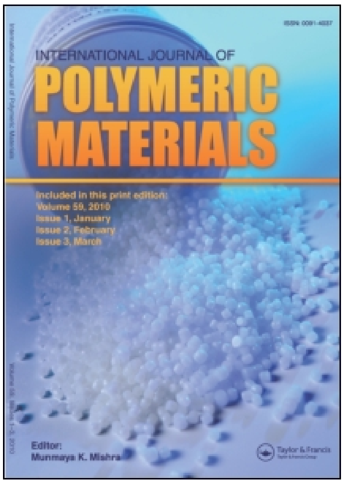

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Characterization of Commercial Grades of Poly(Carbonate of Bisphenol A)

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Characterization of Commercial Grades of Poly(Carbonate of Bisphenol A)

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This study characterized three different commercial grades of poly(carbonate of bisphenol A) samples (for extrusion, CD, and DVD) by several instrumental analysis methods, such as elemental analysis (EA), inductively coupled plasma mass spectrometry (ICP-MS), Fourier-Transform infrared spectroscopy (FTIR), viscosity measurements, differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA). The results of EA and ICP-MS showed that the chemical composition of the samples has no significant differences and the C/H ratio approaches theoretical value. The most abundant metal element in the samples is Fe. FTIR spectra demonstrated they have the same chain structure. Comparing the intrinsic viscosities and viscosity average molecular weights from the results of viscometry analysis, the values fell in the order: extrusion grade > CD grade > DVD grade. Various thermal properties determined by DSC and TG analysis showed the same sequence as the results of viscometry analysis and a close relationship between molecular weight and thermal properties was found.

Keywords: activation energy, poly(carbonate of bisphenol-A), property characterization

INTRODUCTION

Polycarbonate (PC), especially poly(carbonate of bisphenol A), is an important engineering thermoplastic. It was synthesized industrially

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by the following two method: The first is a reaction between sodium salt of bisphenol A and phosgene by interfacial polycondensation and the other one is to react directly bisphenol A and diphenyl carbonate through melt-transesterification [1–2]. Most producers use the phosgene process. Because of its good transparency, excellent thermal stability, low moisture absorbency, and attractive mechanical properties, this useful plastic is now used in a wide range of industrials such as automotive and transportation, building and construction, packaging, medical, optical and ophthalmic, and optical media. It is especially in widespread use in the audio, video, and interactive software media [3], such as CD, CD − R, CD − RW, DVD ± R, and DVD ± RW. PC, however, has some drawbacks such as yellowing and the decreasing physical properties that appear on natural weathering, limiting its use [4].

The price of PC fluctuated over the past few years depending on the price of crude oil, local supply/consumption market situation, and other reasons, such as currency exchange rates. For example, according to the report of *Modern Plastics* [5], the PC price in the European market has fallen by around a third since 2001 due to the strong Euro. Because of many new products and applications are continuing to be designed and manufactured from PC, such as: PC alloy, optical data storage, automotive, and electrical/electronic appliances, this development will support a steady growth consumption rate in the future. The demand of this material is expected to be strong in the future [6]. The world PC market is expected to have a growth rate at 9% per year in the next few years. The global PC consumption in 2005 is about 2.6 million tonnes and it will grow to about 3.1 million tons by 2007 [7].

Different grades of PC raw material are used to manufacture different kinds of consumer products to meet the specific properties requirement. The characterization of PC properties, therefore, is necessary and important [8]. Some of the properties (e.g., rheological, mechanical, thermal, material specific, and others), though, can be found in the catalogue supplied by manufactures or technical data sheet on website. Unfortunately, not all of the properties users would like to know can be found this way.

This study has characterized three different commercial grades of poly(carbonate of bisphenol A) raw materials, including PC for extrusion products, for compact discs (CD), and for digital versatile discs (DVD), manufactured by Bayer Corporation. The following instrumental analysis methods, including elemental analysis (EA), inductively coupled plasma mass spectrometry (ICP-MS), Fourier-Transform infrared spectroscopy (FTIR), viscometry measurement, differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA), were used to characterize the chemical composition, chain structure, molecular weight, and some important thermal properties of the PC samples.

