Aging of a Thermoplastic Polymer Under the Combined Effect of Ultraviolet Ray and Temperature

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1 Introduction

The PC is appreciated for its properties such as transparency, impact resistance and ease of processing. It is used in several applications such as vehicle components, displays as well as in construction and greenhouses. However, its exposure to bad weather triggers physical [1] and chemical [2] aging mechanisms. As a result, these mechanisms cause structural changes and alter its various properties over time [3–5].

In this article, we have studied mixed aging, which consists of exposure of polycarbonate samples to a combined action of UV and temperature. For this, aging under UV-C ($\lambda = 253$ nm) combined with isothermal treatments at 40, 80 and 120 °C for 72, 144 and 216 h were carried out on the polycarbonate of bisphenol A. Observations under an optical microscope, physico-chemical and thermal analyses were then carried out in order to demonstrate the effects of aging on the various properties.

2 Experimental Techniques

2.1 Aging

The polycarbonate samples were aged in a heating chamber with UV lamps made of aluminum with dimensions of 50 × 20 × 40 cm^3. This is equipped with two Philips-type UV lamps producing radiation with a wavelength of 253 nm and energy

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of 4.3 eV. They are mounted under the vault with ventilation to prevent degradation under the effect of heat. Inside the enclosure, an electrical resistance is used to heat the samples to a controlled temperature. A sheet is installed above the resistance to properly distribute the heat in the enclosure. The samples are placed on a metal grid allowing rapid homogenization of the temperature. A sensor records the temperature in the vicinity of the specimens and transmits the information to a Eurotherm type regulator which allows the heating rate to be controlled and the set temperature to be maintained by means of a power dimmer. Thermal insulation is provided by a layer of alumina wool placed on the walls and floor of the enclosure. Note that only one side of the samples is directly exposed to UV radiation.

2.2 Different Analyses Used

Characterization by optical microscopy (OM). Micrographs of virgin and aged PC were obtained using an Olympus BX60 type optical microscope (MO) which can magnify the image up to 1000 times.

X-ray diffraction (XRD). XRD analyses were carried out on samples aged under UV combined with temperature, which revealed a change in crystallinity caused by the aging of this material.

A Brucker D8 Advance type X-ray diffractometer, with a θ-2θ assembly was used for this purpose. It is equipped with a 40 kV high voltage generator, which accelerates the electrons in copper anode X-ray tube with a $K\alpha$ line of 1.54 Å. The scan interval was set from 5 to 60° with a step of 0.02° and an exposure time of one second per step. The software driving the device is Spectrum V5.3.1. The tube remains stationary while the detector is stepping while the sample is rotating. When the sample forms an angle θ with the incident beam, the detector moves to 2θ to record the diffracted radiation.

The 1×1 cm^2 surface sample is placed on a hollow sample holder so that the surface to be analyzed is at the same level as the reference surface of the sample holder in order to avoid line shifts. The sample holder is then fixed in its housing by a magnetization system provided for this purpose.

Differential thermal and thermogravimetric analysis (DTA/TGA). Differential thermal analysis (DTA) consists of recording the endothermic and exothermic effects, which are the consequences of reaction or transformation taking place in the material during a thermal cycle. To do this, the sample is placed in a boat next to a second boat containing a reference sample (alumina powder). The two nacelles are arranged on two thermocouples mounted in opposition so as to be able to record the TDA signal which is the difference between the signals of the two thermocouples. Thus, any release or absorption of heat by the sample will be recorded. This manifests itself on the TDA curve as an exothermic or endothermic peak. This analysis therefore allows the detection of any transformation that is accompanied by a thermal effect such as, for example, melting and crystallization, which are, respectively, endothermic and exothermic.

Thermogravimetric analysis (TGA) is the instantaneous measurement of the variation in the mass of a sample as it is heated. The curves reveal the temperatures of certain phenomena, which are accompanied by changes in mass, such as for example oxidation, decomposition, etc.

