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A study on the relationship between polycarbonate microstructure and performance as determined by a combined experimental and molecular dynamics simulation method

Abstract: The influence of the microstructure of polycarbonate (PC) on performance was systematically investigated by both experimental method and molecular simulation. Yield stress, impact strength, molecular weight, and transmittance were used to distinguish the degradation processes between different PCs, and thermal degradation kinetics was studied to obtain the activation energy. At the molecular level, through ¹³C nuclear magnetic resonance (NMR) spectroscopy, it was observed that PCs have a more polar group of benzene rings, resulting in the high density, dielectric constant, and tensile modulus. Meanwhile, molecular dynamics (MD) simulation was employed under a polymer consistent force field force field. Specific volume and mechanical property were analyzed to investigate the thermodynamic property. The molecular dynamics simulation and experimental results on half decomposition temperature $(T_{1/2})$, refraction index, flow activation energy, average density, cohesive energy density, glass transition temperature (T_c) , and elastic modulus had good agreement. Therefore, it was indicated that the molecular simulation could successfully study the characteristics and properties. The fundamental studies would be expected to supply useful information for designing materials and optimizing processing technology.

Keywords: mechanical property; molecular dynamic simulation; optical performance; polycarbonate; thermal degradation.

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1 Introduction

The practical and theoretical analysis of the stabilization and degradation of materials is significant (1). Disposal of plastic wastes has become a serious problem. Researchers have been prompted to investigate plastic recycling by degradation as an alternative to address the increasing environmental concerns (2). Meanwhile, the degradation of polymers in the environment limits their application. So far, the rate of change of average molecular weight has been the focus of attention in most theoretical research studies (3, 4). The main hypothesis of the theory shows that each link in a chain molecule has an equal strength and that the probability of having a broken link is related to the number of links. However, studies on polystyrene have revealed differences with the theory (5). So, it could be said that the study of plastic thermal degradation is still insufficient.

Poly(bisphenol-A carbonate) has been widely applied in such fields as construction, electronics, and packaging, etc., due to its good physical and mechanical properties, such as optical transparency and tensile strength (6). The structural property and molecular motion of this polymer are very important in the investigation of the molecular origin of its mechanical properties. The small segmental motion and molecular structure can be examined by various techniques such as nuclear magnetic resonance (NMR) spectroscopy (7, 8) and dielectric relaxation (9, 10). Polycarbonate products are easily affected by environmental factors. Thermal degradation affects the structure of the molecular chain, the mechanical property, and the optical anisotropy, so the experimental and theoretical study on the thermal degradation of polycarbonates (PCs) is of particular interest (11). The aging resistance of PCs has been reinforced by aging-resistant fiberglass and

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modified by nano-scale clays (12). The main experimental information is obtained by thermogravimetric analysis (TGA). Trick et al. (13), for example, studied the kinetics of solid-state reactions by tracking the mass loss of a pyrolyzing system as a function of temperature. Nevertheless, the relationship between TGA curves and detailed decomposition mechanisms is vague. These techniques yield important information about degradation, but the actual fundamental understanding between structural and thermomechanical properties is not obtained.

Computer simulation (14, 15) is probably the most effective tool to analyze the microstructure and performance of materials under harsh conditions in the short term. The main reason for the thermal degradation is the differences in chain structure, composition, and state of aggregation. Jussi et al. (16) studied the effect of branching of PCs on the optical and mechanical properties by means of molecular simulation. Jussi et al. (17) used the ab initio method to study thermal degradation reactions and the thermal aging behavior of different molecular weights of PCs.

In this research, thermal stability was studied by $T_{\rm g}$, $T_{1/2}$, and degradation kinetics experiment. Mechanical performance was performed to determine impact strength, tensile modulus, and density. During the MD simulations, the interactions between atoms were based on Newton's laws of motion (18). The static and dynamic physical properties of the polymer were used to investigate the microstructure. Comparisons between the molecular dynamic simulation and the experiments were performed to predict the performance of PCs.

