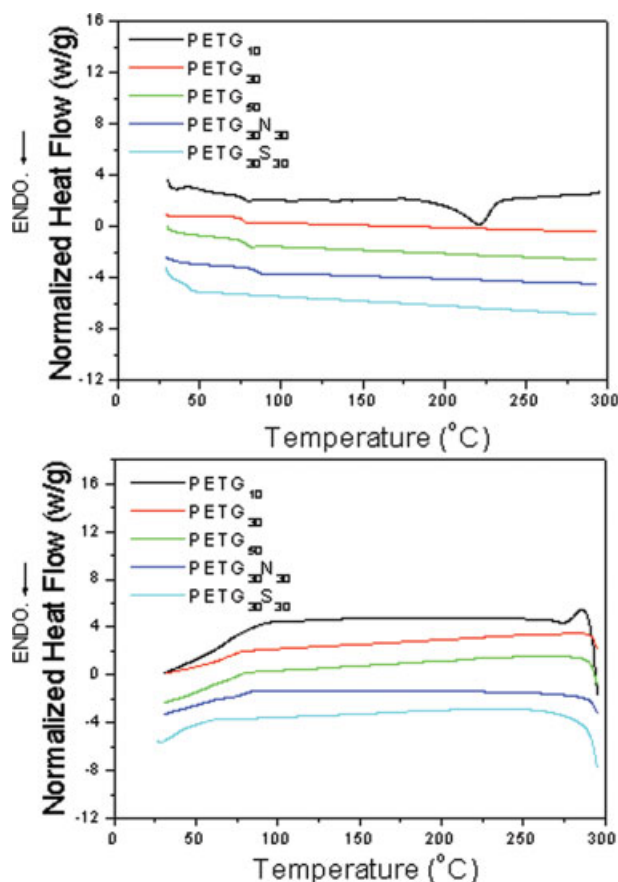
Figure 4 Comparison of DSC traces of PETG$_{10}$, PETG$_{30}$, PETG$_{50}$, PETG$_{30}$N$_{30}$, and PETG$_{30}$S$_{30}$ copolyesters: top - second heating; bottom - first cooling. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

results in Table I reveal that the incorporation of NDA units slightly increases the thermal stability of PETG$_{30}$. This effect must be associated with the pres-

Figure 6 TGA traces of PETG$_{30}$, PETG$_{30}$N$_{30}$ and PETG$_{30}$S$_{30}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ence of naphthalene structures in the polyester chain, because a similar increase in the decomposition temperature of poly(ethylene terephthalate-*co*-2, 6-naphthalate) is observed.[22,14] This trend was reversed, however, when the terephthalic units were replaced by succinic units, perhaps because aliphatic structures were less stable than aromatic structures. Nevertheless, all polymers remained unchanged as the temperature was increased to 380°C. The degradation rate was maximal between 430 and 450°C. Figure 6 plots the TGA traces of PETG$_{30}$, PETG$_{30}$N$_{30}$ and PETG$_{30}$S$_{30}$.

X-ray diffraction

Figure 7 compares the normalized intensity profiles of the X-rays scattered in reflection mode of PETG$_{30}$, PETG$_{30}$N$_{30}$, PETG$_{30}$S$_{30}$, and PET. All samples were prepared as amorphous materials by melt compression followed by immersion into ice-cold water.
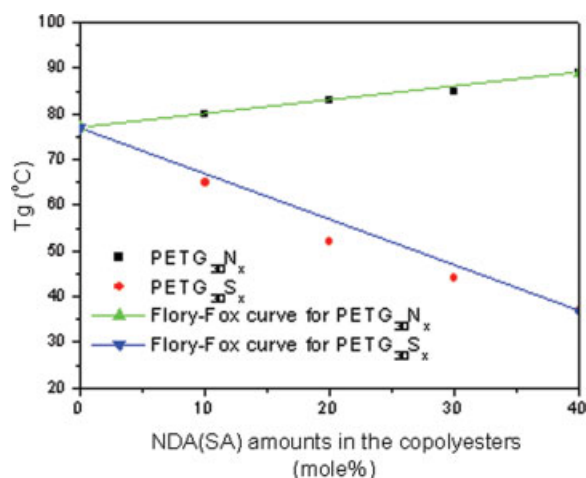

