Study on the Changing Regularity of Structure and Properties of PC Aged Outdoor in Western Areas of China

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ABSTRACT: As an important engineering material, polycarbonate (PC) has been used widely. When exposed to the environment, PC will have aging process, which will reduce its performance and efficiency. This article studies the changing regularities of PCs structure and properties of ageing in western areas of China by measuring the change of intrinsic viscosity (IV), thermal decomposition temperature, glass transition temperature, and the groups within PC. The analysis of its IV, DSC, and thermo gravimetric analysis exhibited the same changing regularity, i.e., the aged PC (in Lasa, Yuli, and Jiangjin) experienced degradation and crosslinking, while degradation occurred earlier in the process of ageing, crosslinking predominated in later period. In addition, the results of UV absorption spectra and infrared absorption spectra showed the evidence of decomposition of the ester groups, resulting in the production of alcohol and phenol. And the results of mechanical tests indicated that the ductility disappeared mainly in the first year of outdoor aging. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2128–2136, 2012

Key words: polycarbonates; ageing; viscosity; thermal properties; glass transition

INTRODUCTION

As a good engineering plastic with high impact strength, good dimension stability, bisphenol A polycarbonate (PC) also exhibits high heat deflection temperature, excellent electrical, and optical properties. Therefore, it is widely used in various areas, such as optical discs, building materials, translucent sheets, window glass, electrical, and electronic product, etc. However, PC has an inevitable problem in ageing, which limits its application and reduces the effective time. When used outdoor, PC will suffer weathering. Weathering is a complex process in which multiple factors, such as UV light, moisture, oxygen and temperature variations, lead to the deterioration of the PC properties, especially in extremely bad weather condition. Thus, it is very important to work out the changing regularity of PCs structure and performance in real environment. The basic data obtained can be used to help predict lifetime of PC and evaluate the field of its application. It might contribute to the anti-ageing research as well. In recent years, many researches have been studying on the ageing process of PC under particular conditions. These researchers mainly focused on the effect of UV light and heat (including photodegradation, photo-oxidative degradation, thermal degradation, and thermoxidative degradation) in the accelerated tests,[1–15] but the ageing process with complex environmental factors has not been explored. Due to the complexity of the factors, the long experimental period, the risk of uncontrollable incident in the experimental process, and the relatively high cost, the studies on the PCs outdoor ageing process are still few. Webba and Czandernaa[16] investigated the influence of terrestrial UV irradiation at different latitude on the unstabilized Bisphenol A polycarbonate (BPA-PC) sheet. The researchers found that different outdoor lifetime has different concentrations of phenolic terminal groups, and the fewer phenolic terminal groups would lead to the less absorbance of UV irradiation. So the outdoor lifetime could increase by reducing the concentration of the groups which induces a crosslinking reaction. Pickett[17] studied the yellowing process of PC when ageing outdoor, noting that the ageing samples could undergo some extent of color shift after being stored for a long time. However, indoor simulated accelerated test cannot reflect truly the outdoor environmental conditions. PC would be used in outdoor environment in many cases, so there is a need to strengthen the researches in this field. In addition, these researches are very important to the anti-

TABLE I
Climate Characteristics of Atmosphere Exposure Test Stations in Western Areas of China

Station	Lasa	Yuli	Jiangjin
Average temperature (°C)	9.0	11.0	18.5
Average rainfall (mm)	580.9	48.9	1201.9
Average hours of sunlight (h)	2750.9	3050.9	1392.0
Average radiation (MJ/m^2)	7646.9	6264.0	2957.0

ageing measurement's application. It could contribute to building a model to evaluate the ageing condition at a specific time point and improving the anti-ageing solution against various environmental factors.

In our research, the outdoor experimental locations were set in western areas of China. In general, the climate in those places was worse than that in other areas of China, and we selected three cities (Lasa, Yuli, and Jiangjin) which have typical different climatic features. Tables I and II (year 2007 only) show the climate characteristics and data in the three cities, respectively; measurements are from local atmosphere exposure test stations. The aim of our work was to investigate the changing regularity of structure and properties of aged PC in western areas of China. In the present work, we also hoped that we could provide some basic data to prepare for the measures that could improve weather resistance of PC. The changing regularity was analyzed by measuring intrinsic viscosity (IV), thermo gravimetric analysis (TGA), DSC, UV–vis spectra, Fourier transform infrared (FTIR), and mechanical tests, and the effects of experimental factors on the outdoor ageing process of PC could be learnt. In addition, compared with the results from different ageing time length, the relation between the ageing time and the change of PC could be understood clearly. By analyzing the results in different ageing areas, the relation between the typical climate characteristic and the change of the PC could be obtained.

EXPERIMENTAL

Materials

PC (injection grade 6109, $M_n = 10{,}645$, $M_w = 35514$) was produced by Chongqing Changfeng Chemical Factory of China (Chongqing, China).

Dichloromethane (AR, purity $\geq$ 99.5%) came from Chengdu Kelong Chemical Factory (Chengdu, China).

