

Influence of Polyacrylate/Titanium Dioxide Composite Particles on the Antiaging Performance of Polycarbonates

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Received 27 August 2008; accepted 26 May 2009

DOI 10.1002/app.30898

Published online 12 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polycarbonate (PC) and PC modified by polyacrylate/TiO₂ composite particles were exposed both in an outdoor environment with typical humid and hot climatic conditions in the Jiangjin area and in an indoor hygrothermal environment for accelerated aging. Then, the effects of the polyacrylate/TiO₂ composite particles on the antiaging performance of PC were investigated by measurement of the mechanical properties of PC before and after aging. The results show that the mechanical properties of PC decreased a lot after aging by the outdoor environment of the Jiangjin

area. After accelerated aging by the indoor hygrothermal environment, the tensile strength and the bending strength of PC increased a little, and the elongation at break of PC decreased. The polyacrylate/TiO₂ composite particles effectively increased the elongation at break of PC aged by the hygrothermal environment and outdoor aging. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3495–3500, 2009

Key words: ageing; composites; mechanical properties; polycarbonates

INTRODUCTION

Bisphenol A-polycarbonate (PC) is used in a wide variety of applications as an engineering thermoplastics because of its excellent balance of properties, including optical clarity, high heat-deformation temperature, toughness, and electrical properties. In particular, it is used in outdoor applications because of its good transparency, light weight per unit volume, and high mechanical strength.

According to the literature,¹ the total demand of PC is around 2.8 million tons, and the annual output was about 3.9 million tons in the year 2006. It has become the second most used plastic, second only to polyamide among the five most important engineering plastics. It is so widely used that it is involved in all fields of the world and in the lives of people. However, when used outdoors, the performance of PC is destroyed due to UV light, moisture, stress, and temperature variations, so it is important and necessary to study the antiaging properties of PC.

Over the years, there have been many studies on the degradation processes of PC by accelerated aging tests. The most attention has been paid to the degradation mechanism at the molecular level.

A deep knowledge of the durability and predictability of the properties has been garnered under different environmental conditions and over long periods of time. Some studies related to the impact properties have been reported. Zhan et al.² investigated the hot-air aging and hot-water aging of notched impact samples of PC and discussed the aging mechanisms. They believed that the main fracture mechanism of unaged PC was shear yielding and that of aged PC was caving. Narkis and Nicolais³ reported that internal cracking and microvoids in PC samples that had previously been exposed to boiling water formed during storage at room temperature.

There has been very little work devoted on the antiaging properties of PC. Tan et al.⁴ blended three core-shell acrylic impact modifiers with the same composition and different particle diameters with PC. In addition to the influence of the aging time on the impact and tensile behaviors, the thermal reversibility was also investigated. They found that tiny differences in the thermal history of neat PC resulted in different fracture modes. When acrylic impact modifiers were introduced into PC, the different fracture modes occurring during the testing of neat PC disappeared.

The bond of carbonate in the PC molecular chains is very sensitive to water and is very susceptible to hydrolysis. The hydrolysis reaction is the main reason for the degradation of the PC molecular chain. In addition, phenols and quinines decompose from

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 50533080.

PC at high temperatures; the former keeps reacting as a catalyst, and the latter causes PC to turn yellow. Products of PC work outdoors most of the time, so higher temperature and higher humidity environments are the most important failure conditions for PC. Because of this, we chose the Jiangjin area for the outdoor aging location because of its typical climate conditions, with high annual average temperature and humidity. Furthermore, to simulate outdoor aging, artificial accelerated hygrothermal aging was done indoors. After these aging experiments, the effects of polyacrylate/TiO₂ composite particles⁵ on the antiaging performance of PC were examined.

EXPERIMENTAL

Materials

The polyacrylate/TiO₂ composite particles were prepared in our laboratory via the *in situ* emulsion polymerization of the monomers in the presence of TiO₂.⁵ Bisphenol A-PC was purchased in a solid pellet state from Chongqing Changfeng Chemical Factory (Chongqing, China). Antioxidant1010 was purchased at the market.

