Study of Poly(methyl methacrylate) Film Doped with Inclusion Complex of *p-tert*-Butylcalix[8]arene

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Received 18 July 2001; accepted 9 January 2002

ABSTRACT: Seven kinds of poly(methyl methacrylate) (PMMA) films doped with [60]fullerene or its inclusion complex of *p-tert*-butylcalix[8]arene were prepared and characterized by FTIR, UV-vis, TG, and DSC. It was found that the thermal stability of PMMA is much improved by doping with the inclusion complex in comparison with [60]fullerene itself, that is, the inclusion complex retards the thermal depolymerization of PMMA very effectively. The influence of incorporating active carbon powder or calix[8]arene on the thermal stability of PMMA was also investigated. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1549–1552, 2002

Key words: fullerenes; inclusion chemistry; thermal properties; composites; films

INTRODUCTION

As an optical resin, poly(methyl methacrylate)[1] (PMMA) has taken the place of optical glass and is extensively used in various fields due to its lighter weight, shock resistance, stable chemical property, good processibility, and insulation character. However, its applications are impeded by its low application temperature, high water-absorbing capacity, poor thermal stability, poor abradability, and poor organic solution resistance. Thus, how to overcome the abovementioned defects, especially, its poor thermal stability, is of great significance.

On the other hand, the unique spherical shape, small size (diameter: 0.71 nm), conjugate three-dimensional π-electric system, high thermal stability, and ability to exhibit donor–acceptor or π–π interactions of [60]fullerene[2–5] promise it to be an attractive doping reagent to incorporate into the polymer to construct new materials.[3–7] It has been proved that [60]fullerene can retard the degradation of polymers in the presence of oxygen.[8–10] Also the amorphous glass transition temperature (T_g) of PMMA late increases with the embedding of *N*-methylfulleropyrrolidine.[11] Another study showed that the interaction of the host PMMA matrix with fullerenes could modify the optical properties of C_{60}, a fact promising potential applications.[12] It is well known that [60]fullerene and *p-tert*-butylcalix[8]arene can form an inclusion complex, and the surface properties, including charge distribution, π–π interactions, compatibility, and aggregated state of the complex, are different from those of [60]fullerene itself. Up to now, no one has reported what happens when polymer is mingled with the fullerene inclusion complex. Here, we report on the preparation of PMMA films mingled with [60]fullerene, its inclusion complex of *p-tert*-butylcalix[8]arenes, active carbon, and *p-tert*-butylcalix[8]arenes. The thermal stability of PMMA was more improved when doped with the inclusion complex in comparison with being doped with [60]fullerene itself or active carbon.

EXPERIMENTAL

Materials

PMMA was purchased from commercial sources, and toluene was refluxed over sodium for 4 h and distilled before use. [60]Fullerens in 99.9% purity was supplied by the Center of Analysis and Measurement of Wuhan University (Wuhan, China). *p-tert*-Butylcalix[8]arenes and its [60]fullerene complex were synthesized according to the literature.[13,14]

Preparation of the doping films

All the films were prepared in the same way. The sample solution was degassed under a vacuum, then spread onto a glass plate (25.4 × 76.2 mm), degassed under a vacuum again, and transferred into a desiccator overnight. The glass plate was further dried at 100°C for 30 min, and the film was peeled from the glass plate after cooling.

Samples $I_{(1)}$ and $II_{(1)}$

PMMA, 2.15 g, was dissolved in 85 mL of dry toluene to obtain sample $I_{(1)}$. The PMMA content was 2.73%.

Correspondence to: Y. Chen.

Contract grant sponsor: Research Fund for Doctoral Program of Higher Education of China; Contract grant number: 98048624.

Contract grant sponsor: Wuhan Chenguang Plan Foundation of Hubei Province of China; contract grant number: 995004079C.

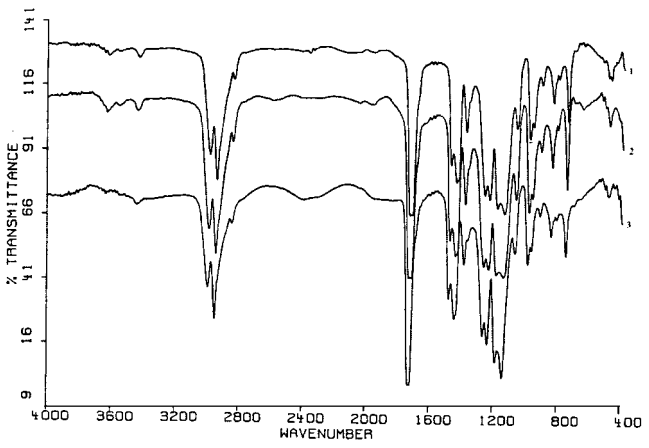

Figure 1 FTIR spectra of three sample films: (1) $I_{(1)}$; (2) $I_{(2)}$; (3) $I_{(3)}$.