Samples

The unaged material was supplied as solid pellets. It was dissolved in dichloromethane to obtain PC/dichloromethane solution. At last, PC film was formed after the solvent volatilized.

In order to get the aged samples, the PC pellets were dried in a vacuum oven at 120°C for 24 h before injection molding, then PC specimens were obtained by injection molding in K2TEC40-111 equipment (Ferromatik Milacron, Germany). The barrel temperatures were 260°C, 260°C, 255°C, and 240°C. Mould temperature was 50°C. The specimens are made according to requirement of Chinese National Standard. The tensile strength test specimens are in dumbbell shape. They are 150 mm long by 10 mm wide and 4 mm thick. The impact strength test specimens and the flexural strength test specimens are both in rectangular shape. They are both 80 mm long by 10 mm wide and 4 mm thick. The specimens were exposed in outdoor weather condition. The outdoor places were three areas of west China, i.e., Lasa, Yuli, and Jiangjin. These areas have typical weather conditions and the climatic data were shown in Tables I and II. The aging time was 1, 2, and 3 years. After the aging experiment, the aged samples were scratched from the surface of specimens after mechanical tests, and then the samples were dissolved in dichloromethane and filtered through two ground-in glass funnel. At last, the film was formed by volatilizing the solvent. The obtained PC films are about 0.3 mm thick.

Measurements and analysis

Measurement of intrinsic viscosity

Ubbelohde viscosity meter (0.38 mm) was used to measure the intrinsic viscosity (IV) of original PC and aged PC. The temperature was (25 ± 0.1)°C and the solvent was dichloromethane. η_0 and η stand for the initial viscosity of pure solvent and the PC solution, respectively, while η_r is relative viscosity and η_{sp} ($\eta_{sp} = \eta_r - 1$) is specific viscosity. C is polymer solution concentration. Through plotting the values of η_{sp} and $\ln\eta_r$ on the C, the IV $[\eta]$ (when $C = 0$) could be obtained, where $[\eta]$ is the intersection point of the two line.

TGA measurement

TGA measurement was carried out with a T2100 analysis system (Dupont, Delaware). In order to get the

TABLE II
The Climate Data of Atmosphere Exposure Test Stations in 2007

Station	Lasa	Yuli	Jiangjin
Average temperature (°C)	9.7	12.9	19.4
Maximum Temperature (°C)	29.0	34.2	38.1
Minimum Temperature (°C)	−11.6	−16.3	4.3
Average relative humidity (%)	36	49	80
Average rainfall (mm)	474.5	37.7	1266.0
Average hours of sunlight (h)	2979.4	3206	1337.1
Average radiation (MJ/m^2)	7470.7	6692.3	2716.6

variation of the thermo-decomposition temperature of PC samples after ageing, TGA measurement was carried out at a heating rate of 10°C/min from 40°C to 600°C under a nitrogen flow of 100 mL/min. The samples weights were between 1.5 mg and 3 mg.

DSC measurement

All the samples were analyzed by using a DSC204 (NETZSCH-Geratebäu GmbH, Germany). To eliminate the thermal history, scans were carried out at a heating rate of 10°C/min from 80°C to 200°C under a nitrogen flow of 20 mL/min. Then the samples were cooled to 80°C at a cooling rate of 10°C/min. At last, the samples were reheated to 200°C at the same heating rate. The glass transition temperature was determined in the second heating scan by the inflection point of the endothermic change. The samples weights were between 5 mg and 6 mg.

UV–vis spectroscopy measurement

UV–vis spectra were recorded on a UV-2300 UV–vis spectrophotometer (Shanghai Tianmei Company, China). The scans were carried out in the range of 190–500 nm at the scanning rate of 200 nm/min. PC samples were dissolved in dichloromethane and the concentration of PC solution was 0.0001 g/mL. Pure dichloromethane was used as a reference.

FTIR measurement

FTIR spectra of samples were recorded on a Nicolet560 (Thermo Fisher Scientific, Massachusetts) spectrometer at a resolution of 2 cm^{-1} in the range of 4000–400 cm^{-1}. The analysis was performed on the films. The films were from the PC/dichloromethane solution after the solvent volatilized at room temperature.

Mechanical test

The tensile properties and flexural properties of the specimens were measured on CMT4204 floor-standing electromechanical universal test machine (Sans Group Company, China) at room temperature. The rate of extension was 50 mm/min and the rate of flexure was 20 mm/min. The impact properties were measured on ZBC1501-2 pendulum impact test machine at room temperature. The impact specimens were performed in Charpy impact test. Before the mechanical tests, all the specimens were stored at 25°C for 48 h. All the tests were in accordance with Chinese National Standard.