The sample, weighed beforehand, is placed in a basket placed at the end of a ceramic rod. A silicon carbide (SiC) resistor furnace is used to heat the sample at a controlled rate. The rod is mounted on an analytical balance to note, via a sensor, any change in the mass of the sample during heat treatment. In this way, it is possible to determine the temperature of the phenomenon, which is at the origin of the change in mass. The signal of the derivative of the TGA "d (TGA)" makes it possible to precisely identify this temperature.

The device used is of the PERKEN ELMER Diamond TGA/DTA type. The 10 mg sample is heated up to 800 °C with a heating rate of 10 °C/min. This device records the thermal effects of reactions or transformations that take place during heating of the sample. At the same time, the mass is weighed instantly, by an analytical balance, which allows a recording of any change in the mass of the sample. In order to avoid oxidation of the sample, we performed our tests in a dynamic nitrogen atmosphere.

The samples for thermal analyses were obtained by cutting strips of one millimeter thick and a few milligrams from the face exposed directly to UV radiation using a wire cutter. These samples are weighed using an analytical balance.

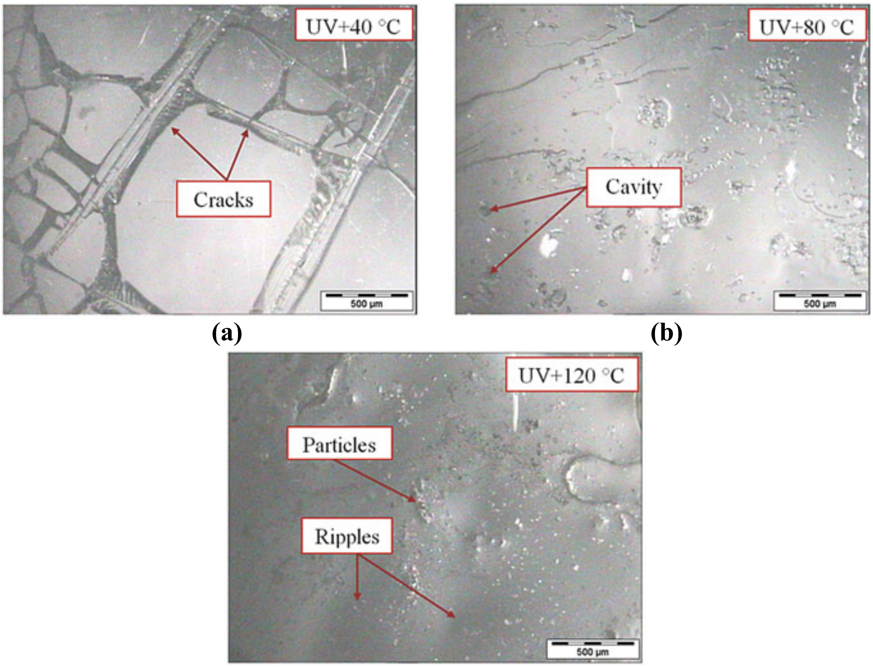
3 Results and Discussions

3.1 Metallographic Observations

We note the presence of cracks on the surface of the sample aged for 216 h under the combined action of UV and the temperature of 40 °C (Fig. 1a). Micrographs of samples aged at 80 and 120 °C show cavities and particles, respectively, as well as surface waves as shown in Fig. 1b, c, respectively.