2 Experimental

2.1 Materials

The PC resins were injection molding grades of OQ2720, ECPC, and EXL112. OQ2720 (M_w =50.1×10³ kg/mol, M_w/M_n =1.63, Poisson's ratio 0.40), ECPC (M_w =49.5×10³ kg/mol, M_w/M_n =1.80, Poisson's ratio 0.41), and EXL1112 (M_w =24.9×10³ kg/mol, M_w/M_n =1.61, Poisson's ratio 0.42), which were all purchased from SABIC Innovative Plastics (Bergen op Zoom, The Netherlands).

2.2 Apparatus and method

¹³C NMR spectroscopy was performed on the samples dissolved in deuterated chloroform (CDCl3) with a Bruker AV 300 spectrometer. The molecular weight was determined on a Waters 410 gel permeation chromatography instrument, with dimethyl formamide as the solvent. Refractive index was studied on a WYA-2S Abbe refractometer, with α -bromonaphthalene as the contact medium. Ultraviolet/visible measurements were acquired on a Shimadzu UV-3150 spectrophotometer. Densities were obtained by the gradient method.

The samples were vacuum dried at 110°C for 24 h to ensure the removal of water. Melt flow index determination was recorded on an XNR-400B melt flow rate meter according to the GB/T3682-2000 standard. Thermal stability and half decomposition temperature were assessed with a Mettler-Toledo TG209C thermogravimetric analyzer. All samples were heated at rates of 5°C/min, 10°C/ min, 15°C/min, and 20°C/min to 700°C, respectively. The maximum weightlessness rate occurred at a temperature $T_{\rm max}$, which can be used to calculate the thermal degradation activation energy. T_{α} was measured by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC-204F instrument under N₂, with a heating rate of 10°C/min from 30°C to 200°C. Raw materials were injected using the HAAKE MiniJet II system (Germany). Tensile testing of the dumbbells was performed on a Shimadzu SLBL testing machine according to the GB/T10403-206 standard. The notched Izod impact strength was measured according to the ASTM D256-04 standard using an impact tester (VJ-40, China) on the standard rectangular bars. Mechanical measurements were carried out at 20±3°C, and the average values reported were derived from five specimens.

2.3 Characterization and thermodynamic performance

2.3.1 Characterization

¹³C NMR chemical shifts are shown in Figure 1. The result indicates that the repeat units of the main chain of OQ2720, ECPC, and EXL1112 were the same as those with the structural formula $-O-C_6H_4$ -C(CH₃)₂-C₆H₄-O-CO-. One end group of OQ2720 and ECPC was the same as that of $-COO-C_6H_5$, and the other end group was the same as those of $-CO-C_6H_5$ and $-C_6H_4$ -OH, respectively. The end groups of EXL1112 were $-OC_6H_5$ and $-CO-O-CH_2-C_6H_5$. Copolymerization of dichlorodimethylsilane led to the absorption peak of Si-CH₃ (19).

2.3.2 Processing and optical properties

Injection molding is usually the processing method of choice for optical PCs. Melt flow index relates to the flow activation energy according to the following equation (20):



Figure 1 PC ¹³C NMR spectrum.

$$\eta = A e^{\frac{\Delta E_{\eta}}{RT}}$$
[1]

where η is the viscosity, ΔE_{η} is the flow activation energy, R is the gas constant, T is the absolute temperature, and A is a constant.

Refractive index is an important parameter of optical materials. The high refractive index can reduce the thickness of transparent parts. According to the theory of classical electromagnetism, the Lorentz-Lorenz formula (21) is shown as follows:

$$R_{\text{index}} = \frac{(n^2 - 1)M}{(n^2 + 2)\rho} = \frac{(n^2 - 1)M}{(n^2 + 2)} V = \frac{4}{3} \prod N_A \varepsilon$$
[2]

where R_{index} is the molar refraction, n is the refractive index, M is the molecular weight, ρ is the density, V is the molar volume, and ε is the dielectric susceptibility.