EXPERIMENTAL

Materials

Three different commercial grades of poly(carbonate of bisphenol A), in pellet form (about 3.0 mm in size) were obtained from Bayer Plastics Taiwan. Samples were named as Makrolon 1243 (PC1), Makrolon CD2005 (PC2), and Makrolon DP1-1265 (PC3) for serving as extrusion products, CD, and DVD, respectively. PC powder was prepared by grinding PC pellets followed by sieving with a standard sieve. The particle size of PC was thus classified as <0.35 mm, $0.35\sim0.50$ mm, $0.50\sim0.71$ mm, $0.71\sim1.0$ mm, and >1.0 mm. Powders ranging from 0.50 to 0.71 mm were used for the following characterization tests. Samples, were stored in an electrical desiccator before characterization.

Characterization Methods

EA

Elemental analysis was performed with a CHNS elemental analyzer (Perkin Elmer 2400 Series II). Helium and oxygen served separately as carrier gas and combustion gas. The combustion furnace temperature and the reduction temperature was kept at 970°C and 500°C, respectively. The EA 6000 (Perkin Elmer, tungsten oxide/ zirconium oxide mixture) was used as a reference standard.

ICP-MS

A Perkin Elmer Optima 2000DV inductively coupled plasma mass spectrometry was used to determine the specific metallic elements concentration in the samples. They were first dissolved in an aqueous solution of H_2SO_4 and then diluted with deionized water to various desired concentrations. The composition analysis was performed according to the standard procedure. The operating parameters used in this study are given in Table 1.

FTIR

Fourier transform infrared spectra were collected using a Perkin Elmer Spectrum 2000 spectrometer in transmittance mode. All spectra were detected in the frequency range from 4000 cm^{-1} to 400 cm^{-1}, with a 1 cm^{-1} resolution, and calibrated with polystyrene standards. The analysis was performed on a sample holder. The sample is

TABLE 1 Operating Parameters of the ICP-MS

ICP-MS instrument	
RF power	1300 W
Plasma gas	Ar, 15 L/min
Auxiliary gas	Ar, 0.2 L/min
cones	platinum
Sample introduction	
Sample uptake	1.5 mL/min
Nebulizer	variable
Nebulizer gas	Ar, 1 mL/min
Data acquisition	
Scanning mode	Peak hop
Dwell time	1000
Sweeps per reading	1
Readings per replicate	1
Number of replicates	3

obtained by well mixing of PC powders with KBr (Acros Organics, IR grade) and the weight ratio of PC/KBr is 0.01.

Viscometry Measurement

The viscometry measurements were carried out using a 0B Ubbelohde (Cannon Co.) viscometer in a thermostatically controlled water bath (Tamson, TV4000), keeping the bath at constant temperature $25 \pm 0.1^\circ C$. Tetrahydrofuran (THF, Acros Organics, assay $\geq 99.8\%$) was used as solvent. The flow time (t) of a range of concentrations (C) was compared with those of the pure solvent (t_0) at the same conditions; the relative viscosity ($\eta_r = t/t_0$) and specific viscosity ($\eta_{sp} = \eta_r - 1$) could be calculated. Two most popular equations, Huggins (Eq. 1) and Kraemer (Eq. 2), were used to measure the intrinsic viscosity $[\eta]$ of the samples.

$$\eta_{sp}/C = [\eta]_H + K_H[\eta]_H^2 C \tag{1}$$

$$(\ln \eta_r)/C = [\eta]_k - K_k[\eta]_k^2 C \tag{2}$$

where K_H and K_k are constants called Huggins and Kraemer coefficient, respectively. Each measurement was started after a 30 min equilibrium time.

DSC

The glass transition temperature (T_g) of PC samples was determined by a differential scanning calorimetry (TA instrument, DSC 2910). DSC was calibrated using Indium standard (melting temperature

156.4°C and enthalpy of fusion is 288.40 J/g). The sample was heated under 50 mL/min nitrogen gas flow rate and the starting weight was 3 mg. The scanning temperature range was from 60°C to 300°C with heating rate 10°C/min and 3 scans were carried out for each sample.