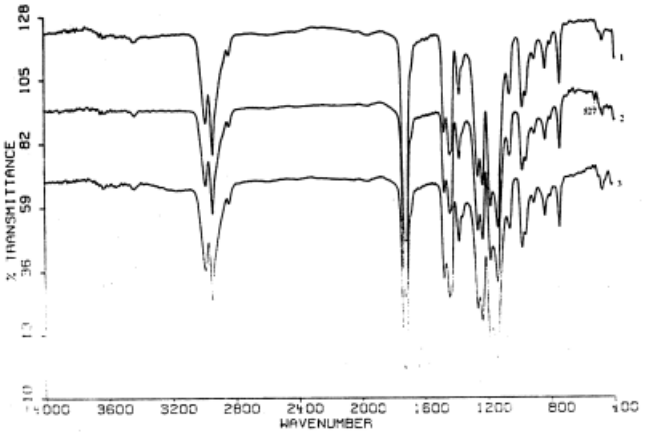

Figure 2 IR spectra of the other three sample films: (1) $II_{(1)}$; (2) $II_{(2)}$; (3) $II_{(3)}$.

When sample $I_{(1)}$ was partially concentrated under reduced pressure, sample $II_{(1)}$ was obtained, and the PMMA content increased to 4.46%.

Samples $I_{(2)}$ and $II_{(2)}$

To 5 g of a 2.73% PMMA toluene solution [Sample $I_{(1)}$], 1 mL of a [60]fullerene toluene solution (containing 3 mg of [60]fullerene) was added and stirred for 3 h. The color of the solution turned purplish red. Sample $II_{(2)}$ was similarly prepared but using 5 g of a 4.46% PMMA solution. It also was purplish red in color. The [60]fullerene contents in the corresponding dry films are 2.2 and 1.4%, respectively.

Samples $I_{(3)}$ and $II_{(3)}$

To 5 g of a 2.73% PMMA toluene solution, 3.2 mg of a *p-tert*-butylcalix[8]arene [60]fullerene complex in 5 mL toluene was added. The mixture was stirred at room temperature for 12 h to obtain sample $I_{(3)}$. When the concentrated PMMA toluene solution (4.46%) was used, the sample $II_{(3)}$ was similarly obtained but using a 8.4 mg *p-tert*-butylcalix[8]arene [60]fullerene complex in 10 mL toluene. The [60]fullerene contents in the corresponding dry film were 0.8 and 1.4%, respectively.

Sample III

Sample III is a PMMA film doped with active carbon powder in 200 mesh; the active carbon content is 2.2%.

Other samples

Sample $I_{(4)}$ and sample $II_{(4)}$ are PMMA films doped with calix[8]arene of 1.4 or 2.5%, respectively.

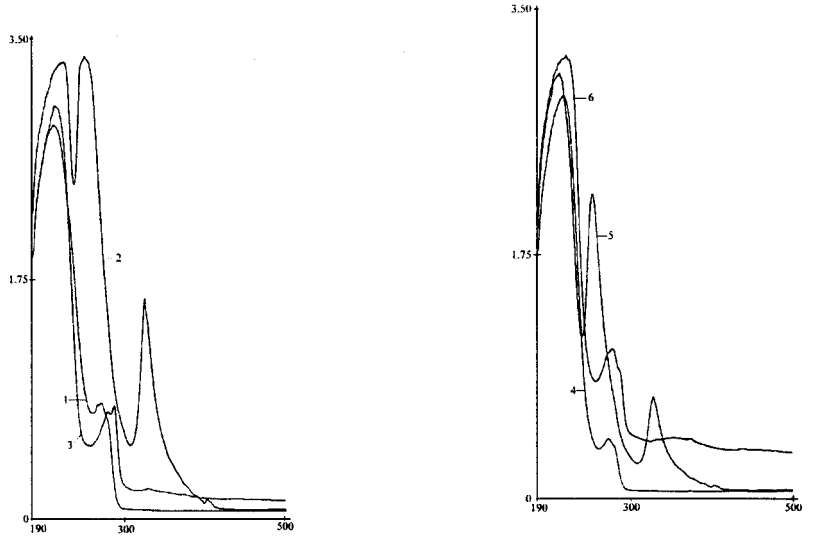

Figure 3 Solid UV-vis curves of six sample films: (1) $I_{(1)}$; (2) $I_{(2)}$; (3) $I_{(3)}$; (4) $II_{(1)}$; (5) $II_{(2)}$; (6) $II_{(3)}$.