RESULTS AND DISCUSSION

Analyses of intrinsic viscosity, thermal stability, and glass transition temperature

Figure 1 illustrates the variation of IV of PC after ageing. The results show that the IV of unaged PC is
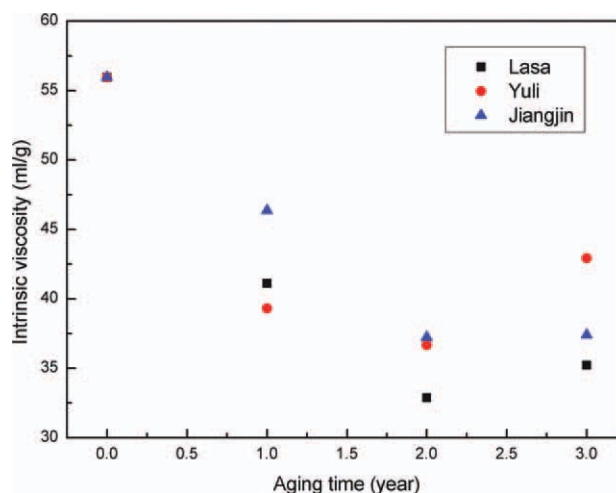

Figure 1 Variation of IV of PC aged in different areas for different time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 55 mL/g, and the IV of aged PC decreases distinctly. Among all the samples, the [η] of samples ageing in Lasa for 2 years decreased more than 40%. In the beginning of the outdoor ageing process (ageing 1 year), the [η] decreased sharply. As showed in Figure 1, the [η] of the samples all reached the lowest point in the second aging year, and then increased in the third aging year. In addition, the IV of PC aging in Lasa decreased the most. After 2 years outdoor exposure, the IV has decreased to 32.9 ml/g. After 1 year outdoor exposure, the IV of samples aging in Yuli decreased the most. The results were related with the climatic conditions. And the relationship between aging process and the weather is to be discussed later.

Figure 2(a–c) shows the thermo gravimetric curves of PC after aging in Lasa, Yuli, and Jiangjin, respectively (in the figure, PC-0 stands for unaged PC, L for Lasa, Y for Yuli, J for Jiangjin, numbers for the aging year). It showed that the thermo-decomposition temperature of aged PC decreased a lot (the initial T_d of PC is 452.32°C). From Table III, the variation of thermo-decomposition temperature was similar to the results of IV—decreased first and increased afterwards. With the increase of exposure time, the variation was not in accord with the aging time, but there was still a recovery trend. The thermal decomposition temperature of aged PC was still far below that of unaged PC. Compared with unaged PC, the range of thermal decomposition temperature and residue rate after aging both increased, indicating that the thermal stability of the samples after aging decreased obviously and the structure changed into some infusible substance. Among the one year aging samples, thermal decomposition temperature in Yuli' dropped the most. The result
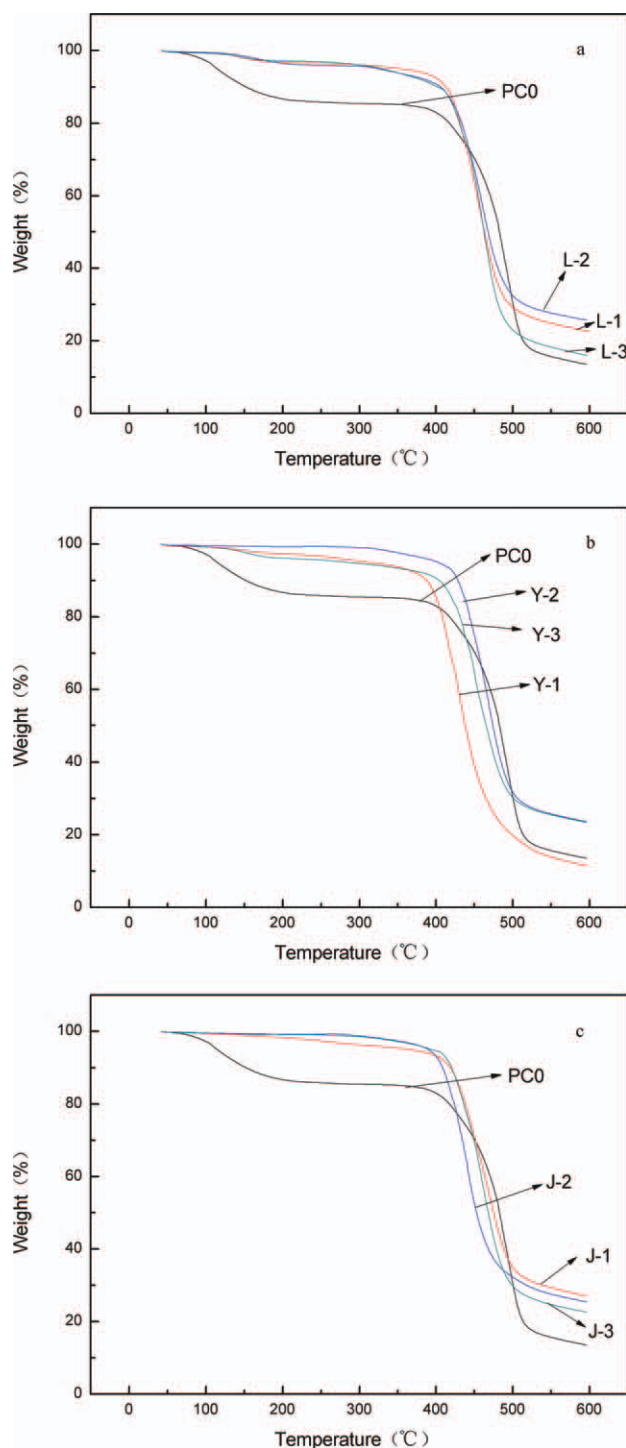
Figure 2 The thermo gravimetric curves of PC unaged and aged in different area for 1 year, 2 years, and 3 years. (a) In Lasa, (b) in Yuli, (c) in Jiangjin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
The Experimental Data of TGA Analysis