TGA

Thermogravimetry analysis was performed under nitrogen flow of 50 mL/min and a purge time of 20 min on the Mettler TGA/SDTA851^{e} thermogravimetric analyzer. For each measurement 10 mg sample was used. The sample was heated from room temperature to 120°C using heating rate 10°C/min and maintained at this temperature 5 min then heated to 700°C at various heating rates 5, 10, 20, and 30°C/min.

RESULTS AND DISCUSSION

EA and ICP-MS

Table 2 shows the data of weight percentage of carbon, hydrogen, and weight ratio of C/H in the PC samples from elemental analysis. The corresponding values for PC1, PC2, and PC3 are almost the same and these values are also quite close to the theoretical values of the PC repeat unit which are 75.59%, 5.51%, and 13.72, respectively. This result demonstrates that the impurities present in the sample have no effect on the main composition of the PC. The balance weight percentage of each PC sample, therefore, should be mostly oxygen and trace elements from additives, impurities, or contaminations. The possible metallic elements presents in the PC samples were detected by ICP-MS. The existence and concentration of the following 23 metallic elements Fe, Cr, Al, Cu, In, Ga, B, Ba, Cd, Co, Li, Mn, Ni, Sr, Ti, Ag, Bi, Ca, K, Mg, Na, Pb, and Zn was measured. Among the quantified

TABLE 2 Elemental Analysis of PC Samples[a]

	PC sample		
Composition	PC1	PC2	PC3
C (%)	75.64	75.52	75.31
H (%)	5.60	5.79	5.65
C/H	13.51	13.04	13.33

[a] The theoretical values of C (%), H (%), and C/H ratio in PC is 75.59%, 5.51%, and 13.72, respectively.

TABLE 3 ICP-MS Results of PC Samples

Composition (ppm)	PC sample		
	PC1	PC2	PC3
Fe	20.1	13.1	20.2
Cr	1.20	1.10	1.12
Al	1.28	0.57	13.2
Cu	0.90	0.61	0.76
In	0.85	0.87	0.87
Ga	0.57	0.60	0.58
B	0.14	0.30	3.39

elements, iron, chromium, aluminum, copper, indium, gallium, and boron are the major elements in the sample and the corresponding concentrations are listed in Table 3. The concentration of other elements was trace or not detected. Iron is the most abundant element for all samples and the concentration ranged from 13.1 ppm to 20.2 ppm. Except for the concentration of aluminum and boron in PC3 begin higher than in PC1 and PC2, the concentrations of the seven major elements in PC samples have shown no significant difference. From practical point of view, in order to produce a high-quality disk and increasing the product yield for the manufacturer, the cleanness and purity of the raw materials is an important factor and the metal residues from impurities or contaminations for the CD or DVD grade of PC raw materials should be reduced to as low value as possible.

FTIR

The FTIR spectra of PC samples are shown in Figure 1. The spectra are very similar for the three samples. The main characteristic absorption peaks of PC are obviously found in the spectrum and identical to the typical results of PC plastics [9]. The wavenumber of the following absorption peaks was used to identify the PC structure. Wavenumbers of 2970, 2875, and 1378 cm^{-1} represent the bonds of C–H in methyl group with symmetrical and asymmetrical bending mode. Wavenumbers of 1775 and 1465 cm^{-1} correspond to the bonds of O–(C=O)–O in carbonyl group and C=C in aromatic ring with stretching vibration mode, respectively. The wavenumber of bonds of carbonate aryl-O-aryl C–O stretch, carbonate C–O stretching, and out-of -plane aromatic CH wags vibration are at 1230, 1160, and 830 cm^{-1}, respectively. The results of FTIR analysis indicate the PC samples have the same

