Nanostructure evolution during thermal treatment of polyimide-fullerene composites as revealed by WAXS and SAXS

M.E. Cagiao¹, A.O. Pozdnyakov², M. Krumova^{1*}, V.V. Kudryavtsev³, F.J. Baltá Calleja¹

¹ Instituto de Estructura de la Materia, CSIC, Serrano, 119, 28006 Madrid, Spain

² Institute of Problems of Mechanical Engineering, Russian Academy of Sciences,
Vasil'evskii Ostrov, Bol'shoi pr. 61, St. Petersburg, 199178, Russia

³ Institute of Macromolecular Compounds, Russian Academy of Sciences,
St.- Petersburg, Bol'shoi pr., 31, V/O, 199004, Russia

*Present address: Department of Engineering, Institute of Materials Science, Martin-Luther University Halle-Wittenberg, D-06099 Halle/Saale, Germany

Abstract

The nanostructure formation in polyimide-fullerene composites during thermal treatment was investigated “in situ”, by means of wide-angle (WAXS) and small-angle X-ray scattering (SAXS) techniques. The WAXS patterns of the PI composites do not reveal the presence of C₆₀ reflections. However, the PI/C₆₀ composite, obtained by adding the C₆₀ solution to the diamines-solution during the first step of the reaction (preparation of the polyamic acid, PAA), shows a maximum at small X-ray scattering angles. Results show that this intensity maximum is markedly affected by thermal treatment of the PI/C₆₀ composite, disappearing at high temperature. From “in situ” X-ray scattering experiments, the “manner” in which the C₆₀ nanoparticles are added to the other reactants and influences the properties of the final polymer is discussed.

Keywords

Nanostructure (A), polyimide (A), fullerene C₆₀ (A), X-ray diffraction (D), heat treatment (E).

Introduction

The development of suitable methods for obtaining fullerenes, particularly C_{60} , in macroscopic amounts [1] has attracted the attention of the researchers in different fields (chemists, physicists, material scientists, etc) due to the special properties (photonic, electronic, superconducting, etc) shown by this molecule. Several chemical transformations have been used in order to obtain a variety of fullerene derivatives [2]. There have been also attempts to prepare fullerene-containing polymers, because they are expected to combine the features of both components, thus allowing the preparation of advanced polymeric materials. For instance, several researchers have obtained polymers with C_{60} ending chains [3, 4]. In other cases, fullerene-grafted polymer chains have been developed [5-10], or chemical combinations of both components [11]. Other alternative is the preparation of blends or composites polymer/fullerene. Several polymer- C_{60} composites, namely C_{60} plus polyethylene [12], polystyrene [13], acrylic [14-17] or vinyl polymers [18], etc., have been studied. Polyimides (PIs) are high-temperature polymers, exhibiting a wide range of applications, as for example, in the preparation of films [19], fibers [20], foams [21] and membranes [22]. Recently, combinations of polyimides (PIs) with fullerene C_{60} have received some attention [23-24] due to their interesting properties. In addition, an introduction of C_{60} into PI matrix is quite promising, due to the molecular nature of this nano filler. In fact, the thermal behavior of C_{60} within the PI matrix is expected to influence the tribological properties of the composite and, therefore, it is a topic of high interest.

PIs having a less flexible backbone, for example, polyimides that contain the bis(phenylene)pyrimidine units show an excellent thermal stability and mechanical

strength due to the specific properties of the bis(phenylene)pyrimidine fragment [25, 26]. We have concentrated the present study in one of these PIs, i.e., the PI based on 3,3', 4,4'-oxydiphthalic anhydride (DPO), and the diamines 2,5-bis(4-aminophenyl)pyrimidine (2,5 PRM) and p-phenylenediamine (PPh) [26]. The molar ratio of the three components is 100:50:50 [25]. The tribological properties of composites formed by PI plus C₆₀ and C₇₀ [25, 27], and the thermally stimulated desorption process of C₆₀ and C₇₀ have been reported [25, 27-29].