Samples	Initial T_d (°C)	Range of T_d (°C)	Residue rate (%)
PC-0	452.32	59.02	13.49
L-1	418.63	66.07	22.22
L-2	422.60	65.26	25.68
L-3	427.43	57.32	15.86
Y-1	396.81	70.83	11.28
Y-2	428.46	65.89	23.58
Y-3	421.15	66.60	23.39
J-1	423.48	72.20	26.94
J-2	409.69	58.18	25.38
J-3	423.82	64.98	22.57

and the samples in Yuli decreased the most among the three first year aging samples. T_g of all samples reached the lowest point in the second year. Compared with T_g of PC before aging, T_g first decreased with aging time and then increased, but the T_g in aging samples were still lower than that of unaged samples. In addition, samples aged in Lasa had the lowest T_g. They were all below 140°C, especially aging for 2 years (T_g = 128.0°C), while samples aged in Jiangjin had the highest T_g.

According to the results above, the outdoor aging process should be a competitive process between degradation and crosslinking—degradation predominates in the beginning, resulting in the obvious decrease of IV, thermo-decomposition temperature, and glass transition temperature. In literature,[16] phenolic terminal groups that produced in degradation stage can arose crosslinking reaction. The degradation and crosslinking process are shown in Scheme 1. It should be emphasized that the Scheme 1 is only
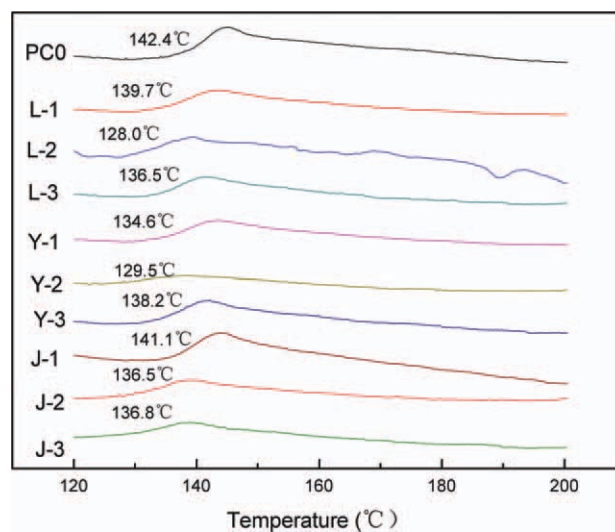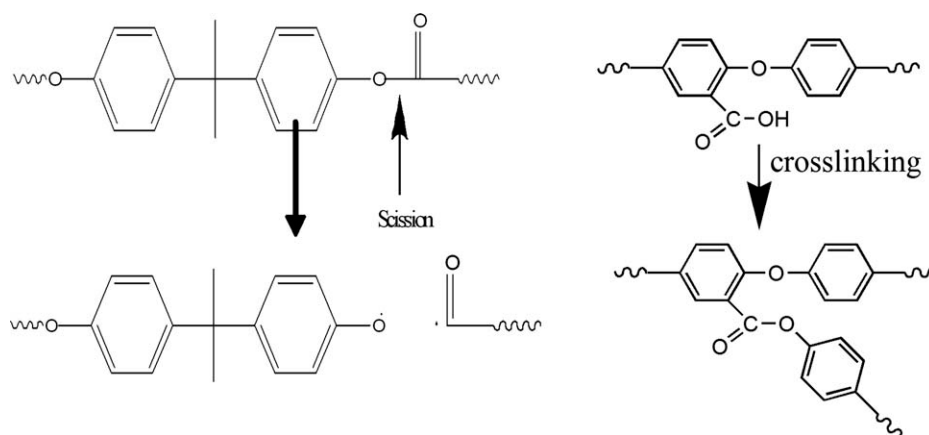

Figure 3 DSC curves of PC unaged and aged in Lasa, Yuli, and Jiangjin for different years. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

agreed with the IV result and could also be explained by the different weather condition.