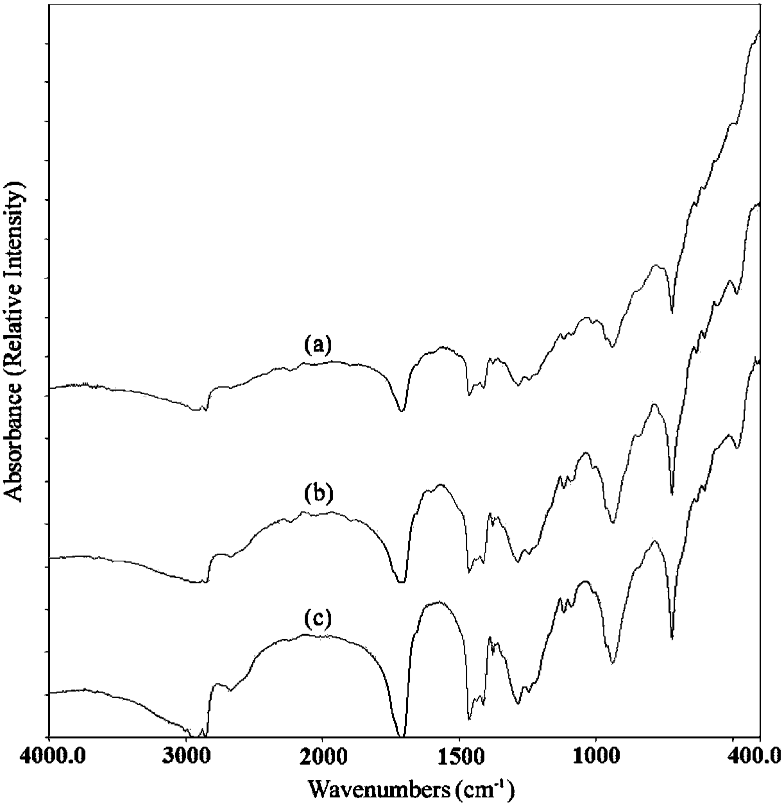

FIGURE 1 FTIR spectrum of PC samples, (a) PC1, (b) PC2, (c) PC3.

chain structure and it was not affected by the possible presence of additives.

Viscometery

By using the results of viscometric experiments and the numerical method of linear least squares, there are several mathematical equations that can be used to determine the intrinsic viscosity $[\eta]$ of a polymer solution. Two of the most popular equations, Huggins (Eq. 1) and Kraemer (Eq. 2), were employed in this article. The viscometric parameters of the PC samples are indicated in Table 4, which were obtained from the intercept and slope of the fitted straight lines. It was found that the intrinsic viscosities of $[\eta]_H$ and $[\eta]_k$ were very close and showed the tendency PC1 > PC2 > PC3, as observed from

TABLE 4 Viscometric Parameters of PC Samples in THF at 25°C

PC	$[\eta]_H^a$	$[\eta]_k^b$	K_H^a	K_k^b	M_v^c
PC1	0.532	0.531	−0.005	−0.432	30,200
PC2	0.386	0.384	−0.010	−0.448	19,000
PC3	0.376	0.376	0.117	−0.341	18,400

[a] Values calculated from Eq. 1 in unit dl/g.
[b] Values calculated from Eq. 2 in unit dl/g.
[c] Values calculated from Mark-Houwink-Sakurada equation in unit g/mol.

a comparison with the values calculated from Eqs. 1 and 2 for each sample. Considering the Huggins and Kraemer coefficients (K_H and K_k), THF is a good solvent for dissolving commercial PC samples as indicated from the results of K_H and K_k values being all smaller than 0.5 and negative, respectively [10].

Viscosity average molecular weight (M_v) of the PC samples could be calculated with the Mark-Houwink-Sakurada equation, $[\eta] = K(M_v)^a$ where K and a are constants whose values are function of the type of polymer, solvent, and temperature of the system. In this experiment, K and a are 3.89×10^{-4} and 0.7, respectively. The calculated viscosity average molecular weight of the samples is also given in the most right column in Table 4. The data reveals the trend of viscosity average molecular weight of PC samples to be the same as intrinsic viscosity, that is, PC1 > PC2 > PC3. Because of the extrusion grade of PC (PC1) is used to manufacture computer boxes, TV or other electronic appliances casing, so the high viscosity or molecular weight is required for the raw materials. On the other hand, to meet the necessity of high flow properties for CD (PC2) and DVD (PC3) manufacturing, a low intrinsic viscosity and molecular weight of raw materials should be used. In industry, in order to enhance the optical product's reproducibility, especially for the DVD discs production whose thickness is always kept thin, the high melt flow rate with a lower molecular weight of the raw material is necessary.

