

UV-Vis DIAGNOSTICS OF THE PMMA-C₆₀ COMPOSITE SYSTEM AND THE KINETICS OF ITS THERMAL DECOMPOSITION

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The influence of polymer-fullerene interactions and fullerene aggregation on the thermal stability of polymethylmethacrylate-fullerene C₆₀ nanocomposite has been studied by means of thermal desorption mass-spectrometry and the UV-Vis absorption spectroscopy.

Keywords: fullerene, polymer, mass-spectrometry, UV-Vis electronic absorption, thermal stability.

1. Introduction

The properties of composite polymer-fullerene systems are influenced by the matrix-filler interactions and the extent of fullerene aggregation. Formation of the composites is implemented by co-dissolution of the components with subsequent film casting and solvent removal from the film. The introduction of the fullerene into the matrix is expected to change the properties of the material. In the majority of works devoted to nanocomposites, the main attention was paid to the influence of the highly dispersed filler on the strength of the material. In previous works (see, e.g., [1,2] and references therein) the thermal stabilities of various polymer-fullerene systems were studied by means of thermal desorption mass-spectrometry (TDMS). TDMS permits to compare the thermal desorption (TD) spectra of the decomposition products of the neat polymer and the spectra of the composite. It was shown that the thermal desorption (TD) spectra of polymethylmethacrylate (PMMA)-C₆₀ nanocomposite can differ from those of neat PMMA. In the current work, we compare the TD spectra of well-characterized neat PMMA with the TD spectra of a PMMA-C₆₀ nanocomposite and with the character of thermally induced changes in the UV-Vis electronic absorption spectra of the composite.

2. Results and discussion

We used the radically polymerized PMMA (trade mark ACRYPET, Diapolyacrylate Co., Ltd, Japan) with molecular weight parameters of $M_n = 3.5 \cdot 10^4$, $M_w/M_n = 7.67$ as determined via gel permeation chromatography (Waters, USA, UV detector, Breeze software), fullerene C₆₀ ("Fullerene Technologies", St.-Petersburg, purity – 99,5 %) and highly pure toluene without further purification. PMMA-C₆₀ blends were prepared by means of the co-dissolution of separately prepared C₆₀ and PMMA toluene solutions. The rated concentration of the components was 5.81 g (toluene)/8.9 mg (C₆₀)/29 mg (PMMA). The dissolution resulted in the formation

The paper is dedicated to the memory of Dr. Oleg F. Pozdnyakov

of a sediment. The real concentration of the components in the solution was, therefore, different from the initial one.

The solutions were cast onto the surface of a stainless steel foil-heater. Details of the TDMS experiments performed with the aid of the reflectron type MS are described elsewhere [1]. UV-Vis spectra were registered with a UV-1800 spectrophotometer in the 190–800 nm wavelength range, the slit thickness used was 1 nm. The films for UV-Vis measurements were prepared by casting PMMA or PMMA-C₆₀ solutions onto a quartz glass plate. Annealing of the samples was carried out at ~ 4 mbar in a Kendro Lab Products (Germany) vacuum oven.

The inset to Fig. 1 shows the full TD spectrum of MMA and the TD spectrum of toluene measured in TD experiments with the neat PMMA films cast from solution. It is seen that along with the main decomposition stage C, the decomposition pattern of PMMA contains two resolved low temperature stages (A and B) of MMA formation. Toluene removal from the film was almost completed at the onset of decomposition stage A. Stage C is interpreted to result from the dissociation of C-C bonds at random sites along the macromolecule. The low temperature stages (A and B) are usually interpreted to result from the decomposition of macromolecules initiated at defect sites along the chain [3]. The formation of the monomer in the low temperature range A can also be related to the depolymerization initiated at macroradicals, formed e.g. upon mechanical treatment or UV irradiation of the polymer [1,4].

