Clustering kinetics of fullerene C\textsubscript{60} in a composite of polymethylmethacrylate – fullerene

Alexander A Bogdanov
Ioffe Institute, 26 Politekhnicheskaya, St Petersburg 194021, Russian Federation

E-mail: a.bogdanov@mail.ioffe.ru

Abstract. The paper presents the results of studying the absorption spectra of a composite polymethylmethacrylate – fullerene C\textsubscript{60}. In this composite, a gradual process of fullerene clustering upon heating is registered. This made it possible to determine the diffusion coefficient of C\textsubscript{60} molecules in this polymer.

1. Introduction
Composite materials based on polymers with nanoparticle additives have great promise for application [1]. The properties of such materials are determined largely by the distribution of nanoparticles over the volume of the composite, as well as their behavior at different temperatures (in particular, diffusion and clustering). Polymers with the addition of fullerenes C\textsubscript{60} are an important class of composites. Previously, when studying the absorption spectra of fullerene in thin films of such composites, it was shown that when a film is cast, the fullerene can be in it in a molecularly dispersed state or in the form of clusters [2]. Such a conclusion was made on the basis of a strong difference in the absorption spectra of individual fullerene molecules (in the gas phase and in solutions) and fullerene clusters (for example, in a thick C\textsubscript{60} film) [3].

In the absorption spectrum of the C\textsubscript{60} film, there is a red shift (at 10–20 nm) and broadening (from 20 to 60–70 nm) of the three main absorption bands at wavelengths 211, 257 and 328 nm. There is also a strong increase in absorption in the forbidden band in the range of 400–500 nm (10–20 times with respect to absorption in the band of 257 nm). It was shown [3] that such a transformation of the spectrum occurs completely already for submonolayer fullerene films with a density of (4–6)\times10\textsuperscript{13} mol/cm\textsuperscript{2}. In such films, fullerenes are in the form of small clusters with a size of 5-10 molecules. The gradual transformation of the absorption spectrum of such a fullerene film with a further decrease in its density could not be registered, since the absorption even for these films is only 0.001–0.01, which is at the limit of sensitivity of the spectrophotometer. However, one can try to use polymer – fullerene composites to study the gradual transformation of the absorption spectrum of fullerene and the associated clustering (aggregation) of fullerene molecules.

The clustering of fullerene in the composite occurs as a result of the diffusion of fullerene molecules and their combination into clusters consisting of a small number of molecules. The diffusion coefficient of fullerene in the composite increases with increasing temperature, which leads to acceleration of clustering. From this it follows that with the help of short-term heating of the composite to a certain elevated temperature, it would be possible to carry out a gradual clustering. In this case, the registration of the absorption spectrum of fullerene in the composite after each short-term heating will give a complete picture of the transformation of the spectrum, and, consequently, the
clustering of fullerene. The purpose of this work was to study the kinetics of fullerene clustering in a polymethylmethacrylate (PMMA)–\(C_{60}\) composite.

2. Description of the experiment
We used PMMA (The Weight Average Molecular Weight \(M_w = 5 \times 10^5\), Fluka), \(C_{60}\) fullerene ("Fullerene Technologies" OJSC, purity - 99.5%) and Toluene OFS. Films of the composite were prepared by mixing separate solutions of fullerene and polymer, holding the mixture solution for several days and casting the solutions onto a quartz glass substrate. The paper presents the results of the study of films with a thickness of less than 1 \(\mu\)m. The absorption spectra of the films were recorded on a Shimadzu UV-1800 spectrophotometer. The substrates with films were heated in a vacuum Heraeus VT 6060P furnace in air.

3. Experimental results and discussion
Preliminary experiments showed that heating to 220–240ºС composite PMMA–\(C_{60}\) with a fullerene content of 0.5 mass% and 1 mass% does not change the shape of the absorption spectrum, there is only a slight decrease in absorption (i.e., there is no clustering). Further heating of the composite to 250–280ºС leads to a strong decrease in absorption (also without changing the shape of the spectrum) and almost completely to the disappearance of characteristic fullerene bands, which can be interpreted as binding fullerene with polymer molecules.