The information of glass transition temperature of PC is shown in Figure 3. T_g has decreased obviously in the first aging year (unaged sample: T_g = 142.4°C),

Scheme 1 The possible way of ageing process: (a) degradation process, (b) crosslinking process.

one possible way of outdoor aging process because of the complicated effect of multiple environmental factors. But with the increase of aging time, cross-linking begins to play a more important role in the process and leads to an increase in IV, thermo-decomposition temperature, and glass transition temperature. Degradation and crosslinking both occur in the outdoor aging and degradation process has more influence on the variation of IV, thermo-decomposition temperature, and glass transition temperature in our 3 years' experiment. The IV decreases with chain scission, resulting in generation of shorter molecular chain. The decrease of T_d indicates a structure change and weaker stability in heat after aging. The variation of T_g in early aging stage may be explained by three reasons. First, the cleavage of ester groups enlarges the movement space and enables the segment to move easily. Second, molecular weight reduction of the sample can raise the proportion of end segments and hence increase the mobility of the whole molecule. Third, the low molecular weight products can act as plasticizer in degradation. However, with the increase of aging time, the molecules start to crosslink, leading to the decrease of free volume and the inhibition of chain movement. So it becomes relatively difficult for the segments to move, resulting in the increase of T_g.

All the results indicate that the distinction between the samples is resulted from the climatic conditions. As shown in Table I, the longer daylight hours and more intense radiation in Lasa and Yulin lead to more photodegradation and molecular structure damage. So even the temperature and relative humidity (RH) are much higher in Jiangjin, the photodegradation is not as much as that in Lasa and Yuli. As for the climate in Lasa and Yulin, both of which have long daylight hours and intense radiation, the main difference was the humidity and moisture. In general, Lasa has more rainfall than Yuli. The multiple factors of water, light, and oxygen

accelerate the outdoor degradation. The moisture and water could also accelerate the aging process with UV irradiation.[15] This is why the degradation is severer in Lasa than in Yuli in the mass. However, PC aged in Yuli for 1 year degrades much. The IV and thermo-decomposition temperature are even lower than those of Lasa's sample. According to Table II, the reason can be explained by the difference of daylight hours in the two areas. Daylight hours in Yuli are longer than those in Lasa, in the beginning of outdoor aging process, longer daylight hours may ensure that the samples could have more chance to suffer from irradiation, and lead to the continuing structural damage.

UV–vis spectroscopy analysis

Different UV absorption spectra of PC samples aged in different areas are reported in Figure 4, including the results of absorbance between 280 and 340 nm (the right three). There were three peaks at 232 ± 1, 264, and 271 nm, respectively. The 232 ± 1 peak belonged to K band, the other two peaks to B band, illustrating the conjugated structure. Compared with the spectrum of unaged PC, the shape and the position of the absorption bands of PC after aging did not change obviously. However, the intensity of the peak at 232 ± 1 nm has reduced, while that of at 264 nm and 271 nm has increased. The fact indicated the decomposition of the conjugated structure, especially the breakage of carbonate group, and production of more aromatic compounds. As shown in Figure 4, in the range of 280–340 nm, the absorption intensity of aged PC increased significantly. Previous studies showed that the photodegradation of PC occurs in two ways: photo-Fries rearrangement and photo-oxidation under UV irradiation [8]. In the photo-Fries rearrangement mechanism, the reaction starts with the cleavage of carbonyl groups, forming two primary radicals to continue the process.[6] And
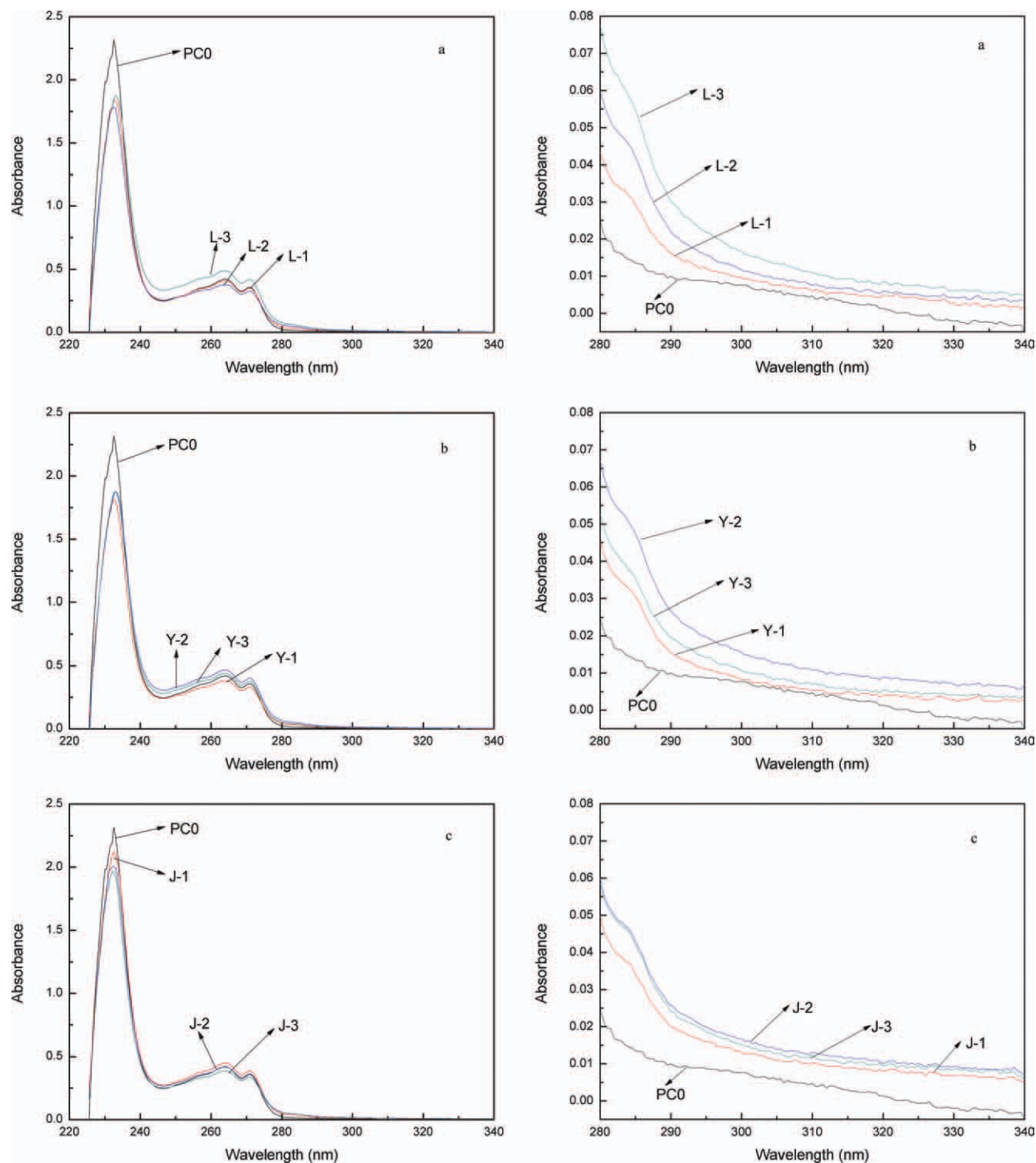
Figure 4 UV absorption spectra of PC aged in (a) Lasa, (b) Yuli, and (c) Jiangjin for different years. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the decomposition and the crosslinking of radicals would produce some derivatives (such as phenylsalicylate and dihydroxybenzophenone). The products would absorb in UV region (phenylsalicylate has the maximum absorption in the range of 290–330 nm, while dihydroxybenzophenone has the maximum absorption in the range of 280–340 nm).[15] So, the results indicated that photo-Fries rearrangement