2.3.3 Thermal degradation kinetics

For the molding of the transparent parts, melt plasticizing time was long and temperature fluctuation was large. The processing performance, thermal stability, and liquidity are more important. TGA is a good choice to understand degradation in terms of mass loss. Most reactions of the type (solid solid+gas) (22) can be described as follows:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A(1-x)^n \mathrm{e}^{\frac{E}{RT}}$$
[3]

where dx/dt is the reaction rate, x is the fraction reacted, n is the empirical order of reaction, E denotes the reaction

energy, *T* is the Kelvin temperature, and *A* is a constant. If the temperature rises during the reaction, dx/dt will arrive at the maximum value. dx/dt returns to zero when the reactant is exhausted. Supposing the temperature rises at a constant rate β , we can get the following equation:

$$\frac{d\left(\frac{dx}{dt}\right)}{dt} = \frac{dx}{dt} \left(\frac{E\beta}{RT^2} - An(1-x)^{n-1}e^{\frac{E}{RT}}\right)$$
[4]

The maximum rate occurs at a temperature T_{max} , defined by setting the above equation equal to zero and taking the logarithm on both sides of the equation:

$$\ln\frac{\beta}{RT_{max}^2} = -\frac{E}{R} \left(\frac{1}{T_{max}}\right) + \ln\left(\frac{nAR(1-x)^{n-1}}{E}\right)$$
[5]

Finally, the thermal degradation activation energy is defined by the following equation:

$$\frac{\mathrm{dln}\left(\frac{\beta}{T_{\mathrm{max}}^2}\right)}{\mathrm{d}\left(\frac{1}{T_{\mathrm{max}}}\right)} = \frac{E}{R}$$
[6]

3 Molecular dynamics simulation

Molecular dynamics (MD) simulations were performed using fully atomistic models to investigate the influence of structure on performance by means of the Materials Studio software suite (Accelrys Inc., USA).

3.1 Simulation methodology

The process of construction of amorphous cells is shown in Figure 2. First, the head and end atom of the repeating unit [Figure 2(A)] were set by the *Build* module and energy minimization was performed before polymerization. Secondly, the *Polymer Builder* and *Amorphous Cell* module were used to form the chain of the required form [Figure 2(B)]. The amorphous cells of PCs were built at low densities of 0.6 g/cm³ to minimize the build time and avert ring spearing (23–25). Each model contained four polymer chains and 80 repeat units [Figure 2(C)]. The length of the chain repeat units was selected for two standards (24): (i) to ensure the computing time at a controlled level and (2) to keep the chains with sufficient movement. The Basic-Refine protocol was initially applied to refine the cells (25). The method used for dealing with van der Waals force was atom based,



Figure 2 Models for the MD simulation of PCs (green atom is H, red atom is O, and gray atom is C).

the electrostatic interaction was Ewald, and the cut-off distance of non-bonded interactions was 15.5 Å. To ensure the cells were well equilibrated before the production runs, the smart minimizer method was applied to minimize the cells (26). The simulated systems were cooled back to the target temperature with 25-K increments. Next, the Andrea et al. (27) thermostat and the Berendsen et al. (28) barostat method were chosen to reach the experimental density with (constant particle number, pressure, and temperature) NPT and (constant particle number, volume, and temperature) NVT simulation. The reason for this choice was that unacceptable inaccuracies could lead to the use of experimental densities as a starting point (26). After the completion of the annealing, the systems were further equilibrated through a series of 500-ps NVT and 150-ps NPT runs at the target temperature before using them to calculate the cohesive energy density, density, specific volume, and mechanical properties. Table 1 summarizes the parameters of the PC models after the equilibration. The Synthia program (23) was used to calculate the properties by applying the predictive capability. In Synthia, performances are shown in terms of topological and geometrical variables. There was good agreement between the experimentally determined $T_{1/2}$ and the value predicted by Synthia within the generally reported range, ~3% (25, 29). The resulting $T_{1/2}$, flow activity

energy, and refractive index values of OQ2720, ECPC, and EXL1112 cells (see Table 2) were in reasonable agreement with experimental and theoretical values.