Heating the PMMA–\(C_{60}\) composite with a high fullerene content (4 mass%) at 180ºС for 50 minutes did not lead to a change in the absorption spectrum of fullerene, only the absorption at maxima 213 and 260 nm decreased by 10%, the maximum of 332 nm remained unchanged. Heating the composite at 200ºС for 40 minutes led to a radical change in the shape of the spectrum, the subsequent heating at 220ºС for 30 minutes resulted only in residual changes in the spectrum. Therefore, to observe the step-by-step clustering of fullerene, a temperature of 200ºС was chosen. It should be noted that the following heating times (the time the substrate with the composite film is in the furnace) are given approximately, since it takes some time to heat the substrate from room temperature to the furnace temperature and conversely to cool the substrate from furnace temperature to the room temperature.

Figure 1 shows the absorption spectra of the PMMA–\(C_{60}\) (4 mass%) composite after successive short-term warm-ups at 200ºС. Curve 1 represents the spectrum of the initial composite heated at a temperature of 100ºС for 10 minutes to remove residual toluene. Heating at 200ºС for 1 and 2 minutes practically did not change the spectrum, only subsequent heating for 4 minutes led to a noticeable change in the spectrum (curve 2). Curves 2-5 show the complete cycle of the transformation of the absorption spectrum of fullerene. Further heating of the film at 200ºС for 20 minutes practically did not lead to a change in the spectrum.
Figure 1. Absorption spectra of the PMMA – C\textsubscript{60} composite film after successive heating at 200°C.
1 – initial film, 2 – heating time 4 minutes, 3 – 3.5 minutes, 4 – 4 minutes, 5 – 9 minutes.

The similarity of the absorption spectrum of fullerene in the initial composite to the absorption spectrum in solution and the gas phase (Figure 2), where fullerene is molecularly dispersed, clearly indicates that fullerene is mainly molecularly dispersed in the initial composite.

Figure 2. Comparison of normalized absorption spectra.
1 – initial PMMA- C\textsubscript{60} composite, 2 – composite after heating at 200°C 20 minutes, 3 — C\textsubscript{60} solution in hexane, 4 — thick C\textsubscript{60} film (98 nm) on quartz [4].

The referred above spectrum transformation is caused by the gradual clustering of fullerene in a polymer matrix. Indeed, in the process of diffusion fullerene molecules meet with each other, often
after meeting they stick together. So small clusters consisting of several molecules arise. In this case, the diffusion coefficient for clusters is lower than for individual molecules and decreases with increasing cluster size. This conclusion can be drawn in particular from the results of [5], in which the diffusion coefficients of gold clusters (with a diameter of 2.5 to 10 nm) in poly-n-butylmethacrylate are measured. So fullerene clustering occurs mainly as a result of the diffusion of individual molecules and their binding to each other or joining small clusters that already exist. It is obvious that clusters of different sizes are present in the composite. The maximum of the cluster size distribution function shifts in the process of clustering towards larger sizes. As the number of free fullerene molecules decreases, the process of increasing the average cluster size slows down and finally stops completely. It is clear that such a clustering mechanism based on the adhesion of individual fullerene molecules to the already existing small clusters (almost immobile) leads to a small average cluster size. Note that the clustering of fullerenes in the composite is irreversible during heating, i.e. fullerene clusters are preserved when the composite is cooled, they do not break up again into individual molecules.

Figure 3. Absorption spectra of the PMMA – C$_{60}$ composite film after successive heating at 200 °C (see Figure 1) in the wavelength range of 300–400 nm.