indeed took place under the irradiation outdoor. In the process, some products absorbed UV light and resulted in the increase of absorption in the range of 280–340 nm. In the three areas, samples aging in Lasa had the most intensive UV absorption in the range, and samples in Yuli took the second place. The different UV absorption might be attributed to the different intensity of UV irradiation. Lasa had
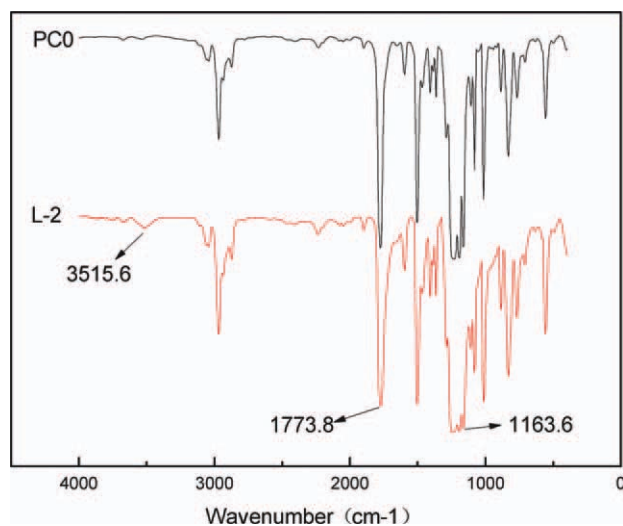
Figure 5 FTIR spectra of PC unaged and PC aged in Lasa for 2 years. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the most intensive irradiation outdoor, resulting in the formation of the most UV-absorbing products in the outdoor aging process. And such products were generated fewest in Jiangjin for lack of sufficient light.

FTIR analysis

In Figure 5, the IR spectra of PC samples before aging and after aging (ageing in Lasa for 2 years) are shown. Most peaks of the sample after aging had not changed. The fact indicated that the aged PC still maintained the main structure. In the spectrum of aged PC, there was a distinct absorption band at 3515.6 cm^{-1}, which belonged to the –OH stretching band, indicating the generation of hydroxy compound in the aging process. It suggested that there should be phenols or alcohols with the C—O stretching in the range of 1300–1000 cm^{-1}. Besides, choosing the peak of 2969 cm^{-1} as reference, the intensity of the stretching band of C=O at 1773.8 cm^{-1} (between 1820 and 1660 cm^{-1}) has decreased to some extent, indicating the reduction of carbonate group. In addition, the intensity of absorption band of aromatic ester at 1163.6 cm^{-1} (between 1200 and 1100 cm^{-1}) has decreased, which indicated disappearance of C—O bond. In literature,[1] phenylsalicylate and dihydroxybenzophenone have absorption at 1689 cm^{-1} and 1629 cm^{-1}, respectively. And the increase of absorption intensity in this range could show the products' existence. Under the combination of UV light and oxygen, the aging process that occurred in Lasa was similar to the photo-oxygen aging behavior. During this process, photo-Fries rearrangement and photo-oxidation reaction occurred, and the main reaction—photo-oxidation reaction would eventually result in generation of phenols, alcohols, acids, and other small molecules.[8] Although the light reaching at ground was mainly in the wavelength of beyond 300 nm, there was also light with wavelength less than 300 nm, which caused photo-Fries rearrangement. The rearrangement would produce substances such as phenylsalicylate and dihydroxybenzophenone, but these substances would be consumed in photo-oxidation reaction, leading to few residues that cannot be detected easily.

