**Thermal imidization of Polyamic Acid - Fullerene Composites:
“In situ” X-ray diffraction study**

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ABSTRACT

“In situ” wide angle (WAXS) and small angle X-ray scattering (SAXS) studies were carried out to characterize the structural changes occurring during the conversion of a polyamic acid into the polyimide in the presence of fullerene, C₆₀. The variations in crystallinity, long period, and the SAXS invariant of the samples are discussed in the light of the various temperature ranges studied. The conversion of the polyamic acid into the polyimide is analyzed according to the different structural steps. Results reveal that C₆₀ affects the degree of order of the composite in the molecular direction, giving rise to slightly smaller crystals than those found in pure polyamic acid. The difference in the SAXS data between the pure PAA and the composite are discussed through the interaction of C₆₀ molecules with the polyamic acid, which seems to hinder the imidization reaction up to 185° C.

Keywords

Polyamic acid, fullerene-composites, imidization, structure, X-ray diffraction.

1. INTRODUCTION

In recent years, the investigation of the polyimide/fullerene C₆₀ composites (PI/C₆₀) has received some attention, owing to the multiple applications (optical, mechanical, biological, etc) of these materials [1]. Also, they show a good combination of properties, i.e., high strength and thermal stability typically found in fullerene-modified polyimides [2, 3, 4]. Other reason for the scientific interest is that the C₆₀ is capable to modify the non-linear optical properties of polyimides [5].

As it is not possible to introduce directly the C₆₀ into the PI matrix, due to the insolubility of the latter, C₆₀ can be added to one of the PI precursors, i.e., either the diamine (DAM), the dianhydride (DAN) or the polyamic acid (PAA). The different routes in which the C₆₀ can be added to a PI matrix are summarized below:

- I) (a) (First step, moderate temperature, solution) DAM (+C₆₀) + DAN →
PAA/C₆₀
- (b) (First step, moderate temperature, solution) DAN (+C₆₀) + DAM →
PAA+C₆₀
- (c) (First step, moderate temperature, solution) PAA (+ C₆₀) → PAA/C₆₀
- II) (a) (Second step, high temperature, solid state) PAA + C₆₀ → PI/C₆₀

Among the PIs, those containing the bis(phenylene) pyrimidine unit are known to exhibit an improved mechanical strength [6] and thermal stability [7, 8]. In the present study, we have investigated the copolyamic acid (coPAA) based on the 3,3', 4,4'-oxydiphthalic anhydride (DPO) and two diamines: 2,5-bis(4-aminophenyl) pyrimidine (2,5 PRM), and *p*-phenylenediamine (*p*-Ph). The molar ratio of the three components is, in our case,

100:50:50 [2]. Chemical formulae of the raw materials and the resultant polymer are shown in fig.1.

In a previous paper, we studied the influence of the fullerene C_{60} on the nanostructure evolution of PI/ C_{60} during thermal treatment [9]. In that study, the pure polyimide PI was compared with the PI/ C_{60} composites prepared by adding the C_{60} , either to the diamine (DAM) solution (route Ia), or to the dianhydride (DAN) solution (route Ib).

C_{60} is a strong electron acceptor molecule. For this reason, one expects that its incorporation into the PI precursor may be affected by the interactions between C_{60} and the electron donor fragments of the precursor [10]. Investigations performed in fullerite samples have revealed that C_{60} molecules can exist in dispersed, amorphous and crystalline states [11-14]. In addition, it has been found that fullerene molecules in polymer matrices can also occur in similar structural states [10, 15-18]. In particular, scanning electron microscopy (SEM), Fourier-transform electron microscopy (FTIR) and thermal desorption spectrometry (TDS) studies performed in the PI/ C_{60} composites, suggest that C_{60} can be present in different states, e.g. molecular dispersion, cluster and crystalline form [2, 19, 20].

Preliminary measurements performed to elucidate the influence of C_{60} added to the polyamic acid (PAA) (route Ic) showed certain differences in the SAXS and WAXS patterns of a PAA/ C_{60} composite as compared to those of neat PAA [12]. The aims of the present study are twofold:

- 1) To describe the structural features of pure PAA, and of the PAA/ C_{60} system prepared by adding the C_{60} to the PAA precursor (route Ic).