Figure 5 Plot of T_g versus NDA (SA) amounts of the copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
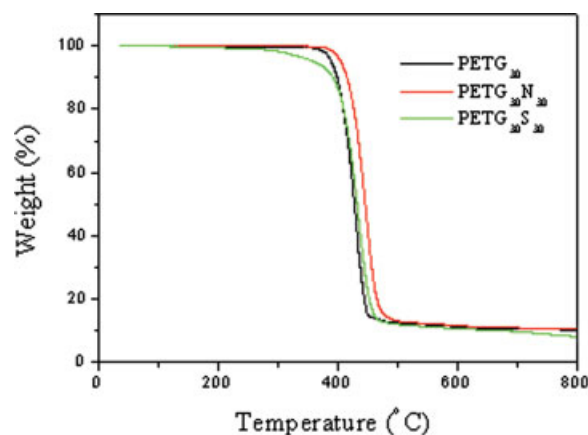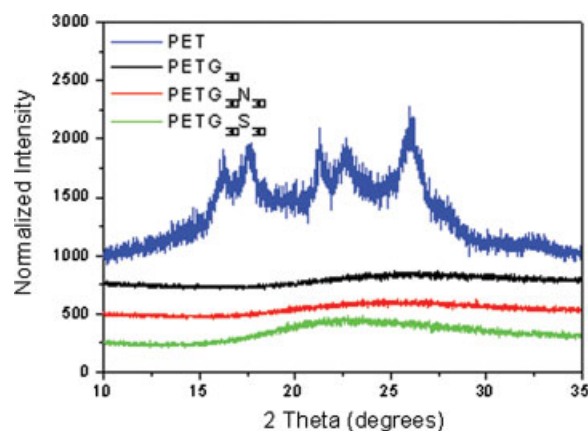

Figure 7 Wide-angle X-ray diffraction pattern of polyesters PETG$_{30}$, PETG$_{30}$N$_{30}$ and PETG$_{30}$S$_{30}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Optical Transmittance and Tensile Properties of Polyesters

Polyester	Transmittance λ (400 nm) (%)	Tensile mechanical properties				
		Young's modulus (Mpa)	Yield stress (Mpa)	Tensile strength at break (Mpa)	Elongation at break (%)	Type[a]
PETG$_{10}$	87.2	1821	57	42	162	HT
PETG$_{20}$	88.4	2027	52	38	152	HT
PETG$_{30}$	88.7	2139	52	27	146	HT
PETG$_{40}$	88.8	2151	53	28	144	HT
PETG$_{50}$	88.7	2163	52	28	145	HT
PETG$_{30}$N$_{10}$	86.9	2159	53	28	148	HT
PETG$_{30}$N$_{20}$	86.9	2208	53	29	145	HT
PETG$_{30}$N$_{30}$	85.5	2233	54	30	143	HT
PETG$_{30}$N$_{40}$	83.5	2290	56	33	144	HT
PETG$_{30}$S$_{10}$	79.3	2103	53	25	137	HT
PETG$_{30}$S$_{20}$	77.5	2087	50	24	146	HT
PETG$_{30}$S$_{30}$	74.2	2054	43	19	154	HT
PETG$_{30}$S$_{40}$	71.7	NT[b]	NT[b]	NT[b]	NT[b]	NT[b]

[a] HT: hard and tough.
[b] NT: not tested because the sample was too soft at room temperature to be tested.

Three high-intensity reflections that were characteristic of the triclinic structure of PET were observed, at 2θ values of about 17.0°, 22.8° and 26.2°.[23] The polyesters PETG$_{30}$, PETG$_{30}$N$_{30}$, and PETG$_{30}$S$_{30}$ yielded broad amorphous X-ray diffraction patterns. These results indicated that the polymers were amorphous and were consistent with DSC measurements.

Optical, tensile and shrinkage properties

The optical property of polyesters is generally evaluated by measuring the transmittance of UV–visible rays through the polyesters. A higher UV-ray transmittance corresponds to a better optical property of that sample. Table II presents the specular light transmission values for λ = 400 nm. Since PET is a semicrystalline polymer, its transmittance for λ =

400 nm is about 80%.[9] When 1,3/1,4-CHDM was incorporated into PET to form amorphous PETG$_{30}$, PETG$_{40}$ and PETG$_{50}$, the optical transmittance of these amorphous copolyester increased up to 89%. In the PETGN series, the transmission decreased as the NDA content increased, from 87% for PETG$_{30}$N$_{10}$ to 84% for PETG$_{30}$N$_{40}$, which still exceeded 70% (the transmittance of PEN for λ = 400 nm).[24] The PETGS series yielded similar results. Figure 8 presents spectrograms of PETG$_{30}$, PETG$_{30}$N$_{30}$, and PETG$_{30}$S$_{30}$.