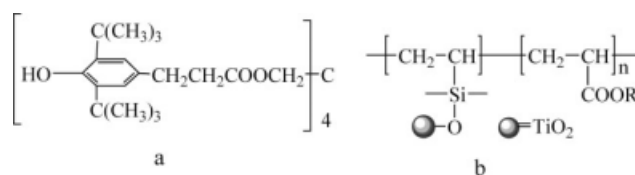
Sample preparation

PC was blended with polyacrylate/TiO₂ composite particles and Antioxidant1010. Then, the mixture was extruded and granulated in a twin-screw extruder (TSSJ225/03, Chenguang Plastics Machinery Institute, Chengdu, China) at 250°C.

All of the samples for aging and testing were obtained by injection molding in a K2TEC40-111 injection machine (Feromatikmlacron, Riegel, Germany). The injection-molding techniques and samples size were chosen according to a Chinese national standard.^{6,7} The process parameters of injection molding in the four areas were 260, 260, 255, and 240°C. Before injection molding, the pellets were dried in a vacuum oven at 120°C for 24 h to exclude water.

Aging test

Two aging tests were carried out in the meantime. Samples were exposed outdoors in the Jiangjin area for 1 year, where the annual average temperature and humidity were 19.4°C and 80%, respectively. The artificial hygrothermal aging was done in a test chamber (SH60B, Chongqing Yinhe Experimental Equipment Co., Ltd., Chongqing, China) for 42 days; the temperature was 70°C, and the relative humidity was 80%. To eliminate the errors and to ensure experimental precision, five pieces of the same material were tested at every aging time point.



Scheme 1 Structural diagrams of (a) Antioxidant1010 and (b) polyacrylate/TiO₂ composite particles.

Measurements

The stress-strain behavior, bending strength, and elongation at break of the samples before and after aging were measured on a CMT4204 floor-standing electromechanical universal testing machine (Sans Group Co., Chongqing, China) at 25°C. The rate of extension was 50 mm/min, and the rate of bending was 20 mm/min.

RESULTS AND DISCUSSION

Results of outdoor aging in the Jiangjin area

We choose the Jiangjin area for the aging location because of its unique climate conditions. According to the annually reported data of the meteorological parameters of some cities in western and middle China, the annual average temperature and humidity of the Jiangjin area were 19.4°C and 80%, respectively, in 2007. Both were the largest values among the cities investigated.

In this study, three kinds of samples, that is, PC, PC/Antioxidant1010, and PC/Antioxidant1010/composite particles, were prepared and tested. Antioxidant1010, shown in Scheme 1(a), was added to protect PC from thermal degradation during processing; the polyacrylate/TiO₂ composite particles, shown in Scheme 1(b), were added to protect PC from ultraviolet photodegradation during the actual course of aging. At the same time, the polyacrylates in the composite particles could improve the compatibility of TiO₂ with PC and, hence, enhance the mechanical properties of PC after aging.

The samples were placed on an aging shelf in the Jiangjin area for 1 year, and then, the mechanical properties of the samples were tested. The results are shown in Tables I and II, and the retention percentage (*E*) was calculated with the following equation:

$$E = V_1/V_0 \times 100\%$$

where *V*₁ is the value of the mechanical property of the sample after aging and *V*₀ is the corresponding value of the same mechanical property of the sample before aging.

TABLE I
Mechanical Properties of the Samples Before and After Aging in the Jiangjin Area for 1 Year

Sample	State	Tensile strength (MPa)	Elongation at break (%)	Bending strength (MPa)
PC	Before aging	65.42 ± 1.50	34.63 ± 4.00	113.73 ± 0.75
	After aging	40.44 ± 5.25	0.72 ± 0.15	125.01 ± 3.50
PC/Antioxidant1010	Before aging	65.29 ± 0.30	86.05 ± 8.10	110.54 ± 2.65
	After aging	37.58 ± 3.50	0.76 ± 0.20	125.25 ± 4.25
PC/Antioxidant1010/ composite particles	Before aging	64.47 ± 0.25	67.27 ± 4.85	110.48 ± 1.20
	After aging	67.74 ± 4.35	18.69 ± 1.25	126.17 ± 5.30

Data are given with the error range after the ± sign.