2) To clarify the influence of fullerene upon imidization of PAA, by comparing the evolution of, both, PAA and PAA/C₆₀ during thermal treatment, giving rise to the final pure polyimide or the PI/C₆₀ composite.

2. EXPERIMENTAL

2.1. Sample preparation

The PAA synthesis and the preparation of the PAA/C₆₀ system, were carried out as follows [2, 4, 10]:

The polyamic acid PAA was synthesized from a mixture of 3,3',4,4'-dipheniloxytetracarboxylic acid dianhydride (DPO), *p*-phenylenediamine (*p*-Ph), and 2,5-bis(4-aminophenyl) pyrimidine (2,5 PRM) taken in the molar ratio 100:50:50. The 2,5 PRM was obtained from N. N. Vorozhtsov Institute of Organic Chemistry (Novosibirsk, Russia) [2, 4]. C₆₀ fullerite with purity higher than 98% was supplied by Fullerene Technologies Co., St. Petersburg, Russia [19]. Prior to the synthesis, the reagent were purified by the following procedures:

DPO was recrystallized from *o*-xylene and heated at 100° C in vacuum ($T_m = 226-227^\circ$ C); *p*-Ph was distilled in vacuum ($T_m = 139-141^\circ$ C); 2,5 PRM was purified by sublimation ($T_m = 226-227^\circ$ C); N, N-dimethylacetamide (DMAA) was, firstly, dried over calcium hydride, and then distilled on a rectification column under reduced pressure; *o*-dichlorobenzene was purified by distillation [10].

Then, 0.6968 g (0.0065 mol) of *p*-Ph and 1.6903 G (0.065 mol) of 2,5 PRM were dissolved with stirring in 47 ml of DMAA. 3.5 g (0.013 mol) of DPO were added by portions to this solution, with permanent stirring [10]. In this way, the PAA solution (molar ratio 100:50:50) in DMAA was prepared. On the other hand, the PAA/C₆₀ system was obtained by pouring an *o*-dichlorobenzene C₆₀-solution into a solution of PAA in DMAA (route Ic), in the required proportion to obtain a C₆₀ concentration of 5% on dry

polymer basis, followed by careful stirring of the mixture for a few hours [2, 4, 19]. It has to be noted that C_{60} was not completely dissolved in the mixed solution obtained, and sediment formation was observed. This effect was also found for C_{60} concentrations higher than 2% (dry basis polymer), being independent of the selected route for the C_{60} addition [2, 15, 19]. Thus, the actual concentration of fullerene inside the PI matrix can be lower than the rated one. The solutions were kept in a refrigerator at 6° C for several days. Films were cast onto flat glass substrates from the PAA or PAA/ C_{60} solutions in DMAA. In the second case, the polymer solution was decanted after the sediment formation. Both solutions were dried at 80° C during several hours to remove the solvent and to form a coating. Film thickness was about 40-80 μm .

2.2. Techniques

To characterize the “in situ” evolution of the pure PAA and the PAA/ C_{60} samples during the thermal treatment, 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 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 PAA or PAA/ C_{60} samples were packed together in Al foil to perform the scattering experiments. The films were placed within the sample holder with their surface perpendicular to the X-ray beam, and maintained under rotary pump vacuum during the experiment. The thermal treatment employed was the following:

- 2 minutes at room temperature.
- Heating from room temperature up to 320° C at 5° C/min.
- Heating from 320° C up to 400° C at 10° C/min.

- Cooling down from 400° C to room temperature at 20° C/min.

The crystallinity, w_c , was derived from the WAXS patterns, by using a curve-fitting program, as the ratio of the area corresponding to the crystalline reflections to the total area of the WAXS pattern.

The values of the long period L , and the invariant Q were derived from the angular position and area of the SAXS maximum, respectively. In semicrystalline polymers, the invariant Q is given by the expression [22]:

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

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.