Mechanical performance

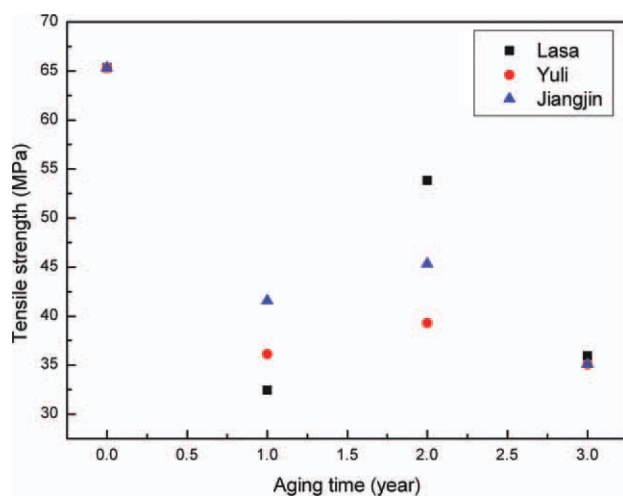Figures 6 and 7 present the tensile properties of PC specimens before and after outdoor aging process.

Figure 6 Variation of tensile strength of PC aged in different areas for different time. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]
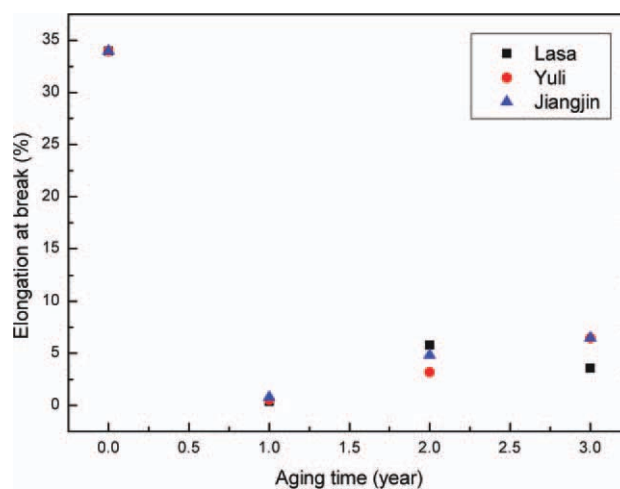

Figure 7 Variation of elongation at break of PC aged in different areas for different time. [Color figure can be viewed in the online issue, which is available at wiley onlinelibrary.com.]

The results showed the effects of outdoor aging clearly. In Figure 6, compared with the tensile strength (65.31 Mpa) of unaged PC, the tensile strength has decreased almost 50% in the first aging year. And when aging for 3 years, the tensile strength of PC specimens reached a very low point about 35 Mpa. Figure 7 showed that the results of elongation at break had a great change in PC ductility. Also in the first year, the elongation at break has already decreased from about 34% to less than 1%, showing the ductility of PC has totally disappeared in outdoor condition. But with the increasing aging time, the elongation at break increased. The results of impact properties are shown in Figure 8. The results showed that the impact strength had decreased more than 50% while the impact strength before aging was 3.655 kJ/m^2. And it decreased much in the first 9 months and became relatively stable later. The results of tensile properties and impact properties demonstrated the loss of ductility in the early outdoor aging process. It could be seen that the PC changed from a ductile material to a brittle material during aging. Figure 9 presents the change of flexural strength in the aging process of PC. It showed that the flexural strength has increased (except the Lasa' aging 3 years specimens, flexural strength was 72.3 Mpa), indicating the hardness of PC after the outdoor aging. The mechanical test results can be explained as follows: The specimens undergo the photo-oxidation aging outdoor. There is the oxide layer in the surface with function of the light and the oxygen. The layer is harder than the bulk, resulting in the higher flexural strength. However the oxide layer has less ductility. When suffering the impact, it cannot dissipate the energy easily, causing the damage of layer. Then the crack
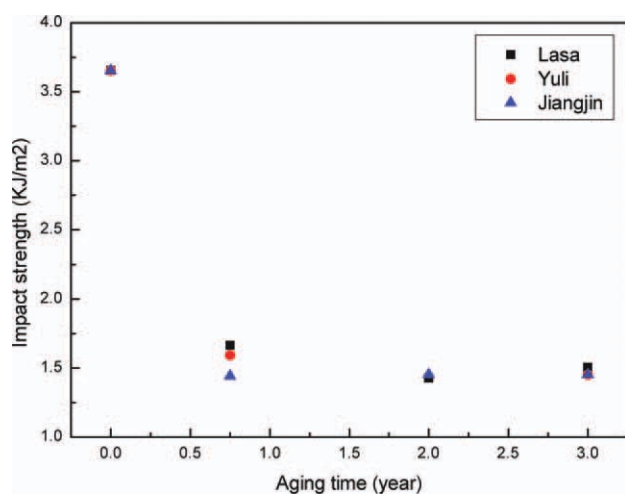

