Synthesis and Thermal Properties of Poly(cyclohexylene dimethylene terephthalate-co-butylene terephthalate)

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Abstract : It is well known that poly(cyclohexylene dimethylene terephthalate)(PCT) is used as the engineering plastics with high melting temperature and fast crystallization rate compared with poly(butylene terephthalate)(PBT). However, poor thermal stability of PCT has limited its practical application due to the drastic decrease of molecular weight during the processing temperature. In order to improve the thermal stability of PCT homopolymer, the copolymer of PCT and PBT was synthesized and the thermal properties of the copolymer have been studied. P(CT/BT) copolymer was obtained by condensation polymerization of DMT, CHDM, and 1,4-butanediol. The chemical structure and composition of the copolymer was investigated by FTIR and NMR analysis. The thermal behavior of copolymer was studied using DSC and it was found that the crystallization-melting behavior of the copolymer was observed for the whole composition range. TGA analysis exhibited that P(CT/BT) copolymer is more stable at the initial stage of thermal decomposition compared with PCT and PBT homopolymers.

Introduction

In early 1950s, the fiber type of poly(cyclohexylene dimethylene terephthalate)(PCT) was introduced to the market as the trade name of KODEL II by Eastman Kodak company.[1,2] General Electric Co. has commercialized the extrusion grade of PCT for the application of construction material and high strength panel in 1980. Recently, the PCT resin for the extrusion purpose was produced from Eastman Kodak Company. The chemical structure of PCT is similar to that of poly(ethylene terephthalate) except the cyclohexylene ring. The presence of cyclohexylene ring of PCT results in the resistance to the hydrolysis of the ester linkages.[3] Cyclohexylene ring has two isomers of cis and

trans type.[4] Depending upon the ratio of isomers, the stiffness of chain, the degree of chain packing, and the intramolecular interaction are different and it affects to the thermophysical properties of PCT.[5] Especially, *trans*-cyclohexane dimethanol (CHDM) could offer high melting temperature just like the aromatic function group. Terephthalate group of PET or PBT increases the stiffness of main chain along the chain direction and this results in the higher melting temperature and glass transition temperature. Both phenylene ring and cyclohexylene ring induce the improved thermal stability of PCT.[6,7]

The commercial CHDM contains two isomers with the ratio of 3 : 7 cis to trans. The melting temperature of PCT made from the commercial CHDM is around 290~295 °C, while PCT made from trans-form CHDM and cis-form CHDM have

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the melting temperature of 315 and 260°C, res-
pectively. Due to the cyclohexylene ring inside
PCT, the melting temperature of PCT is 30~60°C
higher than PET or PBT and the thermal decom-
position temperature is 50°C higher.[5] However,
the thermal decomposition reaction during the
polymerization of PCT occurs very rapidly. Also,
the long residence time during the extrusion pro-
cess results in the drastic decrease of molecular
weight and mechanical properties. It is desirable
to minimize the processing time.[3,8] In order to cir-
cumvent these defects of PCT, the modified PCT
of poor regularity and lower melting temperature
could be obtained by copolymerizing with third
monomer.[9,10] Modified PCT can be synthesized by
reacting with another diacid or diol.

In this study, 1,4-butanediol(1,4-BD) was used
to synthesize P(CT/BT) copolymer. It is well
known that PBT is the engineering plastics with
fast crystallization rate and this enables us to pro-
cess PBT with high extrusion molding speed and
superior dimensional stability. However, due to
the lower thermal decomposition temperature,
PBT has been used by reinforcing with glass fiber.
When PCT is copolymerized with PBT, it can
improve the physical properties as well as dimen-
sional stability due to the similar thermal expan-
sion coefficients of PCT and PBT. Besides,
broader processing window and better thermal
stability are expected.

Experimental

Materials. Monomers of 99% dimethyl tereph-
thalate(DMT) from Acros Ltd., 99% CHDM from
Aldrich Chemicals, and 1,4-BD were used without
purification. 99% of titanium butoxide was used
as catalyst and phosphorus acid from Yakuri Pure
Chemicals was used as thermal stabilizer. Mixture
solvent of phenol and 1,1,2,2-tetrachloroethane
was used with volumetric ratio of 6 : 4 and these
solvent were obtained from Duksan Chemicals
and Shinyo Chemicals, respectively.