The general route to the formation of thermally imidized PIs is known to proceed as follows:

- I) (First step, moderate temperature, solution) DAM + DAN $\rightarrow$ PAA.
- II) (Second step, high temperature, solid state) PAA $\rightarrow$ PI

where DAM and DAN stand for the diamine and dianhydride monomer, respectively, and PAA and PI for the resulting polyamic acid and polyimide. The final properties of, both, the PAA and final PI depend on the structure of the DAM and DAN monomers. In addition, for a given PAA structure, controlled by the first reaction step (I), the resulting mechanical properties of the polyimide PI are determined by the thermal imidization step (II) [25]. It is to be noted that it is not possible to introduce directly the C₆₀ into the PI matrix because of the insolubility of the PIs under study. To overcome this difficulty, the C₆₀ can be added to a solution of one of the PI precursors, i.e., the DAM, the DAN, or the PAA. Therefore, the introduction of C₆₀ into the insoluble PI is performed through one of the following routes:

- I) (a) (First step, moderate temperature, solution) $\text{DAM} (+\text{C}_{60}) + \text{DAN} \rightarrow \text{PAA}/\text{C}_{60}$
 (b) (First step, moderate temperature, solution) $\text{DAN} (+\text{C}_{60}) + \text{DAM} \rightarrow \text{PAA}/\text{C}_{60}$
 (c) (First step, moderate temperature, solution) $\text{PAA} (+\text{C}_{60}) \rightarrow \text{PAA}/\text{C}_{60}$
- II) (Second step, high temperature, solid state) $\text{PAA} + \text{C}_{60} \rightarrow \text{PI}/\text{C}_{60}$

The introduction of these strong electron acceptor molecules into PI, through their incorporation into the PI precursor, (either the diamine, the dianhydride, or the polyamic acid), may be strongly intermediated by certain interactions between C_{60} and electron donor fragments of these precursors [28]. In fact, SEM and FTIR studies [25] indicate the C_{60} presence inside the PI matrix in complex structural states [30]. Preliminary measurements performed to examine the influence of fullerene upon imidization of PAA show certain differences in the SAXS and WAXS patterns of neat PAA as compared to the PAA- C_{60} composite [31].

The aims of the present study are:

- 1) To investigate the influence of the fullerene C_{60} on the nanostructure of the PI/C_{60} composites and on the behavior of these samples subjected to thermal treatment by means of “in situ” X-ray scattering methods.
- 2) To describe the structural characteristics shown by the PI and PI/C_{60} systems resulting from the incorporation of the C_{60} to the DAM solution (route Ia) or to the DAN solution (route Ib) during the heating process.
- 3) To provide more information about the relationship between the $\text{PI}-\text{C}_{60}$ composite nanostructure and the possible interactions between the PI matrix and the fullerene nanoparticles.

Experimental

Samples preparation

The PI used in our investigation was based on: 3,3', 4,4'-oxydiphthalic anhydride (DPO) and two diamines: 2,5-bis(4-aminophenyl) pyrimidine (2,5 PRM) and p-phenylenediamine (PPh) [25, 26]. The molar ratio of the three components was 100:50:50 [25]. The chemical formula of the resultant PI is given in Fig. 1. The PI/C₆₀ system was obtained by pouring a C₆₀ solution in o-dichlorobenzene either into: a solution of PPh and 2,5 PRM in N, N-dimethylacetamide (DMAA) (route Ia), or a solution of DPO in DMAA (route Ib), with subsequent stirring in both cases. The rated C₆₀ content was 5% of the polymer weight (PI basis). Further details of the synthesis are given elsewhere [25]. It is noteworthy that C₆₀ was not completely dissolved in the resultant solution, and sediment formation was observed. This means that the actual concentration of fullerene inside the PI matrix can be lower than the rated one. In fact, this effect had been already observed for C₆₀ concentrations higher than 2% (dry polymer basis), no matter which had been the selected route for the C₆₀ addition [25, 29]. The solutions were kept for several days in a refrigerator at about 6° C. The coatings were cast onto flat glass substrates from a PAA or PAA/C₆₀ solution in DMAA. In the second case, the polymer solution was decanted after the sediment formation. The solutions were dried at 60° C for about 5 h to remove the solvent and to form a coating. They were subsequently heated up to 320°C at a heating rate of 5°C/min to perform the imidization process. After imidization, samples were finally cooled to room temperature at a cooling rate of about 10° C·min⁻¹ [25]. Film thickness was about 40-80 µm.