3.2 Potential function

A reasonable potential function was necessary to study the system of PCs in the simulation. Here, the well-known polymer consistent force field (PCFF) force field (30) was adopted. Also, using this force field, Fan et al. (31) studied the $T_{\rm g}$ and the thermal expansion coefficients of PCs and reported good agreement between experimental and simulated values. More recently, Chang et al. (30) successfully examined the microstructure of amorphous silica. The PCFF force field is one member of the ab initio consistent force-field family, composed of the CFF91, CFF, PCFF, and COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force fields, with the same functional form. The functional form can be illustrated as follows:

$$\begin{split} E &= \sum_{b} \left[K_{2}(b - b_{0})^{2} + K_{3}(b - b_{0})^{3} + K_{4}(b - b_{0})^{4} \right] (a) \\ &+ \sum_{\theta} \left[H_{2}(\theta - \theta_{0})^{2} + H_{3}(\theta - \theta_{0})^{3} + H_{4}(\theta - \theta_{0})^{4} \right] (b) \\ &+ \sum_{\theta} \left\{ V_{1} \left[1 - \cos(\theta - \theta_{1}^{0}) \right] + V_{2} \left[1 - \cos(2\theta - \theta_{2}^{0}) \right] \\ &+ V_{3} \left[1 - \cos(3\theta - \theta_{3}^{0}) \right] \right\} (c) \\ &+ \sum_{b} \sum_{b'} F_{bb'}(b - b_{0})(b' - b'_{0}) (e) \\ &+ \sum_{b} \sum_{b'} F_{bb'}(\theta - \theta_{0})(\theta' - \theta'_{0}) (f) \\ &+ \sum_{\theta} \sum_{\theta'} F_{\theta \theta'}(\theta - \theta_{0})(\theta' - \theta_{0}) (g) \\ &+ \sum_{\theta} \sum_{\theta'} F_{b\theta}(b - b_{0}) \left[V_{1} \cos\theta + V_{2} \cos 2\theta + V_{3} \cos 3\theta \right] (h) \\ &+ \sum_{b'} \sum_{\theta'} (b' - b'_{0}) \left[V_{1} \cos\theta + V_{2} \cos 2\theta + V_{3} \cos 3\theta \right] (i) \\ &+ \sum_{b'} \sum_{\theta'} \sum_{\theta'} K_{\theta_{\theta \theta'}} \cos\theta (\theta - \theta_{0}) (\theta' - \theta'_{0}) (j) \\ &+ \sum_{b' j} \frac{q_{i}q_{j}}{\epsilon r_{ij}} (k) \\ &+ \sum_{b' j} \left[\left(\frac{A_{ij}}{r_{j}^{9}} \right) \cdot \left(\frac{B_{ij}}{r_{ij}^{6}} \right) \right] (1) \end{split}$$

Table 1 Parameters of simulated PC models after equilibration.

Parameters/model	0Q2720	ECPC	EXL1112
Cell length $(x/y/z)$ (Å)	27.65/27.65/27.65	30.15/33.39/31.17	29.80/27.40/33.45
Number of C atoms	1332	1368	1156
Number of O atoms	252	256	168
Number of Si atoms	0	0	8

Samples	Т _{1/2 (ехр)} (К)	Т _{1/2(sim)} (К)	Melt index _(exp) g/(10 min)	Flow activity energy _(sim) (kJ/mol)	Refractive index _(exp)	Refractive index _(sim)	$ ho_{ ext{(exp)}}$ (g/cm³)	ρ _(sim) (g/cm ³)
0Q2720	785	766	10.6	88.1	1.59	1.60	1.25	1.22
ECPC	783	759	4.1	89.2	1.56	1.58	1.20	1.19
EXL1112	779	748	21.4	71.0	1.55	1.57	1.17	1.14

Table 2 Experimental and simulated properties of PCs at 298 K and 0.1 MPa.

The energy terms have three forms: the bonded energy terms, the cross-terms, and the non-bonded energy terms. The bonded energy terms include (a) the covalent bond stretching, (b) the bond angle bending, and (c) the torsion angle rotation energy terms. The improper term (d) is treated as a harmonic function. The dynamic variations of the bond stretching, bending, and torsion angle rotation (e–j) form the cross-terms. The interactive energies between molecules include (k) the Coulombic electrostatic and (l) the van der Waals energy (31).