Synthesis. 1 mol mixture of 1,4-BD and
CHDM with different ratios were prepared and
added to 1 mol of DMT. Total 30 grams of these
prepared monomers were copolymerized with
60 ppm concentration of Ti catalyst under nitro-

gen atmosphere. Due to the high volatility of
DMT at the initial stage, DMT was completely
melted at 130°C under 100 rpm and the temper-
ature was raised gradually up to 220°C in order
to remove the methanol. When the 70-80%
amount of theoretically calculated methanol was
removed, 150 ppm of phosphorus acid was
added with increased temperature of 280°C and
the unreacted monomer was removed. Keeping
the vacuum of 0.3 torr and temperature of 290°C
when the mixing speed decreased down to 40 rpm
completed the copolymerization reaction. For the
polymerization of polyester, the metallic com-
pounds containing Li, Na, Ca, Mg, Mn, Ti, Co etc.
were used as catalyst which affects the reaction
time and reaction efficiency. Since Ti catalyst has
high activation energy during the polymerization
of PCT at lower temperature, it is appropriate to
use Ti catalyst at ester interchange(EI) reaction
stage as well as condensation polymerization.
60 ppm of Ti catalyst was added during EI reac-
tion. When the excess amount of catalyst was
added during the polymerization of PCT, it could
result in the fast decomposition reaction with dis-
coloration. It is required to determine the amount
of catalyst judiciously during the polymerization.
The whole reaction proceeds for 260 min with
150 min of EI reaction and 110 min of polycon-
densation step, respectively. Copolymerization
reaction occurs by reacting 1 : 1 ratio of acid and
alcohol with 60 ppm of Ti catalyst followed by
raising the temperature slowly. When the amount
of methanol was removed around 60-70% of cal-
culated value, the thermal stabilizer was added
and the reaction was completed by keeping the
high temperature and vacuum for 60 min. When
the molar ratio of DMT and CHDM approaches
1 : 1, it induces high inside reaction temperature
rapidly with large amount of extracted methanol
at the initial stage. However, when the reaction
proceeds without appropriate temperature con-
trol, the EI reaction does not occur properly and
the solidification of reactant happens. Since DMT
has high volatility, it was vaporized very slowly
during the EI reaction in order to prevent the
blocking of extraction tube. Also, a vacuum was
applied gradually for 30-40 min for the complete
removal of by-products and the prevention of

262

Korea Polym. J., Vol. 8, No. 6, 2000

incomplete reaction due to unreacted monomer extracted.

Thermal Behaviors. Thermal properties of the copolymer were studied using Mettler DSC 821e model with 4-5 mg sample under aluminum crucible. The sample was in the powder state. The melting temperature was observed with heating rate of 20 °C/min. After keeping the sample in the melt state around 20 degree higher than melting temperature for 2 min, it was quenched down with liquid nitrogen. The glass transition temperature, melting temperature, crystallization temperature and cold crystallization temperature were observed with heating and cooling rate of 10 °C/min repeatedly. Thermal decomposition behavior of the copolymer was studied using Mettler TGA-30 model. The sample was prepared by dissolving the copolymer in the mixture solvent of phenol and 1,1,2,2-tetrachloroethane with weight ratio of 6 : 4, followed by precipitating the solution in the methanol, and then dried under the vacuum for 24 hours at 40 °C. The dried powder sample was tested from 30 to 600 °C with heating rate of 10 °C/min under the nitrogen atmosphere.

Infra-red Spectroscopy. The chemical structure of the copolymer was analyzed using FT-IR Perkin Elmer 1650 model. The samples were prepared using KBr disc method as well as film casting method. The better spectroscopy result was selected depending upon the peak resolution. The film sample was made by pressing between two polyimide films at 20 °C higher than melting temperature followed by quenching at room temperature. When the peak resolution is not satisfactory and excess IR absorption occurs, the film casting method was used using the mixed solvent of 6:4 weight ratio of phenol and 1,1,2,2-tetrachloroethane over KBr disc at 70 °C for 48 hours under vacuum.

Viscosity Measurement. To investigate the relative molecular weight of the copolymer, the intrinsic viscosity was measured using Ostwald viscometer at 25 °C. Temperature was precisely controlled with oil circulator Excel HTRC-20 model. 100 mL solution was prepared by dissolving 0.5 g of sample in the mixed solvent of phenol and 1,1,2,2-tetrachloroethane with the weight ratio of 6 : 4. The average value among five measurements was adopted, then the inherent viscos-

ity was calculated.

Nuclear Magnetic Resonance Spectroscopy. The molecular structure of copolymer was analyzed by ^{1}H NMR with Brucker AMX 500 model. 99% deuterated TFA from Aldrich Chemicals was used as solvent. The copolymer composition was determined by calculating the characteristic peak area of diacid unit and diol unit.