DSC

An important thermal property, glass transition temperature (T_g), can be determined from DSC experiments. The consequence of DSC analysis of the PC samples is demonstrated in Figure 2. The values of T_g obtained for sample PC1, PC2, and PC3 are 147.6°C, 145.8°C, and 144.8°C, respectively. T_g for PC1 is much closer to the theoretical value of 150°C [9] of the amorphous bisphenol A polycarbonate than PC2 and

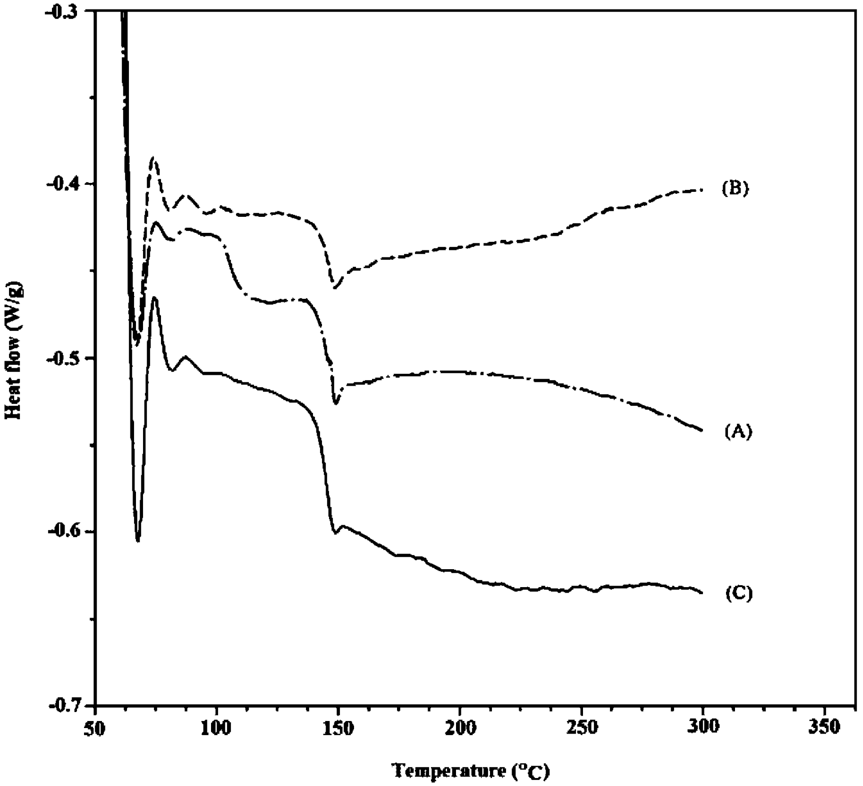

FIGURE 2 DSC curves of PC samples, (A) PC1, (B) PC2, (C) PC3.

PC3. The sequence of the T_g value is identical to the results of viscometrtic experiments, which means that the T_g of the samples is related to the molecular weight. Because the PC samples exhibited to melting points, the amorphous character of the commercial samples was confirmed.