3.2 X-ray Diffraction

Aging under UV combined at a temperature of 40 °C. Figure 2 shows diffractograms of PC aged under UV combined at the temperature of 40 °C for 72, 144 and 216 h. It appears that the intensity of the diffraction peak changes with the duration of aging. An increase in this intensity is observed at the same level for aging times of 72 and 216 h. On the other hand, for 144 h, there is a decrease in intensity to a value lower than that of the virgin material accompanied by a shift of the line toward the

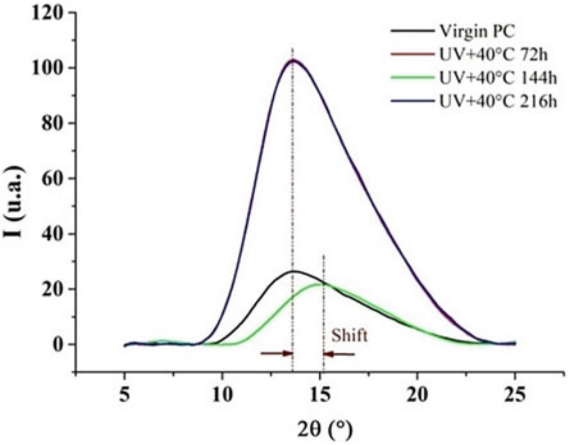


(a) **(b)**

(c)

Fig. 1 Optical micrographs of the PC aged under UV combined at **a** 40, **b** 80 and **c** 120 °C for 216 h

Fig. 2 XRD of PC aged with UV combined at 40 °C for 72, 144 and 216 h



large angles of diffraction. The increase in intensity corresponds to an increase in the rate of crystallinity while its decrease reflects an amorphization of the material. Indeed, at short times, the material begins to undergo the phenomenon of physical aging under the effect of UV and temperature [1, 2]; the molecular chains become mobile and rearrange themselves more in the crystalline areas. When the duration is medium (144 h), the more vulnerable bonds begin to break, which disturbs the order in the crystallites. This then results in a decrease in the intensity of the diffraction peak with a shift corresponding to a tightening of the molecular chains in the crystallites. Over a longer period (216 h), the free radicals, formed by bond breakage, undergo a crosslinking phenomenon which again increases the crystallinity which manifests itself by an increase in the intensity of the diffraction peak [6]. Thus, it seems that the phenomena of bond breaking and crosslinking are successive and contribute to a modification of the structure as a function of the aging period.

UV aging combined at a temperature of 80 °C. When the temperature increases to 80 °C, the increase in diffraction intensity, for 72 h, is relatively smaller than that observed for a temperature of 40 °C (Fig. 3). For 144 h of aging, there is also an amorphization which results in a relatively greater decrease in the intensity of the diffraction peak. We observe a shift of the peak toward the large angles, which is the greater the longer the duration.

UV aging combined at a temperature of 120 °C. Thus, it appears that the increase in temperature disrupts the order in the crystallites for aging times of 72 and 144 h. For the duration of 216 h, the intensity increases again due to the phenomenon of crosslinking favorable to the increase in the rate of crystallinity [7].

Aging at 120 °C causes a gradual increase in crystallinity for 72 and 144 h of aging. On the other hand, for a period of 216 h of aging, the material is strongly amorphized. This is evidenced by the diffractogram of Fig. 4 which shows a strong attenuation of the intensity of the diffraction peak.

Fig. 3 XRD of the PC aged with UV combined 80 °C for 72, 144 and 216 h

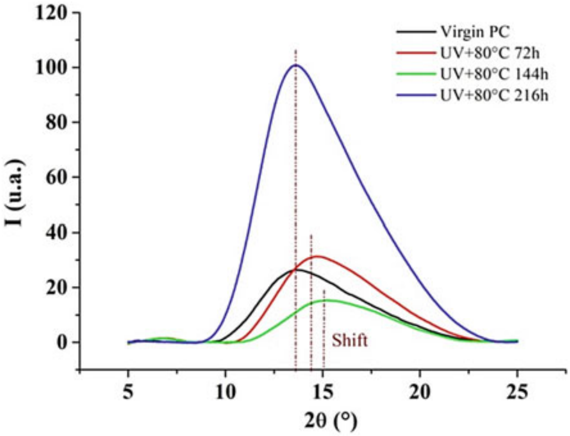
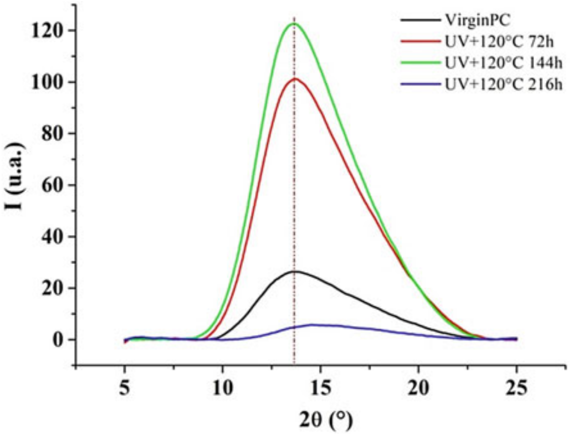