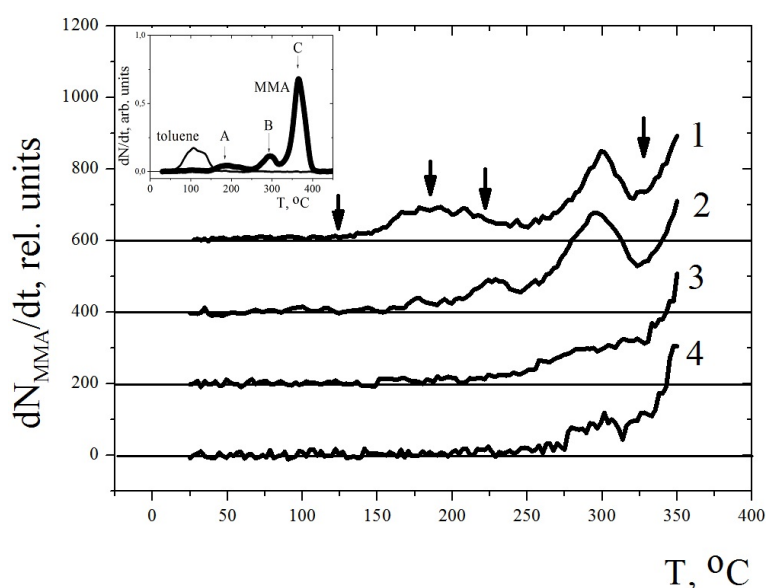


FIG. 1. Low temperature range of the TD spectra of MMA for neat PMMA (curve 1), composite system PMMA-C₆₀ after short, around 1 hour, (curve 2) and prolonged, around 24 hours, PMMA-C₆₀ co-dissolution (curve 3). Curve 4 is the TD spectrum of the sediment of PMMA-C₆₀ solution. The inset shows the full TD spectra of MMA for neat PMMA (thick line) and toluene (thin line). Arrows A, B and C show the characteristic features of TD spectrum of MMA (see text for details). Heating rate $\sim 2 \text{ K}\cdot\text{sec}^{-1}$

Stage C for the composite does not differ from that of neat PMMA. As is seen from Fig. 1, the shape of TD stages A and B for the composite (curves 2, 3) differs strongly compared to that of the neat PMMA (curve 1). The shape of the spectra is determined by the preparation details of the composite film, e.g. by the duration of the initial solution preparation and the conditions of the drying of the films. Nonetheless, we can outline the characteristic features

of the TD spectral shape changes. The intensity of stage A tends to decrease in the case of the composite (curves 2 and 3) compared to neat PMMA (curve 1). Stage B tends to decrease and tail to lower temperatures nonmonotonically with regards to time of dissolution. In order to clarify the question regarding the thermally induced changes in the composite, we have registered UV-Vis spectra of the composite for different annealing regimes. The characteristic temperatures shown by thick vertical lines in Fig. 1 have been chosen. These temperatures are related to the conditions of partial and complete removal (see inset to Fig. 1) of the solvent from the films as well as to the temperatures related to decomposition processes initiated at different defect sites of the PMMA (stages A and B).

Figure 2 shows the electronic absorption spectrum of the as-prepared PMMA-C₆₀ composite film (curve 3). The spectra of C₆₀ in toluene (curve 1) and hexane [6] (curve 2) are given for reference. As is seen, the spectrum of the film resembles the spectrum of the neat C₆₀ in solution (quantity and the position of the band's maxima, their line widths). The strong maxima in the hexane solution are attributed to the allowed transitions at wavelengths 211 nm (transition $8^1T_{1u} - 1^1A_g$), 256.6 nm ($6^1T_{1u} - 1^1A_g$), 328.4 nm ($3^1T_{1u} - 1^1A_g$) and more weak at 408.3 nm ($1^1T_{1u} - 1^1A_g$) with the vibronic structure at 404 nm and the broad weak band at 450–650 nm (vibronic structure of $S_0 - S_1$ transition) [5, 6].