Techniques

To characterize the nanostructure of the samples included in this study, simultaneous wide- and small-angle x-ray scattering (WAXS and SAXS) experiments were performed using the synchrotron radiation source at the A2 beam line of HASYLAB in the synchrotron DESY of Hamburg. A wavelength of 0.15 nm was used. Accumulation times of 30 or 60 s per frame were used for, both, linear WAXS and SAXS detectors. The distance between the sample and the SAXS detector was 180 cm. To improve the scattering intensity, three films of either PI or PI/C₆₀ samples were packed together in Al foil to perform the scattering experiments. The surface of the films was placed, within the sample holder, perpendicular to the X-ray beam and maintained under rotary pump vacuum during the experiment. Samples were first held at room temperature for 2 min, and then subjected to the following thermal treatment: 1) Heating from room temperature to 320°C at a rate of 20°C/min. 2) Heating from 320°C to 400°C at 5°C/min. 3) Isothermal treatment at 400°C for 6 min. 4) Cooling from 400°C to room temperature at 20°C/min. PET and rattail films were used as standards for the WAXS and SAXS calibration, respectively.

From the WAXS study, the crystallinity was estimated by using a curve-fitting program, as the ratio between the area corresponding to the crystalline reflections and the total area of the WAXS pattern. The experimental SAXS patterns were corrected by the Lorentz factor. The area of the SAXS maximum and its angular position were measured to calculate the corresponding values of the invariant, Q , and the long period, L , respectively. As it is well known, in semicrystalline polymers the invariant Q is given by the expression [32]

$$Q \sim (\rho_c - \rho_a)^2 w_c(1-w_c) \quad (1)$$

where ρ_c and ρ_a are the electronic densities of the crystalline and amorphous phases, respectively, and w_c is the crystallinity of the material. Q was calculated as the total area of the SAXS pattern after having performed the Lorentz correction.

Results

Wide angle X-ray scattering

Fig. 2 shows the wide angle X-ray scattering (WAXS) patterns the samples PI (fig. 2a) and PI/C₆₀ obtained through route Ia (Fig. 2b) at room temperature. The WAXS pattern of PI/C₆₀ obtained following route Ib, not shown here, is similar to that of Fig. 2b. The WAXS pattern of C₆₀ is shown in Fig. 2c. The X-ray profiles of the three samples show a crystalline reflection appearing at about 11° (2θ). In case of C₆₀, this is the (111) crystalline reflection [33]. The PI used in this study presents a nanoblock structure [26]. One of the nanoblocks is constituted by a number of DPO-PPh chains, 2-3 monomer units length each, and the other one is formed by chains of DPO-2,5 PRM, with an average length of 4-5 monomer units [26]. Taking these results into account, the reflection appearing at ~ 11° in figs. 2b and 2c could be related to the (003) planes of the DPO-2,5 PRM nanoblocks [26]. It is important to note that, in [26], the material studied was oriented, and several distinct maxima (meridional and equatorial) appeared in the corresponding WAXS pattern. However, the samples in the present study are cast-unoriented films. This is probably the reason why the WAXS pattern shows distinctly the reflection at about 11° (2θ). Furthermore, it is noteworthy that none of the C₆₀ crystalline reflections appears in the WAXS pattern of the PI/C₆₀ sample (Fig. 2b), not