Table II presents the tensile properties of the PETG, PETGN, and PETGS series. In the PETG series, the elongation and tensile stress at break were affected by the content of 1,3/1,4-CHDM comonomers. The crystallizable polymer (PETG$_{10}$ and PETG$_{20}$) was semicrystalline and tended to crystal-
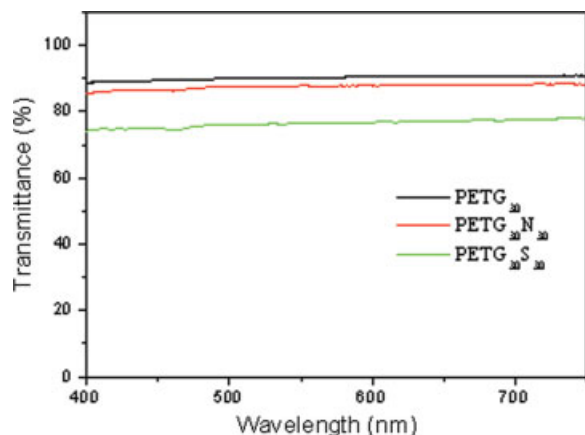

Figure 8 Optical transmittance of polyesters PETG$_{30}$, PETG$_{30}$N$_{30}$ and PETG$_{30}$S$_{30}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
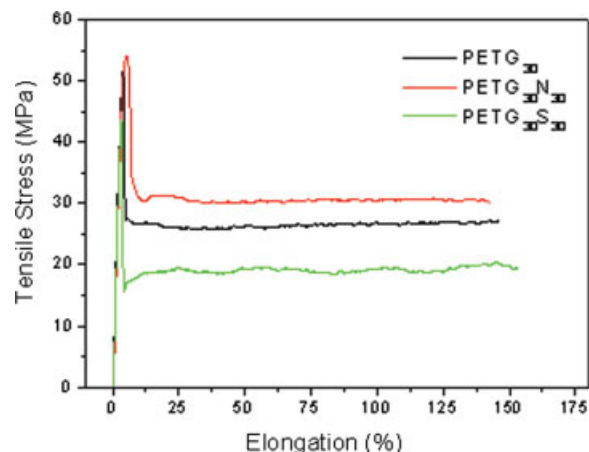

Figure 9 Typical stress-strain diagrams of polyester copolymers of the specified indicated compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
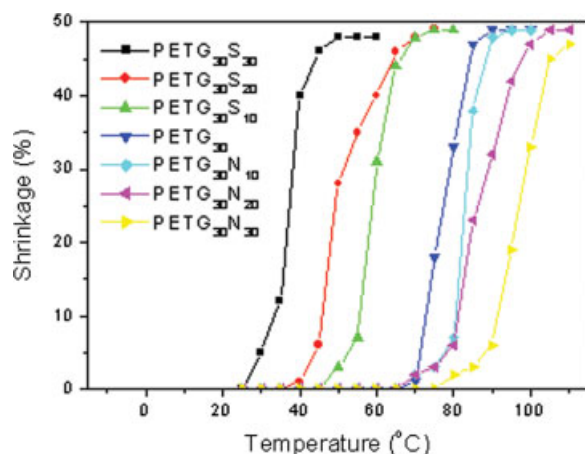
Figure 10 The shrinkage property of copolyesters as a function of the heating temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lize during deformation, contributing to higher tensile stress and elongation at break than amorphous polymer ($PETG_{30}$, $PETG_{40}$, and $PETG_{50}$). However, the Young's modulus of along the series of PETG copolymers increased steadily with the content of CHDM units, perhaps because of the substitution of linear EG for the bulky and cyclic 1,3/1,4-CHDM. The diacid contents also affected the Young's modulus, the yield stress and the tensile strength at the break of copolymers in the PETGN and PETGS series. The Young's modulus, the yield stress and the tensile strength at break increased steadily with the NDA content in the PETGN series. PETGS series exhibited the opposite trends. These results may follow from the effect on stiffness of incorporating diacid monomers into polymer chains. Figure 9 plots the stress–strain traces of polyesters $PETG_{30}$, $PETG_{30}N_{30}$ and $PETG_{30}S_{30}$.