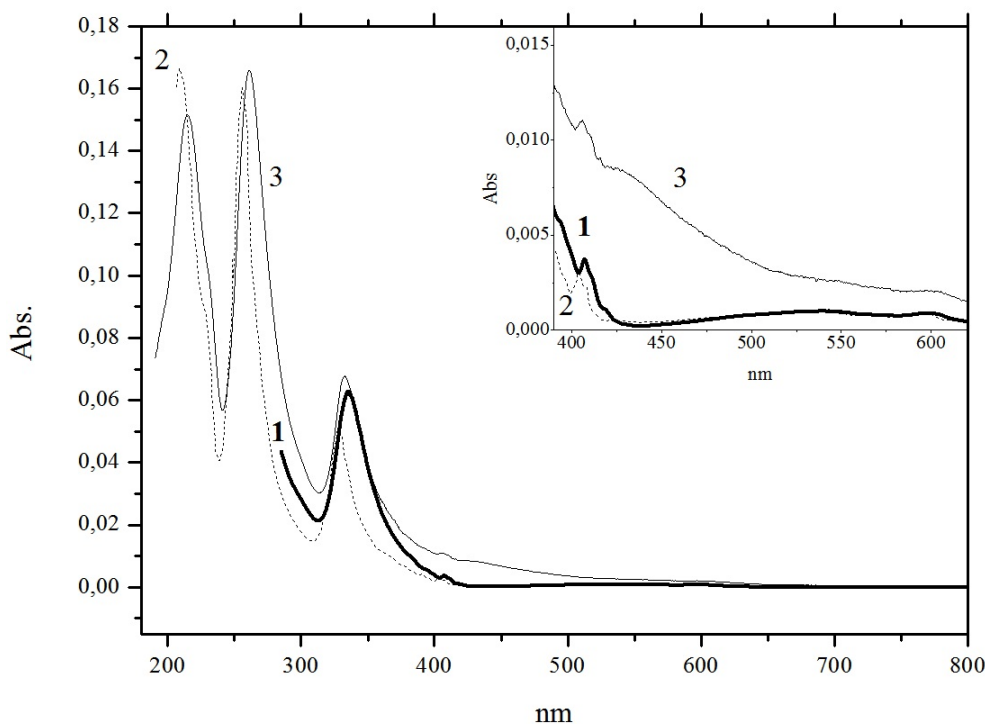


FIG. 2. Electronic absorption spectra of C₆₀ in toluene (curve 1) and in n-hexane (curve 2) (taken from [6]). The absorption spectrum of the initial composite PMMA-C₆₀ (curve 3). The inset shows the blowed-up spectral range 380–620 nm

One can note only a slight red shift of the bands (~ 4 nm for three strong bands) and their broadening. The only spectral change of qualitative character is the additional absorption in the 350–500 nm range. It is worth noting that the absorption maximum around 407 nm remains. From the above, we can conclude that no strong PMMA-C₆₀ bonds are formed of the type discussed, e.g. in [7] and the highly dispersed state of fullerene is preserved. Only