Fig. 4 XRD of the combined UV aged PC at the temperature of 120 °C for 72, 144 and 216 h



3.3 *Thermal Degradation*

Thermogravimetric and differential thermal analysis. Figure 5a–c shows the thermogravimetric curves of virgin and UV aged PC combined at temperatures of 40, 80 and 120 °C, for periods of 72, 144 and 216 h, respectively. These curves all reveal a reduction in the mass of the samples, which reflects a decomposition of material by the release of volatile products; in this case, carbon monoxide and carbon dioxide, as well as water vapor [8]. It can be seen that these curves have different slopes depending on the aging parameters. The rate of degradation corresponds to the slope of the TG curve.

Figure 6a–c shows the derivatives of the thermogravimetry curves of virgin and UV aged PC combined at the temperatures of 40, 80 and 120 °C for periods of 72, 144 and 216 h, respectively. The peak of the derivative corresponds to the temperature at which the rate of degradation is maximum (zoom of Fig. 6).

Figure 7a, b shows the variations of the temperature of the onset of degradation and of the average rate of degradation of the PC as a function of the aging time under UV combined at the temperatures of 40, 80 and 120 °C (Table 1).

This figure shows that the temperature at the start of degradation decreases at the short durations (72 h) of aging of the PC then increases at the long and medium durations for temperatures of 40 and 80 °C. On the other hand, for the aging temperature of 120 °C, the temperature at the start of degradation decreases at low and medium aging times. However, it grows over long durations while remaining less than that of the virgin PC. Thus, it seems that aging under UV combined with a temperature of 40 °C increases thermal stability especially at long periods. On the other hand, as soon as the aging temperature becomes high (120 °C), the thermal stability is affected regardless of the aging period. When UV rays are accompanied by heating at low temperature, the PC undergoes physical aging which makes it more stable at