TGA

The thermal decomposition properties of a polymer can be characterized by TG analysis. TGA curves of the PC samples at heating rate of 10°C/min in nitrogen are illustrated in Figure 3. Thermal decomposition properties including the start temperature of decomposition (T_{os}), the maximum rate of weight loss temperature (T_{max}) and the fractional solid (char) weight remains (α) for each sample could be

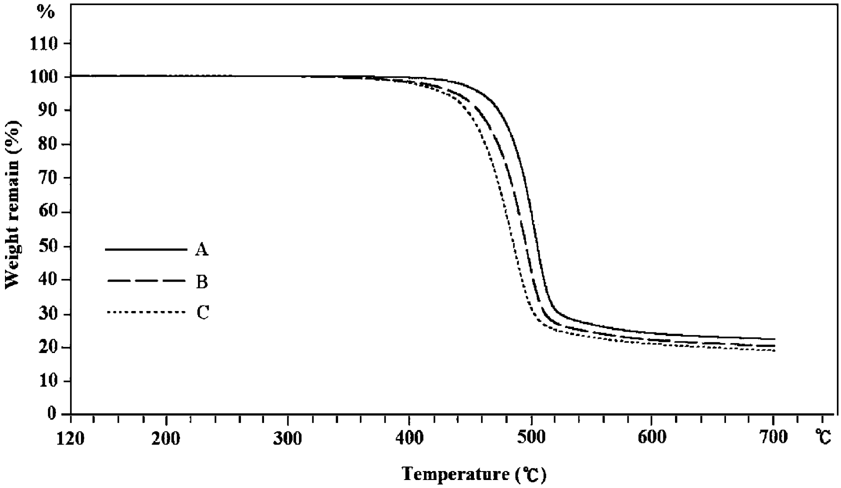

FIGURE 3 TGA curves of PC samples at heating rate 10°C/min, (A) PC1, (B) PC2, (C) PC3.

determined from a single heating TGA curve. The values of thermal decomposition properties of the PC samples are listed in Table 5. The data shows the thermal decomposition values of PC1 are larger than the other two samples and the results also show consistency with the viscometric experiments. They show that molecular weight affects the starting decomposition and the maximum rate of weight loss temperature of PC and both temperatures will increase with increasing molecular weight.

The other important thermal decomposition property can be determined from TG analysis is the activation energy (E_a) of decomposition reaction of a polymer under nitrogen flow at a fixed or variable

TABLE 5 Thermal Decomposition Properties of the PC Samples from TGA curve[a]

	PC sample		
Composition	PC1	PC2	PC3
T_{max} (°C)	524	519	517
T_{os} (°C)	487	482	475
α	0.242	0.235	0.217

[a] Heating rate 10°C/min in nitrogen.

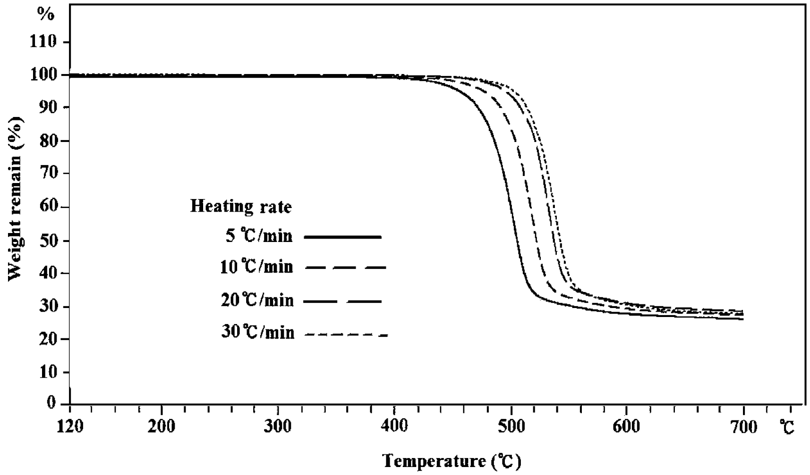

FIGURE 4 TGA curves of PC1 at various heating rates under nitrogen flow.