3.3 Physical property analyses

In this work, three independent molecular models were constructed to check the experimental values and to get the average physical property of the molecular models. Details of the physical property analyses are described below.

3.3.1 Structural features of the packing and cohesive energy density

It is important to generate a representative structure of the polymer before obtaining reliable property predictions. The cohesive energy density (CED) was applied to demonstrate the ability of the model to describe the real material. The intermolecular attractions, consisting of van der Waals and Coulombic interactions, result in the cohesion of a polymer material. Normalization of the echo-to-molar volume yields the CED (32).

3.3.2 Specific volume and the glass transition temperature (T_e)

The cells were cooled from 533 K back to 273 K using 20-K increments. With the first 50 ps discarded, an average density and cohesive energy were obtained for each cell. Values of T_g were obtained by the intersection of lines drawn through points in a plot of specific volume vs. temperature.

Lines were drawn using the best least-squares fit of data above and below the published T_g . This procedure for identifying T_g was reasonably reproducible (31).

3.3.3 Modeling the mechanical properties

The MD run in the *Discover* module of Materials Studio, using the *Analysis* tool, and then *Mechanical* module calculated the static mechanical properties by the full trajectory from Boyer (33). Theodorou and Suter (34) concluded that the contributions originated from the changes in configurational entropy on deformation. Cells were energy minimized with a default setting of 50,000 steps.

4 Results and discussion

4.1 Thermodynamic and optical

EXL1112 has a higher melt index and a lower flow activation energy, as shown in Table 2. There is a negative relation between melt flow index and flow activation energy. EXL1112 has the Si-O and Si-C groups, and the molecular chain is flexible. Therefore OQ2720 has a favorable manufacturing performance for moderate melt index.

It can be concluded that molar refraction is proportional to the dielectric polarization rate (21). The aromatic ring has polarity and the molar refraction is high, which indicates that OQ2720 has a high dielectric constant and a refractive index. Molecular simulation of the flow activation energy and refraction index is consistent with the experimental results of the melt index and refraction index, respectively, which are shown in Table 2.

4.2 Thermal degradation activation energy and influence of thermal degradation

The $\ln(\beta/T_{\text{max}}^2)$ has a linear relation to T_{max} , as shown in Figure 3. The slope–E/R calculated the thermal



Figure 3 Kissinger plot of PCs.

stress and impact strength at 573 K are shown in Figure 4(A). As the plasticizing time increases, the yield strength of OQ2720 and ECPC changes a little. The impact strength decreases but that of OQ2720 is slightly higher than those of other cells. Figure 4(B) shows that the molecular weight (\overline{M}_w) of PCs decreases as the extended time and temperature. It can be inferred that the decrease in molecular weight results in the decrease in impact property. Transmittance determines the optical characteristics and refers to the partial passage of light through a certain structure. Figure 4(C) shows a significant decline in transmittance with the increase in plasticizing time at 593 K. The thermal degradation performance of OQ2720 is better than that of others because of the higher benzene content.

4.3 Model validation

degradation activation energy of OQ2720, ECPC, and EXL1112, which were 216, 208, and 199 kJ/mol, respectively. The result suggests that OQ2720 with high thermal degradation activation energy has good thermal stability.

We studied the effects of plasticizing time of PCs on mechanical and optical properties, which are shown in Figure 4(A)-(C). The effects of plasticizing time on yield

The density (ρ) in Table 2 and the $T_{\rm g}$ in Table 3 were compared to validate the accuracy of the PC models constructed in this work. The relative error is within the generally reported range, ~3%. This agreement suggests that the PCFF force field can provide a reasonable amorphous model for the current study and the models are well equilibrated.



Figure 4 Effects of plasticizing time on (A) yield strength and impact strength, (B) molecular weight, and (C) transmittance.