even the most intense one, at about 18° (2θ). These results are in agreement with those obtained in samples of PI with C_{60} content ranging from 0 to 5% [28, 34]. From the present results, one also observes that PI and PI/ C_{60} X-ray profiles (Figs. 2a and 2b, respectively) at RT are quite similar. Since the evaluation of the scattering pattern in the $12-33^\circ$ (2θ) range during thermal treatment is not straightforward, we concentrated on the analysis of the reflection at about 11° (2θ). This is, indeed, the clearly visible peak and the easiest one to be measured. Therefore, we have analyzed the evolution of the area percentage of the peak at 11° over the total diffracted area, as well as the crystallinity changes undergone by the samples during the thermal treatment.

Figs. 3a and 3b illustrate the relative evolution of the area corresponding to the reflection at 11° (2θ), for PI and PI/ C_{60} (route Ia), respectively, as a function of temperature. PI/ C_{60} obtained by route Ib (not included in Fig. 3) behaves similarly to that obtained by route Ia. It is seen that, whereas the area of this peak for pure PI increases when the temperature raises from 320 to 400°C , in the two PI/ C_{60} systems this contribution remains constant (6-7% of the total area) through the whole thermal treatment. The crystal coherence length, calculated from the integral width of this reflection corresponds to about 12-14 nm in the three systems, and does not vary during the heating process.

Figs. 4a and 4b show the crystallinity evolution of the three samples. Fig 4a corresponds to pure PI, and Fig. 4b, to the PI/ C_{60} composite obtained by route Ia. The behavior of the crystallinity in the composite prepared by route Ib is very similar to that of the other two samples, and has not been included in the plot for the sake of clarity. The initial crystallinity value measured at room temperature is a little higher in the

sample prepared by route Ia than in the other two cases (0.41 against 0.35 in pure PI, or 0.39 in sample prepared by route Ib). From Fig. 4, it is clear that the heating process practically does not affect the crystallinity of the three samples.

Small angle X-ray scattering

It is to be noted that neither pure PI (Fig. 5 top), nor PI/C₆₀ obtained by routes Ib, show SAXS scattering maxima corresponding to the long spacing of PI/C₆₀ prepared by route Ia. One possible reason to explain that this maximum cannot be detected is that the long spacing in the above samples appears at too small angles. However, in case of PI/C₆₀ obtained by route Ia (C₆₀ added to the diamines mixture), the SAXS maximum is clearly visible (compare Figs. 5 top and 5 bottom). In this case the SAXS maximum may be related to the presence of the fullerene C₆₀ molecules, chemically bound to the polyimide chains at regularly spaced distances. From the SAXS maximum, we have derived the long spacing evolution and that of the invariant Q during the thermal treatment. The initial long spacing L (12-13 nm) does not vary as a consequence of the heating process. On the other hand, the invariant Q (Fig. 6) continuously decreases in going from RT to 320°C, and from 320 °C to 400°C, finally almost disappearing at this temperature.

Discussion.

Influence of imidization on structure.

By comparing the evolution of the area under the peak at 11° (2θ) for pure PI (Fig. 3a) and that for PI/C₆₀ composites (Fig. 3b) with increasing temperature, one can

speculate that the presence of C₆₀ inhibits somehow the evolution of this peak in the samples heated from 320 to 400°C. The intensity changes of the peak at 11° (2θ) are probably related to the additional imidization process [25]. In that publication, PI/C₆₀ systems containing from 0 to 5wt% of C₆₀ (dry polymer basis) obtained by routes Ia, Ib and Ic were discussed. All samples were characterized by FTIR, thermal mechanical analysis (TMA), differential thermal gravimetric analysis (DTGA), viscosity measurements, and tensile stress-strain measurements. In addition, the samples were also subjected to friction and wear tests. Results obtained in the FTIR study of the PI/C₆₀ composites showed that, at 320°C, the imidization process is practically complete [25]. However, some chemical changes are still to be expected in this region, as suggested by an exothermic peak appearing in the thermograms of the samples at temperatures higher than 320° C [25]. On the other hand, the TMA study of PI/C₆₀ composite films also indicate that, at temperatures above 300°C, due to the increased mobility of the macromolecules, certain softening of the material takes place. This may result in a higher probability for additional cycle formation, which, in turn, leads to an increase of the stiffness of the whole system [25].