Results and Discussion

The chemical structure of the synthesized copolymer was analyzed using FTIR spectroscopy. Instead of diacid functional group, the characteristic peaks of butylene and cyclohexylene ring functional groups were used. Figure 1 shows the FTIR spectra of P(CT/BT) copolymer with various composition ratio. C-H aliphatic peak, CH_2 peak, and C-H stretching peak of cyclohexylene ring were observed at 2929, 1453.9 and 953.9 cm^{-1} respectively with various CT unit content. It was found that C-H stretching peak of cyclohexylene ring increases with increasing CT unit content.[11]

^{1}H NMR was used for the analysis of chemical composition of the copolymer. NMR spectra of P(CT/BT) copolymer is shown in Figure 2. Proton peak of phenylene ring and multiplet hydrogen peak of cyclohexylene ring are shown at 8.2 and 1.2-2.1 ppm, respectively. The proton peak of methylene group in 1,4 position of cyclohexylene ring occurs at 4.4 ppm in *cis* form and 4.3 ppm in
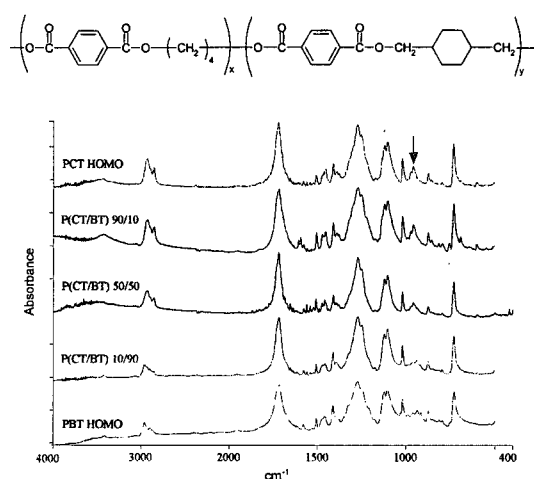

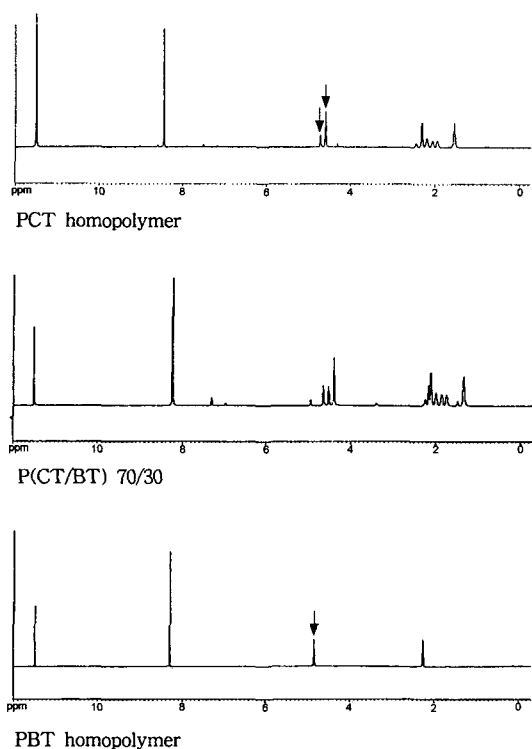Figure 1. FT-IR spectra of P(CT/BT) copolymers.

PCT homopolymer

P(CT/BT) 70/30

PBT homopolymer

Figure 2. ^{1}H NMR spectra of P(CT/BT) 70/30, PCT and PBT homopolymer.

trans form. The proton peak of butylene group in 1,4 butanediol was found at 4.7 ppm. The composition of each unit was calculated by integrating the peak area of each component.

Table I shows the monomer feed ratio before polymerization and determined copolymer composition after polymerization. And the inherent viscosity of P(CT/BT) copolymer is also shown in Table I. In Table I, it was found that P(CT/BT) copolymer shows a little higher composition ratio

of CT unit. This could be due to the higher boiling point of CHDM compared with that of 1,4-BD which results in the less loss during the reaction.

The average value of inherent viscosity of P (CT/BT) was measured between 0.6 and 0.9 dL/g. It was reported that the average molecular weight of PCT with the inherent viscosity of 0.8 exhibits around 200,000.[5]