 Table 3
 Glass transition temperatures obtained from NPT dynamics and the experiment.

Samples	7 _{g (ехр)} (К)	7 _{g (sim)} (К)		
0Q2720	426	440		
ECPC	406	426		
EXL1112	402	424		

4.4 Cohesive energy density

CED is a significant parameter of polymers in the field of thermodynamics. As shown in Figure 5, CED decreases with the increase in temperature. OQ2720 shows a lower CED, for weaker inter-atomic forces. It is consistent with experiment results (Table 4) that OQ2720 has an excellent tensile modulus. Furthermore, the simulated result of CED lies well within the empirical range of 290–420 MJ/m³ (35), giving additional support to the models in this work.

4.5 Specific volumes and glass transition temperature (*T*_)

Specific volumes obtained from the NPT dynamics for each of the PCs are plotted against temperature in Figure 6.



Figure 5 Plot of cohesive energy density vs. temperature of PCs.

Table 4 Simulated mechanical properties of the models.





Figure 6 Plot of specific volume as a function of temperature during NPT dynamic simulation of PCs at 0.1 MPa.

In general, the comparison tendency between simulation results and experimental (DSC) values of T_{g} is identical from Table 3.

An important issue in the discussion of $T_{\rm g}$ relates to the time scale of DSC methods compared to the much shorter effective simulation times. Simulation cooling rates are much higher (ca. 10^{12} K/s) than can be achieved by rapid quenching. Simulations could not be run sufficiently long to sample fully all the complete phase spaces (36). It has been pointed out that the relaxation of a chain in an entangled melt is about 10^{-6} s, and it could achieve a relative equilibrium state during simulation even at temperatures well above T_{a} (37).

4.6 Mechanical property

PC is an amorphous polymer (6). The models were fully annealed and further equilibrated through a series of 500-ps NVT and 150-ps NPT runs to ensure the systems were isotropic. The isotropy of the models could be checked by calculating the elastic constant matrix (38). The minimized structure was strained under deformations. The stress components were calculated by the virial expression (39). The slopes of $\partial \sigma / \partial \varepsilon$ in tension and shear can establish the full 6×6 stiffness matrix (C_{ij} , where i, j=1, 2, 3, 4, 5, 6). The Lamé coefficients λ and μ were calculated as follows (40):

$$\mu = \frac{1}{3} (C_{44} + C_{55} + C_{66})$$
 [8a]

$$\lambda + 2\mu = \frac{1}{3} (C_{11} + C_{22} + C_{33})$$
 [8b]

The stress-strain behavior of isotropic materials could be represented by two independent Lamé coefficients, and the other material properties were calculated from the Lamé coefficients:

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$$
[8c]

$$K = \lambda + 2\mu$$
 [8d]

$$G=\mu$$
 [8e]

where *E* is the tensile moduli, *G* denotes the shear moduli, and *K* is the bulk moduli.

The simulated and experiment mechanical properties are shown in Table 4, which shows that OQ2720 has a higher tensile modulus and shear modulus. This trend is consistent with experimental results. EXL1112 has a higher bulk modulus because of the higher chain movement and mobility. The simulated tensile modulus and shear modulus are higher than the corresponding experimental values. This may be partly due to the fact that the calculated cells represent an ideal structure, while realistic materials have defects in the structures.

5 Conclusions

Molecular simulations and experiments were performed to analyze the correlation between the microstructure and the properties of PCs. The simulated density, $T_{1/2}$, and $T_{\rm g}$ were compared with experiment results, within the generally reported range, ~3%. The simulation results were in good agreement with experiment results. The thermal degradation activation energy of OQ2720 was 216 KJ/mol, which indicated better thermal stability. The experimental tensile modulus of OQ2720 was up to 1.69 GPa among PCs. OQ2720 had a good mechanical property and optical performance because of its high molecular weight and the presence of groups of benzene rings. Therefore, molecular simulations can predict the physical and mechanical data for PCs, as well as provide a molecular insight into the influence of microstructures, which can be used as a method to select the ideal candidates for good optical performance, thermal stability, and injection materials.

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