heating rates. Figure 4 shows the TGA curves of PC1 sample at different heating rates 5, 10, 20, and 30°C/min in nitrogen. The TGA curves of PC2 and PC3 were similar to that of PC1 at the same heating rates, and not shown here. The kinetic parameters including activation energy, preexponential factor (A_0) and order of reaction (n) can be obtained by several mathematical methods. Activation energy, however, is the most interesting and important factor to be known when concerned with the decomposition of plastic products. The rate equation for plastic thermal decomposition is usually represented by general power law with the form of nth order and rate constant k,

$$R = -\frac{d\alpha}{dt} = k\alpha^n \tag{3}$$

where n is the order of reaction and α is the fractional solid residue at any instantaneous time t. The fractional solid residue α can be rewritten in terms of the fractional weight loss (m) during the thermal decomposition as $\alpha = 1-m$. Substituting this relation into Eq. 3 and supposing the rate constant k obeys the Arrhenius equation $k = A_0 \exp(-E_a/RT)$, then Eq. 3 becomes

$$\frac{dm}{dt} = A_0 \exp(-E_a/RT)(1-m)^n \tag{4}$$

where R is gas constant (8.314 J/mol) and T is the absolute temperature (K) of reaction, respectively. If the TG analysis was carried out under multiple constant heating rates, the heating rate (r) can be represented as dT/dt. Upon introducing the heating rate relation into Eq. 4, it can be rewritten as

$$r\frac{dm}{dT} = A_0 \exp(-E_a/RT)(1-m)^n \tag{5}$$

Therefore, Eq. 5 is the fundamental equation to determine the activation energy of the PC samples on the basis of TGA data. The Ozawa [11] and Kissinger [12] methods were applied in this experiment. The former method is based on Doyle's approximation and Eq. 5 can be derived and becomes

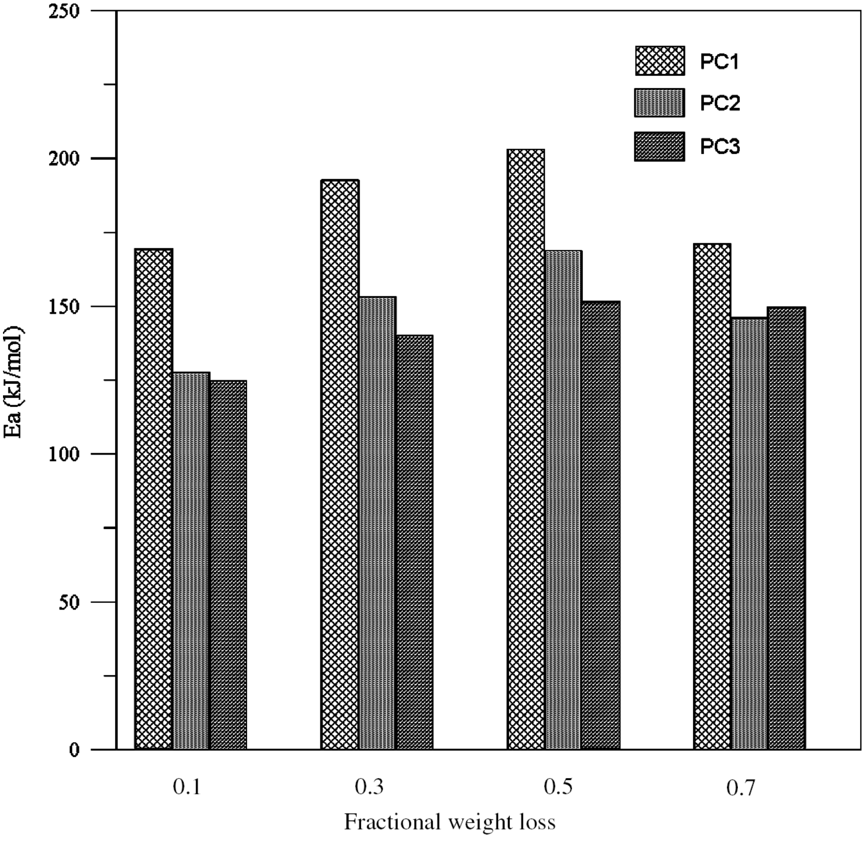

FIGURE 5 Activation energy from the Ozawa method for PC decomposition for various weight losses.

$$\log(r) = C - (0.4567\ E_a/RT) \tag{6}$$

where C is a constant and the activation energy at any particular m can be obtained from the slope of the plot log(r) versus 1/T. If the Kissinger method assumes that at the temperature T_{max} the first derivative of m with respect to t equals the result of second derivative and $n(1-m)^{n-1}_{max} = 1$ [13], then Eq. 5 can be written as

$$\ln(r) = \ln(AR/Ea) - (E_a/RT_{max}) \tag{7}$$

Thus, the activation energy can be computed from the linear dependence of the $\ln(r/T^2_{max})$ versus $1/T_{max}$ plot for various heating rates.