Figure 10 presents the shrinkage property of copolyesters as a function of the heating temperature. The theoretical maximum shrinkage was 50%, because the specimen was stretched to an extension ratio of about 200% in this study. All samples showed that the shrinkage increased with temperature and dramatically arose at the temperature above the corresponding T_g, which was consistent with the previous reports.[8,12,13] The shrinkage was more than 40% when the heating temperature was higher than T_g. This result indicated that the both PETGN and PETGS series could be potentially used as heat-shrinkable materials with a wide range of operation temperatures, from $\sim 35°C$ ($PETG_{30}S_{30}$) to 90°C ($PETG_{30}N_{30}$).

CONCLUSIONS

NDA and SA were separately introduced into the $PETG_{30}$ copolyester formed PETGN and PETGS,

respectively, which were characterized. The thermal, optical, and tensile properties of those polymers were obtained as functions of NDA or SA content. DSC and X-ray analysis indicated that both PETGN and PETGS series were amorphous, although the optical transmittance decreased as the NDA or SA contents increased. The incorporation of NDA and SA widened the T_g range of those polymers from approximately 37°C for $PETG_{30}S_{40}$ to 89°C for $PETG_{30}N_{40}$. It also affected the tensile properties. Furthermore, the shrinkage of these copolymers was more than 40% when the heating temperature was higher than the corresponding T_g. These results reveal that the tuning of the crystallizability and the T_g of copolyester by adjusting the composition can be exploited in designing new amorphous PET materials with a better balance among thermal, mechanical, optical, and shrinkage properties.

References

1. Tirell, D. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Kreschwitz J. I., Ed.; Wiley: New York, 1988; Vol. 4, p 192.
2. Tsutsumi, N.; Nagata, M. In Encyclopedia of Polymeric Materials, Salamone, J. C. Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 8, p 5887.
3. Turner, S. R. J Polym Sci Part A: Polym Chem 2004, 42, 5847.
4. Li, X.; Yee, A. F. Macromolecules 2003, 36, 9421.
5. Lee, S.; Yee, A. F. Macromolecules 2003, 36, 6791.
6. Deepa, P.; Divya, K.; Jayakannan, M. J Polym Sci Part A: Polym Chem 2006, 44, 42.
7. Deepa, P.; Sona, C.; Jayakannan, M. J Polym Sci Part A: Polym Chem 2006, 44, 5557.
8. Shih, W. K. Polym Eng Sci 1994, 34, 1121.
9. Tsai, Y.; Fan, C. H.; Hung, C. Y.; Tsai, F. J. J Appl Polym Sci 2007, 104, 279.
10. Tsai, Y.; Tai, C. H.; Tsai, S. J.; Tsai, F. J. Eur Polym J 2008, 44, 550.
11. Kint, D. P. R.; Martinez de Ilarduya, A.; Munoz-Guerra, S. J Polym Sci Part A: Polym Chem 2001, 39, 1994.
12. Shelby, M. D. U.S. Pat. 6,599,994 (2003).
13. Fukuda, Y. U.S. Patent 4,939,232 (1990).
14. Chrissafis, K.; Paraskevopoulos, K. M.; Bikiaris, D. N. Thermochimica Acta 2005, 435, 142.
15. Sun, Y. M.; Wang, C. S. Eur Polym J 1999, 35, 1087.
16. Amari, T.; Nishimura, K.; Minou, K.; Kawabata, A.; Ozaki, Y. J Polym Sci Part A: Polym Chem 2001, 39, 665.
17. Hill, A. J; Weinhold, S.; Stack, G. M.; Tant, M. R. Eur Polym J 1996, 32, 843.
18. Ha, W. S.; Chun, Y. K.; Jang, S. S.; Rhee, D. M.; Park, C. R. J. Polym Sci Part B: Polym Phys 1997, 35, 309.
19. Li, B.; Yu, J.; Lee, S; Ree, M. Polymer 1999, 40, 5371.
20. Nagata, M.; Goto, H.; Sakai, W.; Tsutsumi, N. Polymer 2000, 41, 4373.
21. Lee, S. W.; Ree, M.; Park, C. E.; Jung, Y. K.; Park, C. S.; Jin, Y. S.; Bae, D. C. Polymer 1999, 40, 7137.
22. Mcdowell, C. C.; Freeman, B. D.; Mcneely, G. W.; Haider, M. I.; Hill, A. J. J. Polym Sci Part B: Polym Phys 1998, 36, 2981.
23. Daubeny, R. P.; Bunn, C. W.; Brown, C. J. Proc R Soc London Ser A 1954, 226, 531.
24. Callander, D. D. Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters; Wiley: New York, 2003, p 328.