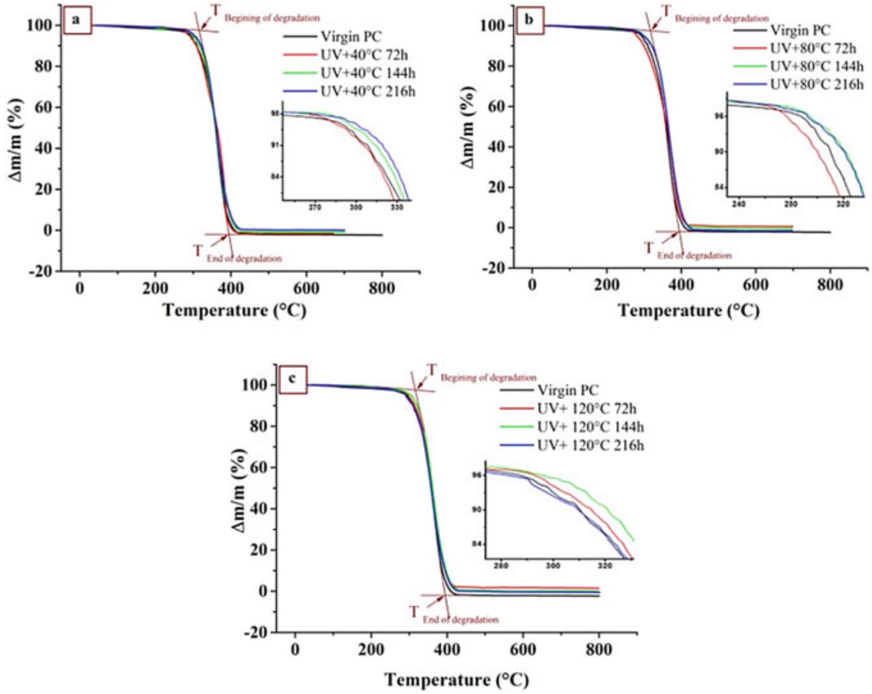


Fig. 5 Thermograms (TG) of virgin and UV aged PC combined at temperatures: **a** 40 °C; **b** 80 °C; **c** 120 °C, for 72, 144 and 216 h

temperature, but as soon as the aging temperature increases, bond breaks are possible which favors the reduction of thermal stability aged material [7].

It is noted that the degradation rate follows the same pattern as the temperature at the start of degradation as a function of the duration of mixed aging (UV + T).

Differential thermal analysis. Figure 8a–c shows the differential thermal analysis (DTA) curves of virgin and UV aged PC combined at temperatures of 40, 80 and 120 °C for periods of 72, 144 and 216 h, respectively. These curves reveal two endothermic peaks (denoted by 1 and 2) for the samples aged independently of the aging temperature. In contrast, the virgin material shows a single endothermic peak of ATD. A third endothermic peak (denoted by 3) is observed only for aging at 40 and 80 °C for 72 h. These endothermic peaks reflect decomposition phenomena that take place by breaking of bonds under the effect of temperature and UV. The surfaces of these peaks correspond to the energies brought into play during the various decompositions.

Note that these peaks have different surfaces, which explains why the decomposition reactions require relatively lower energy when some of the bonds concerned are already broken during aging. On the other hand, when during aging, there is formation of a new substance by crosslinking and oxidation. It will take more energy to

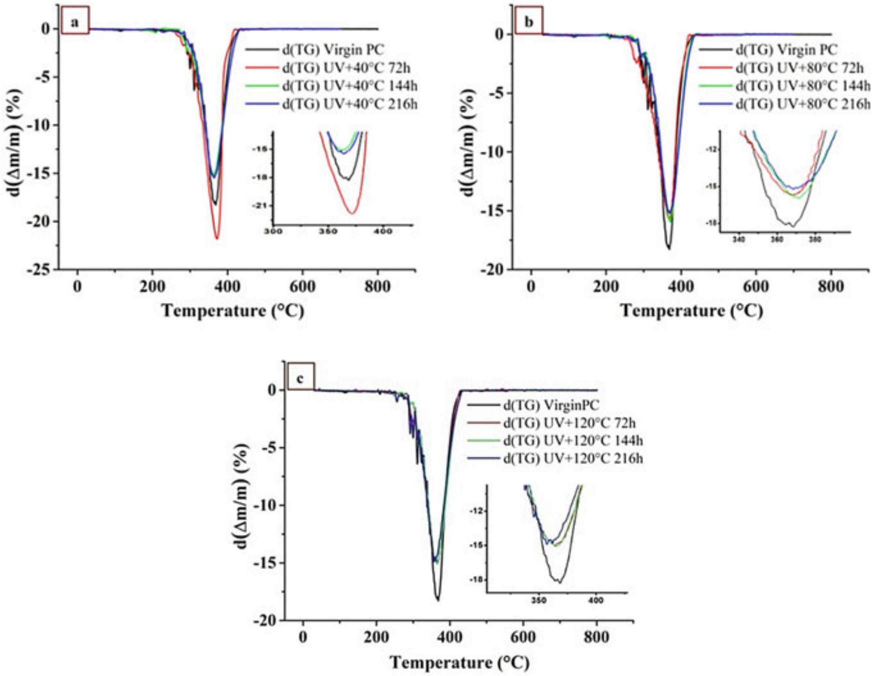


Fig. 6 TG derivatives of virgin and UV aged PC combined at: **a** 40 °C; **b** 80 °C; **c** 120 °C for 72, 144 and 216 h