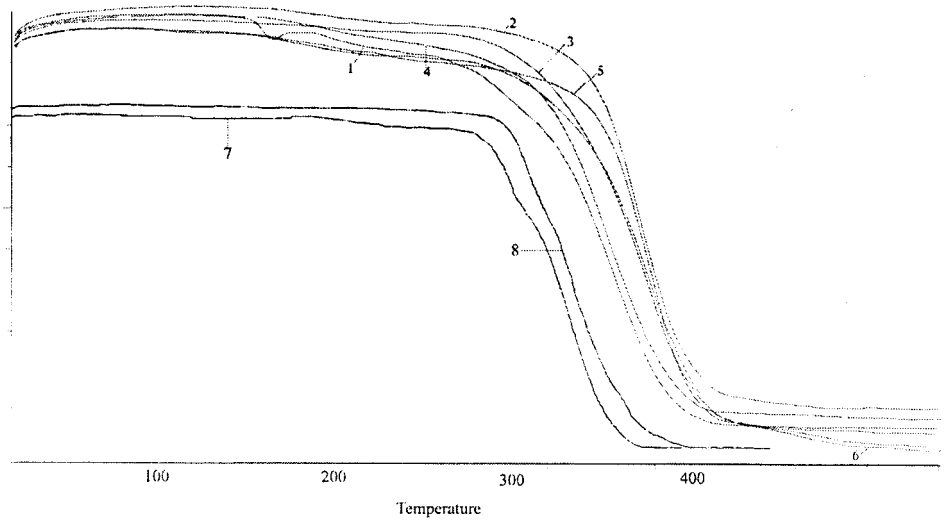

Figure 4 TG curves of eight sample films: (1) $I_{(1)}$; (2) $I_{(2)}$; (3) $I_{(3)}$; (4) $II_{(1)}$; (5) $II_{(2)}$; (6) $II_{(3)}$; (7) $I_{(4)}$; (8) $II_{(4)}$.

Measurements

Infrared spectra were recorded on an IR spectrometer of Nicolet 170 SX, using KBr tablets. Ultraviolet spectra were measured on a Shimadzu UV-240 spectrometer with a scanning range from 190 to 500 nm. Differential scanning colorimetry (DSC) and themogravimetric analysis (TG) were performed on a STA 409C thermal analysis apparatus in a stream of nitrogen (100 mL/min) at 0–500°C with a scanning rate of 5°C/min.

RESULTS AND DISCUSSION

The IR spectra of the six films are shown in Figures 1 and 2. It was found that the spectra are almost all the same and no new peaks or remarkable peak shifts occurred. This can be explained by that the PMMA in each sample is the major component, so the most characteristic absorption peaks of [60]fullerene and its *p-tert*-butylcalix[8]arene may be covered. However, there is a slight difference in the range of 800–400 cm^{-1}. A small skeleton peak of the free [60]fullerene at 527 cm^{-1} can be found in film $I_{(2)}$ and film $II_{(2)}$ but not in film $I_{(3)}$ and film $II_{(3)}$. The major absorption peaks of the six samples are 2995, 2951, 1731, 1483, 1449, 1387, 1272, 1193, 1149, 1070, 987, 966, 842, and 750 cm^{-1}.

UV-vis spectra of the six films are shown in Figure 3. As can be seen from Figure 3, the UV-vis curves of $I_{(1)}$ and $I_{(3)}$ and of $II_{(1)}$ and $II_{(3)}$ are similar except that two peaks assigned to PMMA have a red shift of 5–10 nm. However, the spectra of films $I_{(1)}$ and $I_{(2)}$ and films $II_{(1)}$ and $II_{(2)}$ are quite different. A new adsorption peak appeared at 328 nm and the original second adsorption peak of PMMA at 275 nm shifts from 275 to 260 nm. It can be concluded that the interaction between free [60]fullerene and PMMA are stronger than that between the inclusion complex and PMMA. In other words, free [60]fullerene exerts a stronger influence than does the included [60]fullerene.