The values of activation energy for PC decomposition in nitrogen environment according to Ozawa method vary with the fractional weight loss m as shown in Figure 5. It can be seen that the activation energy for the PC decomposition increased from m = 0.1 to the maximum at m = 0.5 and then decreased as the increasing of weight

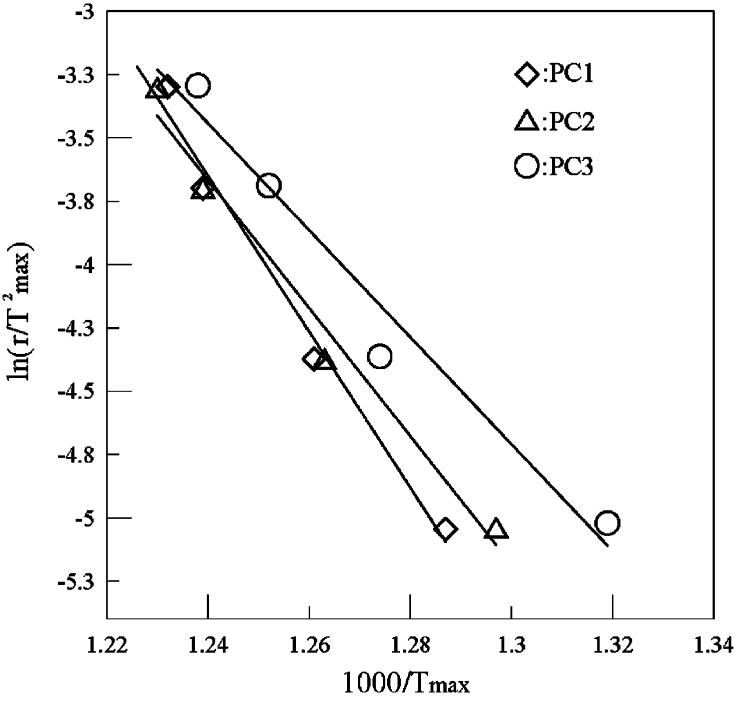

FIGURE 6 The Kissinger method of $\ln(r/T^2_{max})$ versus $1/T_{max}$ for PC decomposition.

loss. The value of activation energy for the decomposition of PC1 is larger than PC2 and PC3 for all fractional weight losses. The variation of activation energy with fractional weight loss represent may a change in mechanism during the thermal decomposition. Kissinger's plot for PC decomposition at temperature T_{max} under various heating rates is illustrated in Figure 6. The estimated activation energies by this method for PC1, PC2, and PC3 are 256, 210, and 176 kJ/mol, respectively. The values of activation energy obtained from Kissinger's method are greater than those calculated by Ozawa's method. The activation energy of PC decomposition are in the order PC1 > PC2 > PC3, in agreement with the previously mentioned thermal properties. PC with higher molecular weight has enhances thermal stability.

CONCLUSIONS

EA, ICP-MS, FTIR, viscometric analysis, DSC, and TGA were applied to investigate the composition, structure, and thermal properties of three different grades of commercial PC samples. EA and ICP-MS shows they have the same composition except for some fluctuations in metal contents. The possible presence of impurities or contaminations does not affect the main composition. FTIR spectrum also demonstrates the samples to have the same chain structure based on the identical spectra. The different behaviors among samples, especially for extrusion grade, were observed from the results of viscometric analysis, DSC, and TGA. The intrinsic viscosity, viscosity average molecular weight, glass transition temperature, starting decomposition temperature, the maximum rate of weight loss temperature, the fractional solid weight retained, and activation energy of thermal decomposition of PC are all in the same order as extrusion grade > CD grade > DVD grade. The molecular weight of PC obviously affects the plastic thermal properties.

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