3. RESULTS

3.1. WAXS

Fig. 2 shows that the WAXS patterns of PAA and PAA/C₆₀ are practically identical; i.e., none of the C₆₀ crystalline reflections appear in the WAXS diagram of the PAA/C₆₀ composite [23]. These results are in agreement with previous observations on PI/C₆₀ composites containing up to 5% C₆₀ [10, 24]. Recent studies performed on polyamic acid-C₆₀ composites indicate that, for C₆₀ concentrations higher than 10 %, crystalline reflections corresponding to C₆₀ appear in the WAXS pattern [20]. The evaluation of the WAXS pattern between 12 and 32° (2 θ) during the thermal treatment is not straightforward. For this reason, we have concentrated on the analysis of the reflection at about 11° (2 θ). In fact, this reflection is most clearly visible and the easiest one to evaluate (see fig.2). We have analyzed the percentage of area of this reflection with respect to the total WAXS area (S_{11}), as well as the crystal coherence length, D , derived

from the integral width, and the variation of both quantities with temperature. Similarly to the case of other polyamic acids [25], the reflection at about 11° can be related to the identity period of the polymeric chain.

The variation of the degree of crystallinity observed during the thermal treatment exhibits a similar stepwise increase in both systems (see fig. 3). Thus, the initial crystallinity, $w_c \approx 0.2$, remains nearly constant till the temperature reaches a value of 185°C . If the temperature is increased to 255°C , then the w_c -value rises up to ~ 0.3 . In the range 255 - 320°C , w_c remains constant. In the range 320 - 400°C , w_c experiences a new increase, reaching a maximum value of about 0.35 . During the first minutes of the subsequent cooling process, w_c slightly increases (up to ~ 0.4) and finally remains constant until the end of the thermal treatment. The evolution of S_{11} (not shown here) is similar to that of the crystallinity, but in the PAA/ C_{60} composite this contribution is always slightly higher (1.1 - 1.8%) than that in case of pure PAA.

Concerning the crystal coherence length, D , derived from the integral width $\delta\beta$ of the peak at 11° ($D \sim 1/\delta\beta$), its variation during the heating process is rather small, and similar in the two samples studied. In pure PAA, D slightly increases from 11 to 13.3 nm, whereas in the PAA/ C_{60} composite, D varies between 10.5 and 12.7 nm. In both systems, the spacing d corresponding to the peak at 11° does not change during the thermal treatment (the peak position at about 11° remains nearly constant).

3.2. SAXS

Fig. 4 illustrates the variation of the long spacing L with temperature for the two samples. In both cases the long spacing L (see fig. 4) shows a constant value in the range RT - 255°C , followed by a gradual increase with temperature and a final leveling off tendency during the cooling process. It is noteworthy that the final L values (~ 12.1 nm) nearly

coincide with the crystal coherence length D as derived from the reflection at 11° (13.3 and 12.7 nm for pure PAA and for the PAA/C₆₀ composite, respectively).

Fig. 5 illustrates the evolution of the invariant with temperature for both samples, Q showing a clear maximum at about 235°C for PAA (fig. 5a), whereas two maxima ($T = 115^\circ\text{C}$ and $T = 235^\circ\text{C}$) appear in case of PAA/C₆₀ (fig. 5b).

4. DISCUSSION

4.1. Pure polyamic acid PAA

For the discussion of figs. 3 and 4, it is convenient to distinguish among the following temperature ranges: I) from RT up to 185°C ; II) from 185 up to 255°C ; III) from 255 up to 320°C ; IV) from 320 up to 400°C ; V) the final cooling step, from 400°C down to RT. It is clear that in the range I, both, w_c and S_{11} remain constant. The progress of the imidization reaction in range II induces w_c (fig. 3) and S_{11} to increase in this region. In range III the material is almost totally imidized [2], and w_c (fig. 3) and S_{11} remain constant. In range IV, the samples are heated from 320 to 400°C . Our preceding differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) results [2] point to the possibility of a chemical transformation (last imidization stages) within the PI matrix at these temperatures. In previous investigations [2, 4], the DTGA curves from PAA films show two maxima: the first one ($T_1 = 180^\circ\text{C}$) is related to the elimination of the residual solvent¹, and also of the water resulting from the imidization reaction. The second maximum ($T_2 = 600^\circ\text{C}$) is related to the decomposition of the PI matrix. From these curves, it appears that the imidization is not complete until a temperature of 400°C is reached.

¹ N. B. : The boiling points of o-dichlorobenzene and N, N-dimethyl acetamide are 180°C and 165°C , respectively.

Thus, in range IV, an additional crystallization seems to take place, and w_c reaches values between 0.31-0.35. The scattering area S_{11} also behaves similarly to the crystallinity in this temperature range.