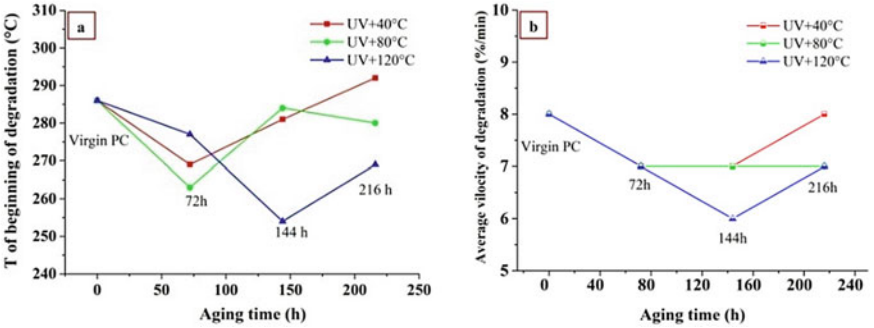


Fig. 7 **a** Temperatures at the start of degradation and **b** Average speeds as a function of time and temperature of aging

ensure its decomposition; in this case, the corresponding ATD peak will have a larger surface as shown in Fig. 8. In addition, the shift of peak 1 toward low temperatures shows that the structure of the material has undergone changes during aging.

The decomposition temperatures corresponding to the various peaks are reported in Table 2 as a function of the aging temperatures and the exposure times.

Table 1 Average speed (V avg) and temperature interval of the start and end of degradation as a function of the aging time of virgin PC and aged under UV combined at 40, 80 and 120 °C

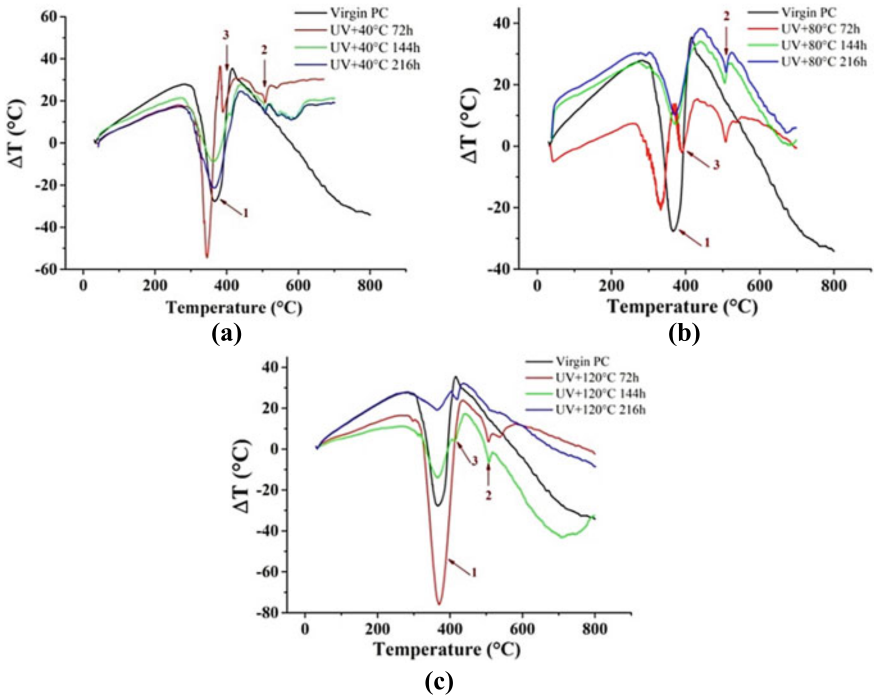
Times (h)	$T_{\text{Beginning of degradation}}$ (°C)	$T_{\text{End of degradation}}$ (°C)	Average rate (%/mn)
UV + 40 °C			
0	286	410	8
72	269	408	7
144	281	418	7
216	292	415	8
UV + 80 °C			
Times (h)	$T_{\text{Beginning of degradation}}$ (°C)	$T_{\text{End of degradation}}$ (°C)	Average rate (%/mn)
0	286	410	8
72	263	413	7
144	284	420	7
216	280	421	8
UV + 120 °C			
Times (h)	$T_{\text{Beginning of degradation}}$ (°C)	$T_{\text{End of degradation}}$ (°C)	Average rate (%/mn)
0	286	410	8
72	277	417	7
144	254	423	6
216	269	419	7