From the WAXS measurements carried out in the present study, it is clear that crystallinity does not change during the thermal treatment (see Figs. 4a and 4b). Results also show that, among the three types of samples studied, only the PI/C₆₀ sample prepared by route Ia presents a long spacing in the SAXS pattern. In fact, according to the results published in [25], some other differences have been found between PI/C₆₀ composites prepared by the routes Ia, Ib, or Ic. For example, the introduction of C₆₀ in the DAM mixtures (route Ia) usually produces tougher coatings after imidization at high temperatures. In particular, if C₆₀ is introduced in the DAN (route Ib) in a proportion

higher than 2%, the coatings upon imidization suffer from spontaneous embrittlement [25]. In addition, SEM observations on composites prepared by all the routes revealed a clear phase separation in the coatings. From the micrographs it can be seen that nanoagglomerates of the second phase (fullerene C₆₀) are included in the PI matrix, growing in size when the C₆₀ content increases [25]. After imidization at 320° C, the surface morphology in the samples prepared by route Ia is more irregular than in those obtained through route Ic (compare Figs. 3a and 3b in ref. [25]). In agreement with these results, it has been found that the viscosity of the PAA solution increases after adding the C₆₀ by routes Ia or Ic, this effect being higher in composites prepared by route Ia. This behavior can be explained assuming that the conditions for the interaction between the PAA and the C₆₀ are more favorable in the first case, thus producing a more relevant crosslinking effect in the PAA molecules [25]. It is worth noting that the initial concentration of C₆₀ inside a coating for the PI/C₆₀ composite, prepared by route Ic, is ~ 10¹⁹ molecules/cm³ [29].

Nanostructure formation

The presence of a long spacing L in the SAXS diagrams in the PI/C₆₀ obtained by route Ia could be thought as related to the capacity of C₆₀ to react with primary [35], secondary [35-37] and tertiary amines [38, 39]. Thus, C₆₀ is probably capable to react with the diamines used in the synthesis process (2,5 PRM and PPh), giving rise to addition products that contribute to a maximum in their SAXS diagram. It is known that the presence of a maximum in the SAXS pattern of a material is related to the coexistence of two phases with different electronic densities (usually, crystalline and amorphous phase in semicrystalline polymers).

It is noteworthy that in the PI/C₆₀ composite prepared by the route Ia, L is initially slightly higher than the crystal thickness as determined from the integral width of the reflection at 11° (13.1 and 12.4 nm, respectively). In addition, both values become closer to each other as the thermal treatment is in progress. From 370°C onwards, L results impossible to be measured, as the Q value approaches to zero (see Fig.6). As pointed out above, the crystallinity for the three samples studied is almost constant during the whole thermal treatment. Therefore, the Q evolution for samples prepared by route Ia as a function of temperature (Fig. 5) can be only ascribed to the diminution of the $(\rho_c - \rho_a)^2$ factor. There is some parallelism between the Q evolution for samples prepared by route Ia as a function of temperature, and the different aspects shown by the SEM micrographs of these samples freshly prepared, and heated at 320 and 420°C, respectively [25]. The sample surface appears more homogeneous in heated samples, especially in those treated at higher temperatures (see Figs. 3a, 4a and 4b in ref. [25]).