According to fig. 4, L first remains constant in ranges I and II, and then in ranges III-IV starts to increase, in a more or less continuous way, until the temperature reaches the maximum value (400° C). The L value slightly increases again during the beginning of the cooling process (range V), and finally levels off. The invariant Q exhibits a quite different behavior (see fig. 5).

The successive steps during the heating process can be explained as follows:

Range I (RT-185°): the invariant Q increases, due to the increase of the $(\rho_c - \rho_a)^2$ factor.

The crystallinity w_c , the contribution of the peak at 11° and the long spacing L remain constant.

Range II: when the temperature rises from 185 up to 255° C, the amount of crystalline material w_c increases, parallel to S_{11} , though L remains constant. Thus, in range II, the crystals grow mainly laterally (D varies from 10.5 to 11.7 nm). Simultaneously, the invariant Q steeply increases until the temperature reaches 235° C. However, when the temperature increases further from 235 to 320° C, then Q diminishes. The initial strong increase of Q in this region is caused by a parallel increase of, both, w_c and the $(\rho_c - \rho_a)^2$ factor, which could be related to the further progress of the imidization reaction.

The subsequent lowering of Q from 235° C to 320° C is originated by the $(\rho_c - \rho_a)^2$ decrease, provided w_c and S_{11} remain constant.

Range III: in the range 255-320° C, L gradually increases.

Range IV (320-400° C): the parallel increase of w_c , S_{11} , L and Q suggest that crystals increase in number and lateral size, as there are no changes in the crystal coherence

length D in the molecular direction. The L increase may be explained by the progress of the imidization reaction, finally reaching the L -value corresponding to the pure PI.

4.2. PAA/C₆₀ composite

Fig. 3 illustrates the evolution of w_c during the thermal treatment for the PAA/C₆₀ sample. It is seen that the composite behaves in a similar way to the pure PAA. Only a small contribution due to the C₆₀ presence is observed in the WAXS pattern:

- a) S_{11} is a little higher (1.1-1.8%) in case of the sample PAA/C₆₀.
- b) D varies from 11.0 to 13.3 nm in pure PAA, while in the PAA/C₆₀ composite from 10.5 to 12.7 nm.

From the SAXS results it can be seen that L in the PAA/C₆₀ composite behaves similarly to that of PAA alone (see fig. 4). The Q evolution is, however, different from that shown by pure PAA (compare fig. 5b to fig. 5a), particularly between 25 and 185°C. The different behavior shown by the Q evolution in both systems in this temperature range might be due to the presence of C₆₀ in the composite. Fullerene C₆₀ is a strong electron acceptor, being capable to react with primary [26], secondary [26-28] and tertiary amines [29, 30]. Analysis of the thermal desorption spectra of PAA/C₆₀ composite coatings indicate that C₆₀ molecules, in the initial PAA/C₆₀ solutions, interact with terminal amine groups of the polyamic acid [15, 19, 20]. Such an interaction is confirmed by the increase of the intrinsic viscosity in the PAA/C₆₀ solutions compared to that of the pure PAA solutions [2]. FTIR and SEM studies performed in PAA/C₆₀ films heated at different temperatures [2] additionally confirm this assumption. Therefore, in the range 25-185° C, there appears to be a competition between the C₆₀ tendency to react with the electron donor groups of the polyamic acid (CO and NH₂), and the imidization reaction (closing of cycles and water evaporation). In fact, Sazanov et al [31] indicate that, in PAA/C₆₀

composites, C_{60} is capable to react with CO and NH_2 , and even with carboxyl groups, thus, hindering the imidization reaction. In our system, this effect disappears for temperatures higher than 185° C.

The electron acceptor character of C_{60} has also been stressed out by comparing the thermal behavior of the PI under study and the composite PI/ C_{60} , prepared by adding the C_{60} to the diamines solution [9]. It has been shown that the composite presents a clear SAXS maximum that could be related to the tri-dimensional location of the C_{60} molecules within the PI/ C_{60} composite. From this fact, and also, from other experimental evidences, it seems clear that the C_{60} molecules are able to react with the nitrogen atoms of the diamines present in the solution. It is interesting to note that the TSD studies performed on the PI/ C_{60} composites allow one to distinguish between the material prepared by adding the C_{60} to the diamines solution, and that obtained by adding the fullerene to the PAA solution [20]. In the first case, the results suggest that the C_{60} is present in three forms, namely, molecularly dispersed, amorphous and crystalline phases. However, the crystalline phase of the C_{60} is absent in the second case [20]. In any case, the FTIR and TSD studies performed on the PAA/ C_{60} and the PI/ C_{60} composites suggest the presence of covalent chemical bonds between the C_{60} and the matrix [2, 15, 19, 20].