As shown in Table I, before exposure, Antioxidant1010 and the composite particles had no significant influence on the tensile strength of PC. After 1 year of exposure in the outdoors, PC exhibited a significant property change, with a rapid drop in the tensile strength, and the retention percentage was only 61.82% (Table II), which indicated that the hygrothermal environment fatally destroyed the tensile strength of PC. Antioxidant1010 did not enhance the antiaging performance of PC revealed by the tensile value because the retention percentage of the tensile strength of the PC/Antioxidant1010 was even smaller than that of PC (Table II). When the polyacrylate/TiO₂ composite particles were added, the antiaging effect in the samples was quite obvious. The tensile strength of the PC/Antioxidant1010/composite particles did not decrease but increased after aging, which showed that the polyacrylate/TiO₂ composite particles inhibited the decline of the tensile strength of PC.

Before aging, the elongation at break of PC increased to 86.45 and 64.47% from 34.63%, respectively, with the addition of Antioxidant1010 and Antioxidant1010/composite particles. These results occurred because Antioxidant1010 and the composite particles play the role of a plasticizer and improved the fracture toughness of PC. After aging, the elongation at break of PC decreased to 0.72%, whereas that of the PC/Antioxidant1010 reduces to 0.76%. The retention percentages of the elongation at break of the two samples were 2.08 and 0.88%, respectively. A possible reason for the result is that the low-molecular Antioxidant1010 migrated from the inside to the surface of the samples, and the additive effect became almost nil. For the PC/Antioxidant1010/composite particles, migration did not occur on TiO₂ because it was encapsulated by macromolecular polyacrylates. Polyacrylate is an elastic resin that can be compatible with most polymers, and it improved the dispersity of TiO₂ in PC. The interface was fuzzy with a strong adhesive force, and the compatibility of TiO₂ with PC increased, so the retention percentage was 27.78% for the PC/

Antioxidant1010/composite particle sample, which was much larger than that of PC and PC/Antioxidant1010.

The bend strength of PC without any additive was 113.73 MPa, and this value decreased to 110.54 and 110.48 MPa, respectively, with the addition of Antioxidant1010 and Antioxidant1010/composite particles. These results illustrate that the effect of Antioxidant1010 and composite particles on the bending strength of PC made no difference. As we know, the bending force is vertical to the orientation of the molecular chain in the bending process. Stress loss caused by chain scission had less of an influence than the increase in stress caused by crosslinking on the bending strength, so after aging, the bending strength of all of the samples increased slightly. The difference is that the retention percentage of the bending strength of the PC/Antioxidant1010/composite particles and PC/Antioxidant1010 were higher than that of PC.

The stress–strain curves of the PC, PC/Antioxidant1010, and PC/Antioxidant1010/composite particles are listed in Figure 1. Before aging, there was a peak that indicated strain softening in the stress–strain curve of PC, showing the longest elongation at break [Fig. 1(a)]. After outdoor aging for 1 year, strain softening did not appear [Fig. 1(b)]. Comparing the results of PC before and after aging, we drew the conclusion that the climate in the Jiangjin area caused serious damage to the mechanical properties of PC, making the ductile PC sample

TABLE II
Retention Percentage of the Mechanical Properties of the Samples After Aging in Jiangjin Area for 1 Year

Sample	<i>E</i> of tensile strength (%)	<i>E</i> of elongation at break (%)	<i>E</i> of bending strength (%)
PC	61.82	2.08	101.13
PC/Antioxidant1010	57.56	0.88	113.31
PC/Antioxidant1010/ composite particles	105.07	27.78	114.20

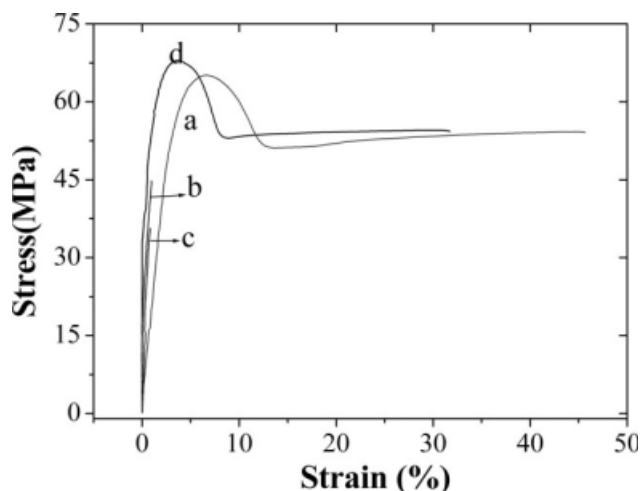


Figure 1 Stress–strain curves of the PC (a) before and (b) after aging, (c) PC/Antioxidant1010 after aging, and (d) PC/Antioxidant1010/composite particles after aging.