During the study of the wear behavior of PI/C₆₀ composite coatings, the addition of C₆₀ was shown to lower the specific wear rate in PI/C₆₀ heated at 420°C [27]. This indicates the possibility of some reaction occurring between PI and C₆₀, even if the majority of C₆₀ is desorpted at this high temperature, as can be deduced from the Q evolution (see Fig. 6). Note also, that thermodesorption studies performed on polyimide-fullerene C60 systems [28, 29] provide grounds to assume that strong chemical bonds, formed between fullerene molecules and polymer chains already in the diamines-C₆₀ solution or the PAA-C₆₀ solution, are decomposed at the onset of thermal decomposition of the PI matrix. The disappearance of C₆₀, due to a desorption process,

and/or complicated chemical transformations of C_{60} in the presence of PI molecules, is a subject of further research [25]. It is important to note that the thermal decomposition of this PI takes place between 500 and 700°C, with a maximum appearing at about 600°C [25, 27]. This means that, at 400°C, the thermal decomposition of the PI has not started yet.

Fig. 7 schematically illustrates a possible structure of the PI/ C_{60} composite, which might explain the periodicity, L , derived from the SAXS pattern ($L \sim 12\text{-}13\text{ nm}$) and its evolution during the thermal treatment. This model could explain the gradual decrease of scattering intensity observed (see Fig. 5 bottom). In this scheme the fullerene molecules are represented by circles, the DPO-PPh molecules by the thinner lines, and the DPO-PRM chains by the thicker lines. Figure 7 has not been scaled to the actual dimensions (the C_{60} mean diameter is about 0.71 nm, i.e., too small to be properly represented in the scheme [40]). On the other hand, it should be stressed out that an important amount of C_{60} is probably also present in the initial PI/ C_{60} material in the form of aggregates (see Fig. 3a in ref. 25). These aggregates have been included in Fig. 7, but their size in this figure does not correspond to the real one.

In support of the model of Fig. 7, SEM evidences the presence of agglomerates inside PI- C_{60} composite ranging in sizes from about 5 microns down to the resolution limit of the method [25]. FTIR results indicate [25] the presence of characteristic bands of neat C_{60} and also the forbidden bands of C_{60} , in support for their occurrence in certain structural conditions [30]. Thermal treatment of the PI- C_{60} composite results in the decrease of the intensity of these bands, which is adequately explained by thermal desorption of C_{60} at elevated temperatures. These results suggest that, in the PI/ C_{60}

composites, C₆₀ can be present in different phase states, including the occurrence of C₆₀ clusters [25].

Conclusions

The obtained results reveal that the WAXS profiles of the PI/C₆₀ composites do not show the presence of the C₆₀ reflections. However, the SAXS pattern of PI/C₆₀ sample prepared by route Ia presents a clear scattering maximum which does not depend on temperature, and might be related with the 3-dimensional location of the C₆₀ molecules within the PI/C₆₀ composite. On the other hand, the SAXS intensity decrease with increasing temperature suggests the disappearance of the 3-dimensional order of the C₆₀ molecules because of the heating process.

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Figure captions

Fig. 1: Chemical formula of the polyimide studied in this paper.

Fig. 2: WAXS profiles of: a) pure PI; b) PI/C₆₀ prepared through route Ia (see text); c) pure fullerene C₆₀.

Fig. 3: Evolution of the area corresponding to the (003) reflection during the thermal treatment in: a) pure PI; b) PI/C₆₀ prepared through route Ia (see text).

Fig. 4. Evolution of the crystallinity during the thermal treatment in: a) pure PI; b) PI/C₆₀ prepared by route Ia.

Fig. 5. Variation of the SAXS profile during the thermal treatment in: top) pure PI or PI/C₆₀ prepared by route Ib; bottom) PI/C₆₀ prepared by route Ia.

Fig. 6. Evolution of the Invariant Q for the PI/C₆₀ composite prepared by route Ia during the thermal treatment.

Fig. 7. Schematic model showing the changes in the PI/C₆₀ composite structure during thermal treatment at selected temperatures. Circles: fullerene molecules; thinner lines: chains constituted by DPO-PPh molecules; thicker lines: chains of DPO-PRM molecules.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Room temperature

320° C

400° C

Fig. 7