4 Conclusion

PC subjected to the combined action of UV and temperature undergoes a significant deterioration of its properties. The modification of these properties is a consequence of the splitting of molecular chains induced by the action of UV energy and temperature and the appearance of surface damage is presented by ripples revealed by optical microscopy.

Ordered areas after aging are evidenced by increased intensities of the X-ray diffraction peaks as well as an increase in crystal volumes is revealed by a shift in the diffraction peaks of aged materials. On the other hand, there is an amorphization of the PC as a function of the aging time, revealed by DRX.

An increase in thermal stability, due to the physical aging of the material, signifies a delay in the thermal degradation of the PC which has been demonstrated by thermogravimetry and by differential thermal analysis. Additionally, ATD shows that exposure of the PC to high temperatures results in breaks in the chemical bonds of the material indicated by decreasing peaks in ATD curves, meaning that the aged material requires less energy than the reference material.



(a)

(b)

(c)

Fig. 8 TDA curves of virgin PC and aged under UV combined at **a** 40, **b** 80 and **c** 120 °C for 72, 144 and 216 h

Table 2 Decomposition temperatures

Times (h)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
UV + 40 °C			
0	360	/	/
72	345	508	390
144	363	508	409
216	366	507	404
UV + 80 °C			
Times (h)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
0	360	/	/
72	334	508	387
144	371	505	/
216	368	508	/
UV + 120 °C			
Times (h)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
0	360	/	/
72	371	506	418
144	365	506	413
216	363	508	/

References

1. Ho CH, Vu-Khanh T (2003) effects of time and temperature on physical aging of polycarbonate. Theoret Appl Fract Mech 39(2):107–116
2. Schnell H (1964) Chemistry and physics of polycarbonate, inter-science, New York
3. Sharma T, Aggarwal S, Sharma A, Kumar S, Mittal VK, Kalsi PC, Manchanda VK (2008) Modification of optical properties of polycarbonate by gamma irradiation. Radiat Eff Defects Solids 163(2):161–167
4. El-Ghazaly M, ShAydarous A, Al-Thomali TA (2013) Ultraviolet radiation of short wavelength (UVC) induced-modifications in optical properties of PADC. Life Sci J 10(4):2446–2450
5. Gogotov IN, Barazov SKh (2012) the effect of ultraviolet light and temperature on the degradation of composite polypropylene. PLAST Massy 12:55–58
6. Claude B, Gonon L, Duchet J, Verney V, Gardette JL (2004) Surface cross-linking of polycarbonate under irradiation at long wavelengths. Polym Degradation Stab 83:237–240
7. Diepens M, Gijsman P (2009) Outdoor and accelerated weathering studies of bisphenol A polycarbonate. Polym Degrad Stab 96:649–652
8. Yan Ch, Jian H, Zhang J, Zhao F, Liu Ch, Shen Ch (2016) The influence of sub-Tg annealing on environmental stress cracking resistance of polycarbonate. Polym Test 56:364–368