rigid; that is, the hygrothermal environment had a great effect on PC, so it is important and necessary to improve the antiaging properties of PC for use in outdoor environments, especially in hygrothermal environments. After the addition of Antioxidant1010, there was no good effect reflected by the stress–strain relationship. The sample after outdoor aging for 1 year was also rigid [Fig. 1(c)] because of the migration of Antioxidant1010 from the inside to the surface of the samples, and the additive effect became almost nil. When the polyacrylate/TiO₂ composite particles were added to PC, however, the effect was different compared with the effect caused only by Antioxidant1010. Strain softening still existed after the sample was aged for 1 year [Fig. 1(d)]. The stress softening was higher and narrower than that of the nonaged neat PC. This result reflected the fact that the polyacrylate/TiO₂ composite particles had an active influence on the mechanical properties of PC used outdoors and effectively enhanced the antiaging performance of PC.

Results of the artificial accelerated hygrothermal aging indoors

Because we established that the hygrothermal environment had a great influence on the mechanical properties of PC on the basis of the results obtained by the outdoor aging in the Jiangjin area, it was necessary to make clear the influence of an individual hot and humid environment on the mechanical properties of PC. Therefore, we conducted another experiment to simulate the hot and humid environment. The experiment was conducted in an aging oven, where the temperature was 70°C and the relative humidity was 80%. The samples were exposed in the oven for periods from 2 to 42 days, and then,

they were removed and stored at room temperature. The mechanical properties were tested after all of the samples were aged.

Hygrothermal aging has two effects, those caused by hot air and steam. Hot led to a conformation rearrangement and free volume decrease in PC.² The water molecule was smaller than the PC molecule, so it could move easily and provide free volume for the macromolecular segment movement, which resulted in an increase in the fracture toughness of PC. On the other hand, the PC molecule decomposed after the absorption of water, and the molecular weight decreased. These factors caused the macromolecular segment to become contrarily brittle.

Figure 2 shows the effect of the aging time on the bending strength of the samples. The bending strength of PC increased dramatically after hygrothermal aging for 2 days and then increased gradually with aging time over the timescale investigated [Fig. 2(a)]. This result was similar to that obtained by outdoor aging. A similar result was also reported by LeGrand⁸ and Hutchinson et al.⁹ The bending strength was somewhat equal to that of others after aging for different times. After PC was blended with Antioxidant1010 and polyacrylate/TiO₂ composite particles, the bending strengths also increased dramatically after hygrothermal aging for 2 days and then increased gradually with aging time. The changes in the three curves shown in Figure 2 were similar to each other. In contrast, the bending strength of the PC/Antioxidant1010 had a higher increment than that of PC after hygrothermal aging for 2 days [Fig. 2(b)]. The bending strength of the PC/Antioxidant1010/composite particles had an equal increment to that of PC after hygrothermal

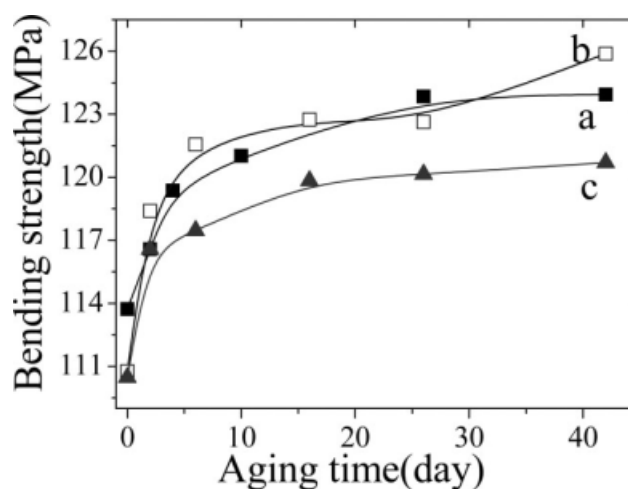


Figure 2 Effects of the aging time on the bending strength of the (a) PC, (b) PC/Antioxidant1010, and (c) PC/Antioxidant1010/composite particles at a temperature of 70°C and a relative humidity of 80% (measuring deviation $\approx \pm 5\%$).