The glass transition temperatures of the copolymers with various compositions are shown in Figure 3. It was observed that glass transition temperature decreases with decreasing CT unit content. This could be due to the hard segment of CHDM unit which induces lower glass transition temperature with decreasing CT unit. Figure 4 exhibits melting behavior of copolymer with varying composition. In general, random copolymers do not show any crystallization melting behavior
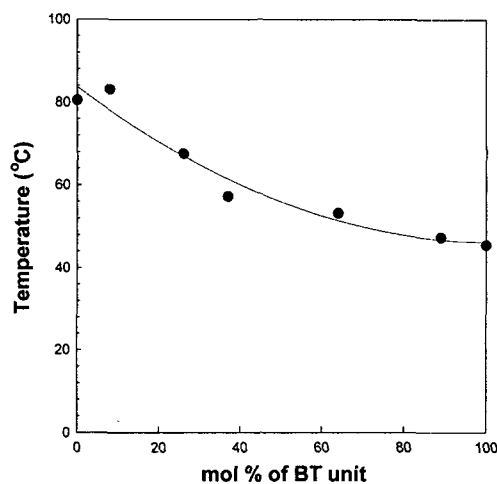

Figure 3. Effect of the copolymer composition on the glass transition temperature of P(CT/BT).

Table I. The Composition and the Inherent Viscosity of P(CT/BT) Copolymers

Samples	CHDM/1,4-BD Feed Ratio (mole)	P(CT/BT) Unit Ratio (mole)	Inherent Viscosity(η_{inh})
PCT Homopolymer	-	-	0.91
P(CT/BT) 10/90	0.1/0.9	0.11/0.89	0.79
P(CT/BT) 30/70	0.3/0.7	0.36/0.64	0.90
P(CT/BT) 50/50	0.5/0.5	0.63/0.37	0.72
P(CT/BT) 70/30	0.7/0.3	0.74/0.26	0.83
P(CT/BT) 90/10	0.9/0.1	0.92/0.08	0.61
PBT Homopolymer	-	-	0.82

264

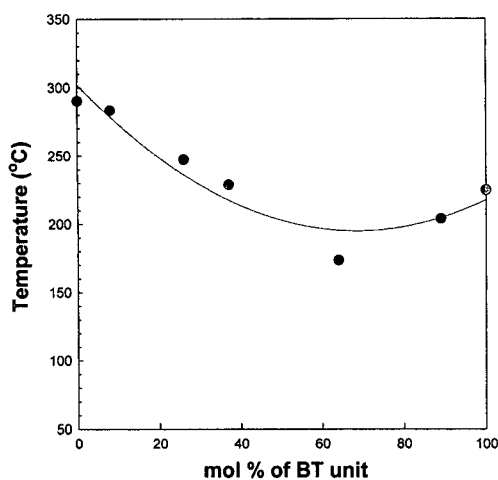Korea Polym. J., Vol. 8, No. 6, 2000

Figure 4. Effect of the copolymer composition on the melting temperature of P(CT/BT).
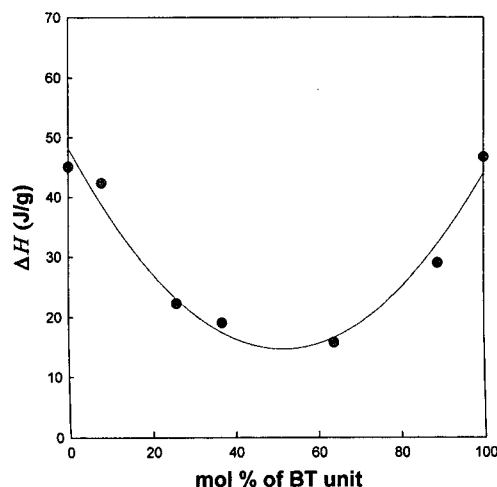

Figure 5. Effect of the copolymer composition on the heat of fusion of P(CT/BT).

at the composition of mid range, P(CT/BT) copolymer shows melting behavior for whole composition range. It can be thought that the cocrystallization occurs in P(CT/BT) copolymer. If cocrystallization occurs in the copolymer, the cocrystallization should be observed also for the blend of PCT and PBT. Table II shows the melting temperature of solution blended sample of PCT and PBT. As seen in Table II, two melting peak were found for whole composition range. This result suggests that crystallization melting behavior of P(CT/BT) copolymer occurs not by the cocrystallization, but by another reason from the similarity of chemical structure. In other words, it can be thought that the chain length of each unit is similar and this results in the ease folding of chain during the crystallization. It is known that the total number of atom in the each repeat unit as well as repeat

cycle of helix structure are same.[12,13] Also melting peak becomes broader with decreasing content of each unit. This could be due to the hindrance effect during crystallization. When the composition of each unit is similar, unstable state of spherulite forms due to the crystallization hindrance effect. Figure 5 exhibits heat of melting with various BT unit in P(CT/BT) copolymer. When the crystallization occurs in P(CT/BT) copolymer, different structure of CT unit and BT unit induces lower crystallinity and lower heat of melting.