Fig. 6 attempts to illustrate schematically the influence of the heating process on the PAA/ C_{60} system. Fig. 6a shows the initial state of the system. Some of the C_{60} molecules have reacted with the nitrogen atoms of the polyamic acid. As the long spacing L_1 is practically identical to that of the PAA alone (see fig. 4), we suggest that a fraction of the reacted C_{60} molecules is located within the amorphous regions between the crystals (see fig. 6a). The rest of the reacted C_{60} is incorporated into the non-crystallized regions. The non-crystallized chains are represented as having a rigid and a flexible component, according to the characteristics of the two diamines involved in the PAA synthesis [6].

Fig. 6b shows schematically the situation when the temperature is about 185° C. According to the Q evolution (see fig. 5), at this temperature the C₆₀ molecules have been partially removed from the amorphous regions between the crystals while L₁ remains unchanged (see fig. 4). Fig. 6c corresponds to the final PI/C₆₀ system at 400° C. At this temperature, the long spacing L of the polyimide is about a 50% higher than that of the PAA (see fig. 4). This could be explained by the growth of new, larger crystals as a consequence of the imidization progress. We designate L₂ as the long spacing originated from heterogeneities of these new crystals. The final L value should be an average of the two long spacing.

From the foregoing, the main differences between the PAA and the PAA/C₆₀ samples can be summarized as follows:

- 1) The PAA/C₆₀ crystals are slightly smaller than those present in pure PAA. This difference is maintained during the thermal treatment, even if the evolution in both cases is parallel.
- 2) S₁₁ is always higher in the PAA/C₆₀ composite than in pure PAA. This is an indication of the influence of C₆₀ in the PAA material, suggesting the occurrence of a better packing in chain direction.

4.3. Final state of the PI/C₆₀ composites

Concerning the final state of the PI/C₆₀ composites at the end of the thermal treatment, from preceding studies [2, 4] it is known that the tribological properties of the PI/C₆₀ composites depend mainly on the structural transformations of the matrix in the temperature range 300-400° C, i.e., during the last imidization stages. On the other hand, from thermo-desorption studies performed on polyimide-fullerene C₆₀ systems [10, 15, 19, 20] one can assume that strong chemical bonds formed between fullerene molecules

and polymer chains, either in the diamines- C_{60} solution or the PAA- C_{60} solution, disappear at the beginning of the thermal decomposition of the PI matrix. The disappearance of C_{60} in this high temperature range might be due to: 1) a desorption process, 2) some complicated chemical transformations of C_{60} in the presence of PI molecules, 3) a combination of both effects.

Within this context, it is noteworthy that the thermal decomposition of the studied PI takes place between 500 and 700°C, with a maximum appearing at about 600°C [2, 4]. This result suggests that the thermal decomposition of the PI does not start below 500° C. In pure PAA and in the PAA/ C_{60} system, the peak position at about 11° remains nearly constant (the corresponding d spacing does not vary). According to Shukanova et al [6], this reflection is related to the (003) planes of the DPO-2,5 PRM nanoblocks of the PAA and PI molecules in pure polymers, copolymers and composites. Therefore, it can be concluded that our samples are relatively rigid in the molecular direction. This is in agreement with the concept of a nematic structure of the PAA and PAA/ C_{60} systems, proposed by Sidorovich et al [25]. According to these authors, the creation of these structures in the PIs [25] takes place into two steps: 1) a mesophase formation in PAA concentrated solutions, 2) the improvement of the mesophase order, at 120-135° C (thermal treatment previous to the imidization step). A subsequent heating at higher temperatures (imidization step) results, either in the crystallization of the material, or in its transition to a better-ordered mesophase.

It has been shown that, both, the PAA and the PAA/ C_{60} composite studied in the present paper show initially certain degree of order in the molecular direction, characterized by a well defined reflection at 11° (2θ), a crystallinity of about 0.2, and the presence of the long spacing L . The order improvement during the heating process is shown by the parallel increase of w_c , S_{11} and L .

