Study on the behavior and mechanism of polycarbonate with hot-water aging

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Abstract. The present work was concerned with hot-water aging behavior and mechanism of Bisphenol A polycarbonate (PC) used as food and packaging materials. It indicated that with the aging time prolonged, PC sample had internal defects and the mechanical properties of PC materials changed not too much, molecular weight decreased, thermal stability declined. Phenolic hydroxyl absorption intensity enhanced in IR spectra and the maximum absorption wavelength red shift of benzene in UV-Vis spectra, the level of BPA increased. The color change of PC sample was not apparent.

1. Introduction
PC has outstanding impact resistance, good optical transparency, excellent thermal stability, cold resistance, creep resistance. It is widely used in food packaging field, such as tableware, cups, pure water bucket, etc. [1-2]. The ester group of PC molecule is easy to hydrolyze when exposed to warm, humid environment, or hot water for a long time, which quite reduced the transparency, toughness, etc. So that it is limited in the application [3-5].

To know the effect of hot-water aging on properties and structure of PC, the aging degree and the water resistance of the aging samples were evaluated by periodically examining the changes of the appearance and the performance. Study on aging mechanism and the relationship between aging precipitation BPA content and the degree of aging, providing a convenient to judge the aging properties of PC and the content of BPA, further providing a theoretical basis for the research of PC aging and aging protection.

2. Experimental
2.1. Sample preparation and aging process
The PC was produced by Taiwan’s Chi Mei Industrial Co., Ltd. Dry the PC pellets at 120°C in a vacuum drying oven for 24h before injection molding, then made several PC standard samples with F2v130 type (Donghua Machinery company) injection molding machine. An annealing process lasting 4h at 135°C was performed to relieve the residual stress before aging tests. The PC specimens were exposed in glassware and added in de-ionized water. Put the glassware in aging oven GT-7017(GOTECH, Taiwan), aging instrument was under 95°C for 0h, 48h, 96h, 144h, 192h ,and 240h, respectively.
2.2. Characterization
The surface morphologies of PC samples were recorded on a 1500 stereomicroscope (Olympus Corporation). Infrared spectra of PC samples were carried out with a Vertex70 spectrometer (Bruker, Germany). The absorption peak at the 2968 cm\(^{-1}\) was used as a reference which was asymmetric stretching vibration of the methyl, and that at the 3515 cm\(^{-1}\) was characteristic peak of BPA. The ratio of their absorbance \(A(3515\text{~cm}^{-1})/A(2696\text{~cm}^{-1})\) reflected the relative amount of precipitated BPA after PC degradation. Mechanical properties were measured on the universal testing machine GT-TCS-2000(GOTECH, Taiwan). A U-4100 UV–Vis spectrophotometer (Hitachi, Japan) was used to test the absorbance and the light transmittance of PC samples, and used light transmittance at wavelength 445 nm, 555 nm, 600 nm to calculate the yellow index \(Y1\), chromatism \(\Delta C\), transparency \(T\%\) according to the formula in the literature [6]. An 1100 type GPC (Agilent, America) was used to measure molecular weight and molecular weight distribution of PC samples. DSC analysis of all samples was carried out with a DSC-Q20 (TA, America)

3. Results and Discussion

3.1. Surface morphology of PC after hot-water aging
Figure 1(a-f) shows the pictures of the surface morphology of the PC sample after hot-water aging time. There were lots of defects which became more and bigger in the surface of PC sample with the aging time.

![Figure 1. Surface morphology of PC after hot-water aging.](image)

(a)0h, (b)48h, (c)96h, (d)144h, (e)192h, (f)240h
3.2. BPA relative content analysis of aged PC

![FTIR spectra and BPA relative content of PC at the different aging time.](image)

Figure 2. FTIR spectra and BPA relative content of PC at the different aging time.

(a) FTIR spectra  
(b) BPA relative content

Figure 2(a, b) reports the effect of the aging time on the FTIR spectra and the BPA relative content of PC samples. As the extension of the aging time, the 3515cm\(^{-1}\) characteristic absorption peak which belonged to the -OH of phenolic groups became sharp, indicating the generation of BPA in the process of aging degradation [3]. The relative amount of BPA migration from PC samples enhanced with the aging time prolonging.