The experimental data obtained allow us to estimate the diffusion coefficient of fullerene molecules in PMMA. When the content of fullerene in the composite is 4 mass%, the concentration of fullerene molecules is $4 \times 10^{19}$ cm$^{-3}$ (PMMA density is 1.2 g/cm$^3$). This corresponds to the average distance between fullerene molecules in the composite: $\bar{r} = 1/(4 \times 10^{19})^{1/3} = 3 \times 10^{-7}$ cm, provided that the fullerene in the original composite is only in the form of individual molecules. A noticeable transformation of the C$_{60}$ absorption spectrum occurred during the time $\tau = 4–8$ min $\approx$ 200–500 s of heating at 200°C (Figure 1, curves 2, 3). Such a transformation means that during this time the C$_{60}$ molecules began to meet each other (they had time to diffuse into the distance $\bar{r}$) and form clusters. The characteristic time of particle diffusion over a distance $\bar{r}$: $\tau_0 = \bar{r}^2/(6D)$, where D is diffusion coefficient. The
estimate shows that the real value of the diffusion coefficient at a temperature of 200°C \( D(200) \) is in the range of \( 10^{16} \)–\( 10^{15} \) cm\(^2\)/s for the values \( \mathcal{F} \) and \( \tau \) given above. This range is determined by the uncertainty of the characteristic time of the spectrum transformation \( \tau \) and the uncertainty of the initial concentration of particles (the possibility of the presence of \( C_{60} \) dimers). Heating the composite at \( T = 180^\circ\text{C} \) for 50 minutes did not lead to a change in the absorption spectrum, i.e. not even traces of clustering are observed. This means that \( D(180) \) is more than 10 times less than \( D(200) \). At the same time, an experiment showed that \( D(220) \) is much larger than \( D(200) \).

It is interesting to compare the obtained estimate for the diffusion coefficient of \( C_{60} \) in PMMA with the data available in the literature. The PMMA–\( C_{60} \) composite with a \( C_{60} \) concentration of less than 5 mass% was also studied in [6]. In the manufacture of composite residual solvent (toluene) was removed by drying in vacuum at a temperature of 180°C for 15 hours. After that, in composites with a \( C_{60} \) concentration of less than 1 mass%, TEM images revealed fullerene clusters with an average size of 20 nm. At concentrations of 1 mass% and more, along with these clusters, clusters about 1 \( \mu \text{m} \) in size were found. The appearance of such large clusters as compared to the small clusters that were found in this work can be explained by the fact that the heating time at 180°C in [6] was 20 times longer than in this work. During this time, even a very slow diffusion of small clusters, which appeared at the first stage of heating, could lead to the formation of such huge clusters.

The features of fullerenes \( C_{60} \) diffusion in polyimide at \( T = 600\text{K} \) (glass transition temperature \( T_g = 479 \) K) were established in [7] using computer modeling on base of all-atom molecular dynamic simulation. The presence of three modes of diffusion – ballistic, subdiffusion and normal was shown. In the normal diffusion regime, the diffusion coefficient of \( C_{60} \) turned out to be \( D = 2.4 \cdot 10^{-7} \) cm\(^2\)/s. When comparing this result with \( D(200) \) obtained in this work, it should be noted that the simulation was carried out for temperatures exceeding the glass transition temperature of polyimide by 120K. In addition, the diffusion coefficient also depends on the polymer matrix. This may explain such a large difference in the values of the diffusion coefficient in PMMA (experimental, in this work) and in polyimide (calculated).

4. Conclusion

Thus, the clustering of fullerene in the PMMA – \( C_{60} \) composite is shown using absorption spectra. The stepwise heating of the composite made it possible to register the whole process of clustering from individual molecules to small clusters. The obtained experimental data showed a very sharp increase in the diffusion coefficient of fullerene molecules in PMMA with temperature, and also made it possible to estimate this coefficient at 200°C. A comparison is made with known data on the diffusion coefficient of fullerene molecules.

Acknowledgments

The author is grateful to A O Pozdnyakov for assistance in conducting the experiment.

References
[1] Volgin I V, Larin S V and Lyulin S V 2018 Polymer Science, Series C 60 Suppl.1 S122–34
[2] Bogdanov A A and Pozdnyakov A O 2016 Technical Physics Letters 42(1) 102–4
[3] Bogdanov A A 2018 Technical Physics 63 1006–9
[4] Hebard A F, Haddon R C, Fleming R M and Kortan A R 1991 Appl. Phys. Lett. 59 2109–11
[5] Grabowski C A and Mukhopadhyay A 2014 Macromolecules 47 7238–42
[6] Kropka J M, Putz K W, Pryamitsyn V, Ganesan V and Green P F 2007 Macromolecules 40 5424-32
[7] Volgin I V, Larin S V, Abad E and Lyulin S V 2017 Macromolecules 50(5) 2207–18

Macromolecules 50 6977