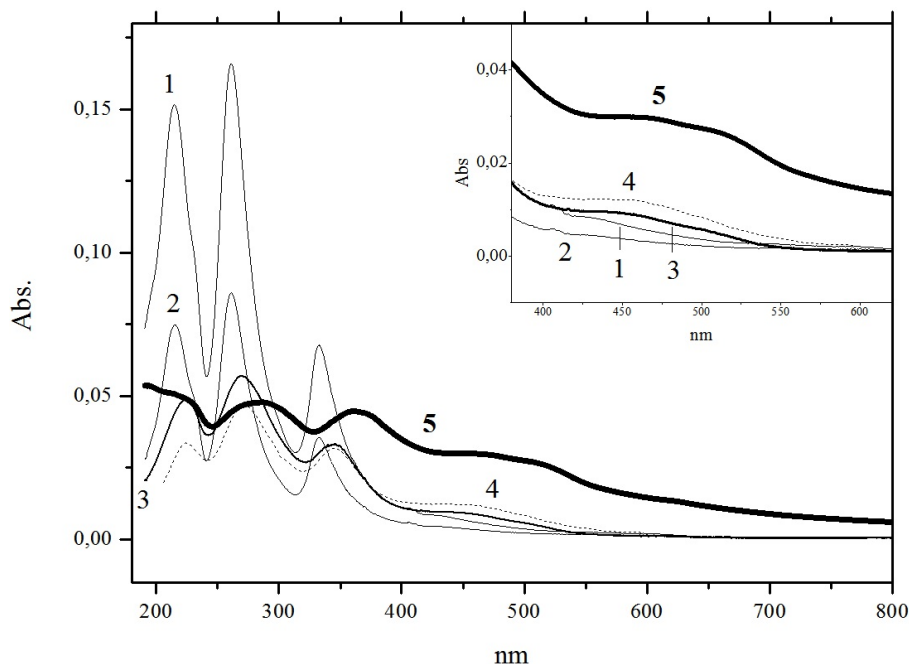


FIG. 3. Absorption spectra of the initial PMMA-C₆₀ film (curve 1), PMMA-C₆₀ composite film after heating up to 120 °C for 40 minutes (curve 2), after heating at 220 °C for 20 minutes (curve 3), after heating at 330 °C for 10 minutes (curve 5). Absorption spectrum of C₆₀ film (taken from [8]) at Al₂O₃ surface (curve 4). The inset shows the blowed-up spectral range 380–620 nm

additional absorbance in the 350–500 nm range can reflect the slight fullerene aggregation in the initial composite.

Figure 3 shows the absorption spectra of the initial PMMA-C₆₀ composite film (curve 1) prior to annealing, as well as the same film after annealing at 120 °C for 40 minutes (curve 2) and at 220 °C for 20 minutes (3). The absorbance spectrum (curve 4) of a neat fullerene C₆₀ film on a clean Al₂O₃ surface (taken from Ref. [8]) is additionally presented for comparison. Comparison of spectra 1 and 2 shows that they are similar. The decrease in the absorption in spectrum 2 is related to the changes in the film's thickness at different sites over the substrate surface. Such similarity of the spectra remained upon heating to 180 °C. The similarity of the spectra enables us to conclude that heating does not result in the formation of strong bonds between fullerene and the polymer, thus the fullerene dispersion state is not altered upon heating up to 180 °C. Note that the absence of strong PMMA-C₆₀ interactions is in good agreement with the results of Near-edge X-ray absorption fine structure spectroscopy [2]. Therefore, the decrease in monomer formation intensity at stage A for the composite may not be related to the formation of the strong interactions between the components and can be explained by the changes in the macromolecular dynamics in the presence of well dispersed fullerene molecules [9].

After annealing at 220 °C (curve 3), the spectrum of the film is radically changed: a significant broadening and red shift of the absorption bands is seen. The absorption band at 407 nm disappeared, while a broad band in the 380–550 nm appeared. The spectrum of the film became similar to the spectrum of a neat C₆₀ film. From these observations, one can suggest that heating of the composite results in the aggregation of almost total amount of the fullerene molecules present in the film. Such strong aggregation of the fullerenes in the narrow temperature range may indicate the growth of the mobility of the fullerene molecules

in the matrix. Upon further heating to 330°C (curve 5), additional strong changes were noted in the spectra: the maxima were strongly broadened and red shifted, while the band at 400–550 nm grew strongly and a strong absorption appeared in the 550–800 nm region. These high temperature changes in the spectra for PMMA decomposition at random sites (stage C in the inset to Fig. 1) requires further detailed studies.

We have therefore given evidence for the absence of strong polymer-fullerene interactions and an increase in the aggregation of fullerene molecules upon thermal annealing of PMMA-fullerene nanocomposites over a broad range of temperatures. These observations suggest that the thermal decomposition pattern of the PMMA matrix may be related to the changes in the macromolecular mobility in the presence of fullerene molecules.

Acknowledgements

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