TGA thermograms of P(CT/BT) copolymers are shown in Figure 6. And, in other to compare with PCT/PBT blends, TGA thermograms of the blends are shown in Figure 7. As shown in Figure 6 and Figure 7, the serious thermal decomposition is observed at around 450~490°C. The

Table II. Melting Temperatures of PCT/PBT Blends

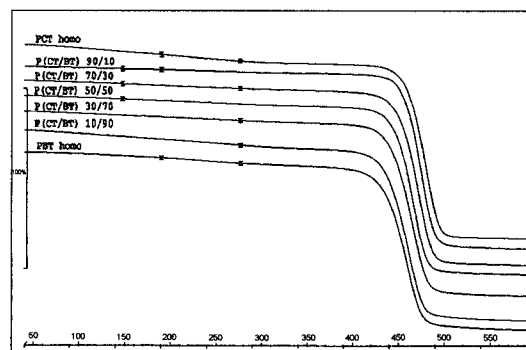| Composition	T_m of PCT/PBT (°C)
PCT Homopolymer	287
PCT/PBT 90/10	275/211
PCT/PBT 70/30	287/223
PCT/PBT 50/50	282/221
PCT/PBT 30/70	282/226
PCT/PBT 10/90	276/204
PBT Homopolymer	228

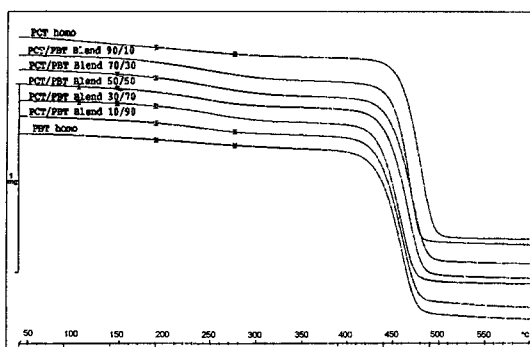**Figure 6.** TGA thermograms of P(CT/BT) copolymers.

Figure 7. TGA thermograms of PCT/PBT blends.

more the content of PCT component, it shows the higher the thermal decomposition temperature(T_d). T_d's of the copolymers and the blends are summerized in Table III. For the same composition the copolymer shows higher T_d than the blend. Table IV shows the weight loss percents of the copolymers and the blends up to T_d. As shown in Table IV, PCT/PBT blend, even also the PCT and PBT homopolymers, exhibit more weight loss than P(CT/BT) copolymers until the stage of serious thermal decomposition(T_d). This

suggests that P(CT/BT) copolymer is more stable than PCT and PBT homopolymers at the initial stage of thermal decomposition.

Conclusion

The copolymerization of P(CT/BT) was made to improve the processibility during the processing and thermal decomposition in the reaction. The chemical structure and thermal properties of copolymer were studied. With addition of 1,4-BD, thermal decomposition was not observed during copolymerization. And the unusual behavior of crystallization melting for whole composition range was found. This might be due to the similarity of chain folding length of CT unit and BT unit as well as similar crystal structure. It is thought that P(CT/BT) copolymer is more stable than PCT and PBT homopolymers at the initial stage of thermal decomposition.

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Table III. Thermal Decomposition Temperatures of P(CT/BT) Copolymers and PCT/PBT Blends

Copolymer Sample	T_d (onset) °C	Blend Sample	T_d (onset) °C
PCT Homopolymer	461	PCT Homopolymer	461
P(CT/BT) 90/10	458	PCT/PBT 90/10	453
P(CT/BT) 70/30	452	PCT/PBT 70/30	449
P(CT/BT) 50/50	447	PCT/PBT 50/50	444
P(CT/BT) 30/70	443	PCT/PBT 30/70	436
P(CT/BT) 10/90	438	PCT/PBT 10/90	436
PBT Homopolymer	436	PBT Homopolymer	436

Table IV. The Weight Loss % of P(CT/BT) Copolymers until the Thermal Decomposition Onset Temperature

Copolymer Sample	Weight Loss (%)	Blend Sample	Weight Loss (%)
PCT Homopolymer	0.11	PCT Homopolymer	0.11
P(CT/BT) 90/10	0.05	PCT/PBT 90/10	0.15
P(CT/BT) 70/30	0.03	PCT/PBT 70/30	0.16
P(CT/BT) 50/50	0.03	PCT/PBT 50/50	0.12
P(CT/BT) 30/70	0.07	PCT/PBT 30/70	0.13
P(CT/BT) 10/90	0.12	PCT/PBT 10/90	0.11
PBT Homopolymer	0.11	PBT Homopolymer	0.11

266

Korea Polym. J., Vol. 8, No. 6, 2000

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