Summarizing, the present X-ray experiments allowed us to distinguish among the various steps that take place during the conversion of PAAs to PIs: solvent and water evaporation (RT-185° C), imidization progress (185-255° C), increase of only the long spacing L (255-320° C), and last imidization stages (320-400° C).

5. CONCLUSIONS

- 1) By means of WAXS and SAXS analysis, it is possible to distinguish among the different steps taking place during the conversion of PAA into PI through thermal imidization: a) solvent and water evaporation during the first imidization stage; b) imidization progress, giving rise to an increase of the crystalline perfection; c) parallel increase of crystallinity and long spacing L during the last imidization stages.
- 2) The presence of C₆₀ seems to affect the degree of order within the material in the molecular direction, showing a higher contribution of the peak at 11° (S₁₁) for the PAA/C₆₀ composite than for the pure PAA system. The composite crystals are, however, slightly smaller than those of pure PAA.
- 3) The Q evolution in the range of temperatures 25-185° C shown by the PAA/C₆₀ composite can be explained through the interaction of the C₆₀ molecules with the CO and NH₂ groups of the polyamic acid, and also, with the carboxyl groups. This interaction seems to hinder the imidization reaction in this temperature range. For temperatures higher than 185° C, the two systems behave similarly.

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FIGURE CAPTIONS

Fig. 1: Chemical formulae of: the dianhydride DPO, the two diamines *p*-Ph and 2,5 PRM, and the resultant polymer: copolyamic acid based on DPO, *p*-Ph and 2,5 PRM in the molar ratio 100:50:50

Fig. 2: WAXS patterns of: (a) pure PAA and (b) the PAA/C₆₀ composite.

Fig. 3: Variation of degree of crystallinity, w_c , during the thermal treatment investigated.

Fig. 4: Variation of the long period, L , with increasing temperature.

Fig. 5: Plot of the invariant Q as a function of increasing temperature for: (a) pure PAA and (b) PAA/C₆₀ composite.

Fig. 6: Schematic model, illustrating the changes in the structure of the PAA/C₆₀ composite at various temperatures of the thermal treatment. Circles: fullerene molecules.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

a) Room temperature-125° C

b) 185° C

c) 400° C

Fig. 5

From: Prof. F.J. Balta Calleja <embalta@iem.cfmaac.csic.es>
To: "Margarita Cuevas" <Cuevas@brill.nl>
Subject: RE: URGENT: CI2337
Date sent: Tue, 06 Mar 2007 10:44:47 +0100

Estimada Sra Cuevas,

Observamos con preocupación que la dirección (Present address) de uno de los coautores de nuestro trabajo, la Dra. Marina Krumova, es incorrecta. La dirección correcta es la siguiente:

University of Konstanz, D-78457 Konstanz, Germany.

Mucho le agradeceríamos si pudiera subsanar esta equivocación.

Con nuestros mejores deseos,

Francisco J. Balta Calleja

From: Prof. F.J. Balta Calleja <embalta@iem.cfmac.csic.es>
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Estimada Sra. Cuevas:

En contestación a su escrito, tenemos el gusto de incluirle adjunta la lista de referencias con los títulos de los artículos publicados.

Contestando a su pregunta, no es posible que hubiera sido profesor de Física suyo en la Universidad Complutense, ya que en 1967 dejé mi puesto en la Cátedra de Electricidad y Magnetismo y me fui a Estados Unidos.
Con mis mejores deseos, atentamente le saluda,

Francisco J. Balta Calleja

Estimado Prof. Balta Calleja,

Agradezco la rapidez con que nos ha enviado las correcciones a las pruebas de imprenta de su artículo CI2337 y los correspondientes formularios. Por favor, ¿podría enviarme lo antes posible una lista con las referencias incluyendo los títulos de los artículos publicados en revistas? Este es el estilo de Composite Interfaces y nos gustaría que su artículo estuviera en un formato consistente con el resto de la revista.

Por curiosidad: ¿puede que yo haya recibido clases de física o cristalografía de usted en la Universidad Complutense en los años 1969 o 1970? Entonces es cuando empecé mis estudios de Geología en Madrid, para acabarlos en Holanda.

Atentamente le saluda,

Margarita

Attachments:

D:\My documents\References