3.3. Mechanical properties of aged PC

![Mechanical properties of PC at different hot-water aging time.](image)

Figure 3. Mechanical properties of PC at different hot-water aging time.

(a) tensile properties  
(b) notched impact strength and hardness  
(c) flexural properties
Figure 3(a) reported that tensile strength of PC decreased slightly, and elongation at break of PC reduced with hot-water aging time. After aging for 48h, the elongation at break of PC descended mildly. Figure 3(b) reveals the notched impact strength and hardness of PC at the various aging time. The notched impact strength of PC decreased lightly after aging. The hardness of PC before and after aging showed almost no change. Figure 3(c) represents the effect of hot-water aging on PC flexural properties. The effect of aging time on flexural modulus and flexural strength of PC was basically consistent and had a small impact on the change of the whole rigidity.

3.4. UV-vis spectrum analysis of aged PC

Figure 4. UV-vis spectra and light transmittance of PC at different hot-water aging time.

(a) UV-vis spectra  (b) Light transmittance

Figure 4(a) reports the UV-Vis absorption spectrum of PC. It can be seen that the characteristic absorption peak of benzene ring (270nm) showed red shift. The red shift was arisen from n→π* conjugation between benzene ring (chromophores) and –OH (autochrome), that is the aging degradation migrated BPA. Red shift lessened with the extension of aging time, because water into the PC sample produced a blue shift solvent effect, blue shift increased with the prolonging of aging time. In a word, the red shift was larger than the blue shift, and the overall performance was a red shift.

From Figure 4(b) it can be seen that as the aging time prolonged, the UV transmittance of PC samples decreased.

Chromatism, yellow index and transparency of PC at the different aging time are represented in Figure 5.

![Figure 5. Chromatism, yellow index and transparency of PC at different hot-water aging time.](image)

(a) chromatism, yellow index; b- transparency

With the hot-water aging time, chromatism of PC increased slightly, the yellow index of PC changed a trifle, and transparency of PC did not change obviously, the reason for this due to the
increasing number of defects within the samples. And the hot-water aging made the PC specimen surface edge in fine lines. Visibly hot-water aging had a slight effect on the color change of PC.

3.5. Relative molecular weight and its distribution of aged PC

![Figure 6. Chromatograms of PC at the different hot-water aging time.](image)

**Table 1.** Molecular weight and its distribution of PC at the different hot-water aging time.

| Ageing time | Mw×10⁴ | Mn×10⁴ | Mw/Mn |
|-------------|--------|--------|--------|
| 0h          | 6.972  | 6.114  | 1.140  |
| 48h         | 5.881  | 4.211  | 1.397  |
| 96h         | 5.804  | 4.293  | 1.352  |
| 144h        | 5.772  | 4.557  | 1.267  |
| 192h        | 5.417  | 3.585  | 1.14   |
| 240h        | 4.367  | 3.813  | 1.145  |

Figure 6 and Table 1 report the GPC analysis of PC sample with hot-water aging time. The weight average molecular weight (Mw) and the number average molecular weight (Mn) of aged PC decreased compared with that of the unaged PC when PC was aged for 240h, Mw reduced by 37.4%. The molecular weight distribution width index of hot-water aging PC increased than unaged PC, the relative molecular weight fell, which suggested that the degradation of PC occurred.

3.6. Glass transition temperature of aged PC

![Figure 7. DSC curves of PC before/after aging in hot-water.](image)
In Figure 7, Tg of PC had dropped after aging. When PC sample was immersed in hot water, hydrolysis made PC chain scission which generated the shorter molecular chain. Molecular weight abatement of the PC sample can increase the proportion of end segments and hence heightened the mobility of the whole molecule so that the Tg of PC decreased.

4. Conclusions
The pictures of the surface morphology of hot-water aging PC show that micro defects occur and its number raise with aging time. FTIR analysis reports that BPA migrates out of aged PC and BPA relative content increase with aging time. Hot-water aging has no obvious effects on the mechanical properties of PC. UV-Vis test shows the red shift of the characteristic absorption peak of the benzene ring. Hot-water aging has a small impact on the color change of PC, and chromatism, yellow index of PC have no obvious changes, transparency of PC decrease slightly. The DSC analysis reports that the Tg of PC drop after aging. GPC analysis indicates that the degradation of PC occurs during hot-water aging.

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