Figure 8 Variation of impact strength of PC aged in different areas for different time. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

Figure 9 Variation of flexural strength of PC aged in different areas for different time. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]
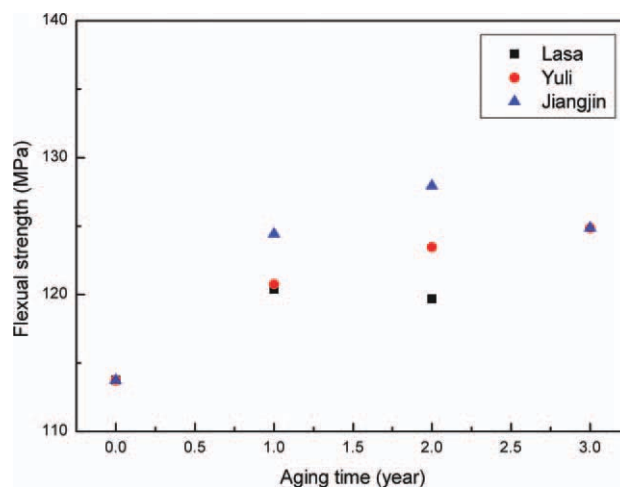
may develop, leading to the sharp decrease of impact strength of aged PC.

CONCLUSION

The results show that IV, thermal decomposition temperature, and glass transition temperature of the aging samples decrease in the beginning and then increase slightly. And the variation shows that the outdoor aging is a combinational and competitive process between degradation and crosslinking behavior—degradation dominates in the first or the second aging year, but crosslink gradually takes over it with the increase of aging time. UV absorption spectra and infrared absorption spectra show that PC samples may generate alcohol, phenol, and dihydroxybenzophenone ketones in the outdoor aging process. And the decomposition of ester groups occurs. After aging, the tensile strength, elongation at break, and impact strength decrease sharply, while the flexural strength increases. The mechanical test results indicate the loss of ductility in the first year. All the results show that aging time length is an important factor in PCs outdoor aging. PC samples aged in Lasa degrade the most, and samples in Jiangjin degrade the least. Degradation is related with the climate condition outdoor, especially the daylight hours and radiation. The significant degradation of samples in Yulin for one year might be attributed to the longest daylight hours.

Daylight hours and radiation are the critical environmental factors in PCs outdoor aging process. The light plays a primary role in early stage of aging. Levels of rainfall and oxygen have synergistic effects on photo-ageing reaction.

References

1. Diepens, M.; Gijsman, P. Polym Degrad Stab 2007, 92, 397.
2. Diepens, M.; Gijsman, P. Polym Degrad Stab 2008, 93, 1383.
3. Diepens, M.; Gijsman, P. Polym Degrad Stab 2009, 94, 34.
4. Nagai, N.; Okumura, H.; Imai, T.; Nishiyama, I. Polym Degrad Stab 2003, 81, 491.
5. Nagai, N.; Matsunobe, T.; Imai, T. Polym Degrad Stab 2005, 88, 224.
6. Gereotovszky, Zs.; Hopp, B.; Beroti, I.; Boyd, I. W. Appl Surf Sci 2002, 186, 85.
7. Claude, B.; Gonon, L.; Duchet, J.; Verney, V.; Gardette, J. L. Polym Degrad Stab 2004, 83, 237.
8. Gao, W. B.; Han, S. M.; Yang, M. J.; Jiang, L.; Dan, Y. Polym Mater Sci Eng (Chinese) 2008, 24, 67.
9. Gao, W. B.; Han, S. M.; Yang, M.; Jiang, L.; Dan, Y. Polym Degrad Stab 2009, 94, 13.
10. Montaudo, G.; Carroccio, S.; Puglisi, C. J Anal Appl Pyrolysis 2002, 64, 229.
11. Jang, B. N.; Wilkie, C. A. Polym Degrad Stab 2004, 86, 419.
12. Jang, B. N.; Wilkie, C. A. Thermochim Acta 2005, 426, 73.
13. Melo, N. S.; Weber, R. P.; Suarez, J. Polym Test 2007, 26, 315.
14. Kjellander, C. K.; Nielsen, T. B.; Ghanbari-Siahkali, A.; Kingshott, P.; Hansen, C. M.; Almdal, K. Polym Degrad Stab 2008, 93, 1486.
15. Tjandraatmadja, G. F.; Burn, S. L.; Jollands, M. C. Polym Degrad Stab 2002, 78, 435.
16. Webba, J. D.; Czandernaa, A. W. Sol Energy Mater 1987, 15, 1.
17. Pickett, J. E. Polym Degrad Stab 2004, 85, 681.