Both Figure 4 and Table I show that [60]fullerene and the inclusion complex could improve the thermal stability of PMMA, but the small amount of calix[8]arene did not exert a large influence on the thermal stability of PMMA. Moreover, the elevating extent is connected with the content of [60]fullerenes in PMMA and the nature of the doping reagent. The more the content of [60]fullerene, the higher is the thermal stability [$I_{(2)}$ and $II_{(2)}$]. With a similar percent-

TABLE I
Temperature of Starting Weight Loss in TG Analysis (°C)

	Sample							
	$I_{(1)}$	$I_{(2)}$	$I_{(3)}$	$I_{(4)}$	$II_{(1)}$	$II_{(2)}$	$II_{(3)}$	$II_{(4)}$
	Temperature							
Material	296	332	312	294	299	322	336	304
C_{60}/PMMA (w/w, %)	0	2.2	0.8	0	0	1.4	1.4	0
C_{60}/PMMA (mol/w, %)	0	0.003	0.001	0	0	0.0019	0.0019	0
Calix[8]/PMMA (w/w, %)	0	0	1.4	1.4	0	0	2.5	2.5
Calix[8]/PMMA (mol/w, %)	0	0	0.001	0.001	0	0	0.0019	0.0019

w/w, % and mol/w, % mean that 1 g of PMMA contains the mass or mol of doping.

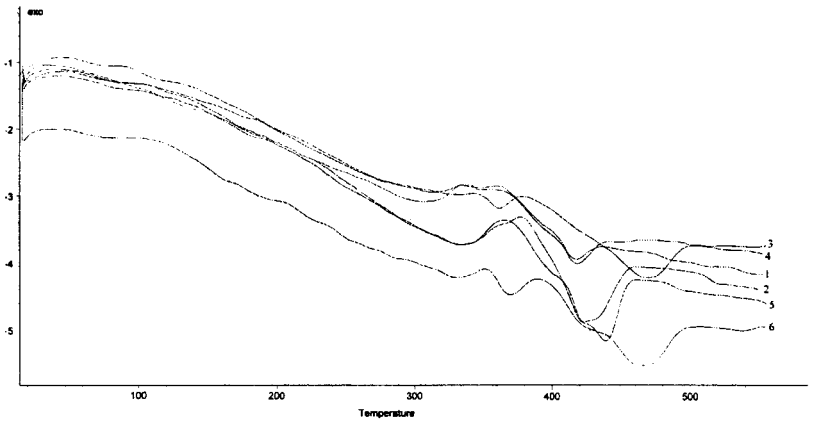

Figure 5 DSC curves of the six sample films: (1) $I_{(1)}$; (2) $I_{(2)}$; (3) $I_{(3)}$; (4) $II_{(1)}$; (5) $II_{(2)}$; (6) $II_{(3)}$.

age of fullerene, the included [60]fullerene is more effective for improving the thermal stability than the free [60]fullerenes [$I_{(2)}$ and $II_{(3)}$].

In Figure 5, we can see that in comparing the DSC curves of samples $I_{(1)}$ and $II_{(1)}$, that is, pure PMMA, the adsorption peaks of other four samples, which were mingled, with [60]fullerene or the included complex shift to right. The shifted extent is also connected with the content of [60]fullerene in PMMA and the nature of the doping reagent, and the same relationship was established as mentioned above.

Table II shows the influence of the incorporating substance on the peak values in the DSC curves. Again, the results show that the mingled substance plays an important role, and the inclusion complex is more effective than is [60]fullerene itself, although the latter also shows a remarkable effect compared with PMMA itself [$I_{(1)}$ and $I_{(2)}$]. No remarkable effect occurred when active carbon was used as the incorporating substance, as shown in the data in the first row. However, it is difficult to explain the lowest value of sample III in the second row.

TABLE II
Influence of Incorporating Substance on the Adsorption Peak

Measurement	Sample			
	$I_{(1)}$	$I_{(2)}$	$I_{(3)}$	III
First peak value (°C)	318	334.2	362	320
Second peak value (°C)	417.6	438.6	469.9	375.5
Content of the incorporating substance (%)	0	2.2	0.8	2.2

CONCLUSIONS

It is concluded that the thermal stability of PMMA could be improved by being doped with [60]fullerene or its inclusion complex of *p-tert*-butylcalix[8]arenes, and the latter exhibits more efficiency than that of the free [60]fullerene.

The authors are grateful to the Research Fund for Doctoral Program of Higher Education of China (98048624) and the Wuhan Chenguang Plan Foundation of Hubei Province of China (995004079C).

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