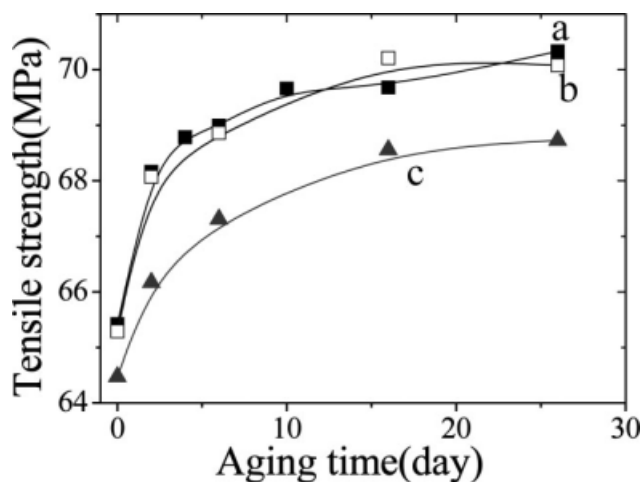


Figure 3 Effects of the aging time on the tensile strength of the (a) PC, (b) PC/Antioxidant1010, and (c) PC/Antioxidant1010/composite particles at a temperature of 70°C and a relative humidity of 80% (measuring deviation $\approx \pm 5\%$).

aging for 2 days [Fig. 2(c)], although the bending strength was smaller than that of PC.

Figure 3 shows the effect of aging time on the tensile strength of the samples. Just as with the bending strength of PC, the tensile strength of PC increased dramatically, about 4%, after hygrothermal aging for 2 days and then increased gradually with increasing aging time over the timescale investigated [Fig. 3(a)]. This result was different from the result obtained by outdoor aging in the Jiangjin area. The tensile strength is intimately related to the intermolecular force, and the tensile fracture is related to the molecular chain orientation and aggregation state. In our studies, the simulation of accelerated aging was only conducted for 42 days; chain scission and crosslinking may take place simultaneously. However, for the outdoor aging, the aging time was so long that chain scission was the major aging mode. The different aging modes induced different results.

The tensile strength of the PC/Antioxidant1010 had the same change tendency as that of PC [Fig. 3(b)], and the two curves were very similar to each other or almost coincident with each other, whereas for the system of the PC/Antioxidant1010/composite particles, the tensile strength of the samples aged for 28 days displayed little difference [Fig. 3(c)] compared to that of the PC samples. First, the curve was more abatable than the two curves described before for the earlier aging stage. Second, the tensile strength of the sample was smaller than that of PC at the same aging time; this indicated that the composite particles had a toughening effect on PC.

Figure 4 shows the effect of the aging time on the elongation at break of the samples. As discussed previously, the Antioxidant1010 and polyacrylate/

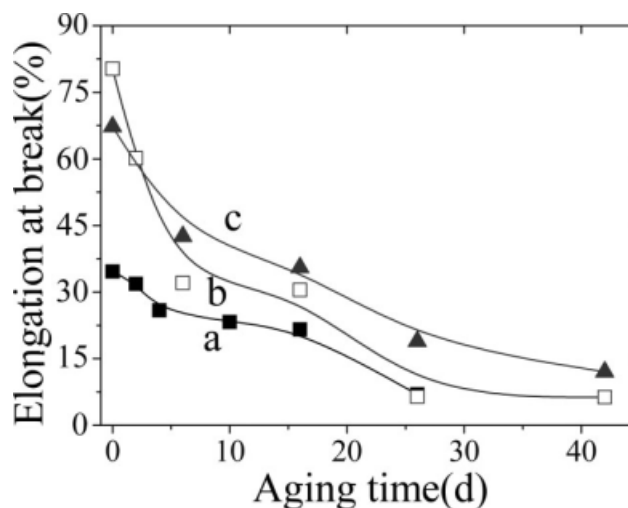


Figure 4 Effects of the aging time on the elongation at break of the (a) PC, (b) PC/Antioxidant1010, and (c) PC/Antioxidant1010/composite particles at a temperature of 70°C and a relative humidity of 80% (measuring deviation $\approx \pm 5\%$).

TiO₂ composite particles played the roles of plasticizers so that the samples were more ductile than the PC sample. After 5 days of aging, all of the samples showed relatively brittle behavior, as indicated by a significant reduction in the elongation at break. As shown in Figure 4(a), the elongation at break decreased gradually all the time with increasing aging time over the timescale investigated. After aging for 26 days, the elongation at break was so small that it was unnecessary to do more testing. This result was similar to the previous results. As shown in Figure 4(b), which represents the PC/Antioxidant1010 sample, the elongation at break decreased about 60% after the sample was aged for

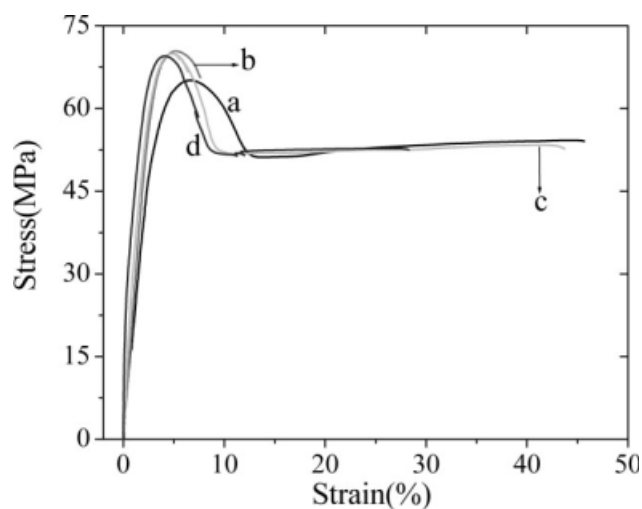


Figure 5 Stress–strain curves of the PC (a) before and (b) after aging, (c) PC/Antioxidant1010 after aging, and (d) PC/Antioxidant1010/composite particles after aging at a temperature of 70°C and a relative humidity of 80%.

6 days. Despite this, the real value was apparently bigger than that of PC. The curve in Figure 4(c) nearly moved in a parallel line with the curve in Figure 4(a) with increasing aging time over the time-scale investigated. The elongation at break of the PC/Antioxidant1010/composite particles was bigger than the value of the other two samples at the same aging time. This again demonstrated that the polyacrylate/TiO₂ composite particles had an active influence on the mechanical properties of the PC aged in the hygrothermal environment.

The stress-strain curves of the PC, PC/Antioxidant1010, and PC/Antioxidant1010/composite particles are listed in Figure 5. Each curve had a peak at the point that strain softening took place. The stress-strain curve of the nonaged PC [Fig. 5(a)] revealed that the sample had a higher elongation at break. Postyield stress drop behavior was observed. The term *postyield stress drop* was introduced by Haward et al.¹⁰ to indicate the extent of strain softening behavior and was then discussed by Bubeck et al.¹¹ and Hill et al.¹² in connection with physical aging. After they were aged for 42 days, the samples broke at the same time or just after the strain softening took place [Fig. 5(b)]. This also demonstrated that the PC sample changed to brittle from tough and that brittle fracture became the main fracture mode. The peak became higher and narrower after aging for 42 days with the addition of the antioxidant1010 and the polyacrylate/TiO₂ composite particles; this indicated that the PC/Antioxidant1010 and PC/Antioxidant1010/composite particles had a higher yield stress and earlier necking behavior.

CONCLUSIONS

The climate conditions in the Jiangjin area caused serious damage to the mechanical properties of PC.

The simulation of artificial accelerated hygrothermal aging also induced a decrease in the elongation at break of PC. Both aging experiment results illustrate that the PC samples changed to brittle from tough after they were aged in a hygrothermal environment. The humid and hot environments had caused severe destruction to PC via outdoor aging and artificial accelerated hygrothermal aging. The polyacrylate/TiO₂ composite particles obviously improved the mechanical properties of PC after outdoor aging, as revealed by all of the retention percentages of the mechanical properties of the samples. The active effect was also displayed after accelerated aging by the indoor hygrothermal environment. The polyacrylate/TiO₂ composite particles were effective in increasing the antiaging performance of PC.

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