

Effect of the cure temperature on the morphology of a cyanate ester resin modified with a thermoplastic: characterization by atomic force microscopy

C. Marieta, M. del Rio, I. Harismendy, I. Mondragon*

Escuela Ingeniería Técnica Industrial, Departamento Ingeniería Química y M. Ambiente, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1 B. 20011, San Sebastián/Donostia, Spain

Received 25 January 1999; received in revised form 19 May 1999; accepted 16 August 1999

Abstract

A bisphenol A dicyanate (DCBA) resin has been modified with bisphenol-A polysulfone (PSU) at a concentration of 15 wt%. Mixtures, postcured at the same conditions, have been precured at different temperatures. The effect of the curing temperature on the morphology has been studied by Atomic Force Microscopy (AFM). In the present study, we have also compared Scanning Electron Microscopy (SEM) and AFM in order to demonstrate that AFM is a powerful tool for the characterisation of polymer mixtures morphology. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cyanate resins; Polysulfone; Morphology; AFM; SEM

1. Introduction

Cyanate esters have found use for applications in the electronic and composite industries where their excellent properties like low dielectric losses, good adhesive properties, glass transition temperatures in the range of 250–300°C, solubility in ketone solvents, and low moisture absorption are demanded [1]. Though cyanate resins are known to be relatively tough compared with other thermosets, some applications require improved fracture toughness. Toughening of thermo-

sets has been achieved through various methods [2]. In this work, the incorporation of a thermoplastic was used. The uncured cyanate resins are compatible with a number of amorphous thermoplastic polymers, including copolyester, polysulfones, polyether sulfones, polyarylates and polyether imides [3–5]. During the course of curing, most of the mentioned polymers phase-separate into micron or sub-micron sized domains exhibiting a co-continuous or phase-inverted morphology at concentrations > 15wt% because of the high molecular weight of the thermoplastic [6].

There is a wide range of microscopic instruments available, which allow characterising polymeric microstructural features. Scanning Electron Microscopy (SEM), undoubtedly one of the most used, and Scanning Probe Microscopy (SPM), a more recent technique which seems to have a big future for its wide

* Corresponding author. Tel.: +34-943-455022; fax: +34-943-471097.

E-mail addresses: iaamagoc@sp.ehu.es (C. Marieta), iapmoegi@sp.ehu.es (I. Mondragon).

range of potential applications [7–12], have been the techniques used in this work.

2. Experimental

2.1. Materials

The cyanate ester resin used in the present work was AroCy B10, kindly supplied by Ciba. The catalyst system used was a mixture of 360 ppm of copper (II) acetylacetonate, $\text{Cu}(\text{AcAc})_2$, and 2 phr of nonylphenol, both supplied by Aldrich [13].

The thermoplastic used was a polysulfone of bisphenol A (PSU) commercially available as Udel P-1700 from Amoco Chemical ($M_n = 38,000$) [14].

Chemical structures of the materials used in this work are shown in Table 1.

2.2. Mixing and curing procedure

The mixture was prepared by dissolving PSU (15

wt%) and DCBA monomer in methylene chloride at room temperature. The solvent was evaporated at 90°C on hot plate and the residual solvent was removed at 110°C for 2 h under vacuum. The catalyst system was added to the mixture at 90°C during 5 min. This catalysed mixture was cured for 3 h at: (a) 160°C and (b) 180°C, and both systems were post-cured for 2 h at 200°C and 1 h at 250°C.

2.3. Microstructural study

Morphology of the mixtures was studied by SEM and AFM, analysing the fracture surfaces of specimens tested by bending.

The SEM examinations were performed in a JEOL JSM-6400 scanning electron microscope at an accelerating voltage of 15 kV. Samples were coated with a thin layer of gold. The thickness of these Au coatings was approximately around 44 nm.

The AFM scanning was carried out using a Scanning Probe Microscope (Nanoscope IIIa, Multimode™ from Digital Instruments) by using contact with

Table 1
Chemical structure of the materials used

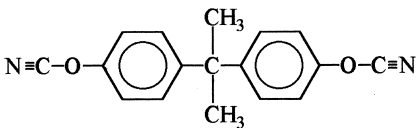
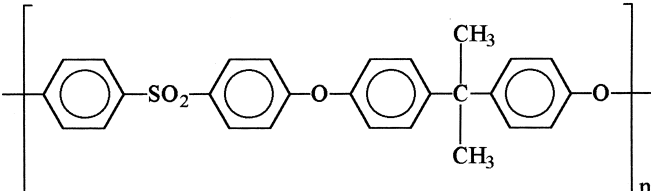
Product	Formula
2,2'-Bis (4-cyanatophenyl) isopropylidene AroCy B10 (Ciba)	 <p style="text-align: center;">Tm: 79°C</p>
Polysulfone of Bisphenol-A Udel P-1700 (Amoco Chemical)	 <p style="text-align: center;">Mn 38000</p>

Table 2
Characteristics of the probe tips provided by Digital Instruments [15]

Characteristics	Contact mode	Tapping mode
Material	Silicon nitride	Etched silicon
Cantilever configuration	V-frame	Single beam
Cantilever length	200 μm	125 μm
Cantilever thickness	0.4–0.6 μm	3.5–5.0 μm
Cantilever width	35–40 μm	30–40 μm
Spring constant	0.12 N/m	20–100 N/m
Nominal tip radius of curvature	20–40 nm	5–10 nm

lateral force mode and tapping with phase imaging under ambient conditions.

The AFM images shown in the present work have been obtained by using a ($15 \times 15 \mu\text{m}$) scanner. Table 2 provides information about the characteristics of the probe tips used.

Several samples were scanned and each sample was imaged at different areas. Similar images were

obtained, so demonstrating the reproducibility of the results. All images are shown without any image processing except horizontal levelling and contrast enhancement.

3. Results and discussion

This section is organised in two parts: in the first part, the effect of curing conditions on the morphology of the mixture is studied by AFM, and in the second part the performance of AFM as technique for characterisation of polymer surfaces is discussed.

For this system the critical composition appears at around a 12 wt% PSU in the uncured mixture.

3.1. Effect of precuring conditions on the morphology: characterisation by AFM

The DCBA/PSU mixture at the studied composition (15 wt% PSU) was transparent at the earlier stages of polymerisation, indicative of homogeneity. However, as curing proceeded, the mixture became opaque. This

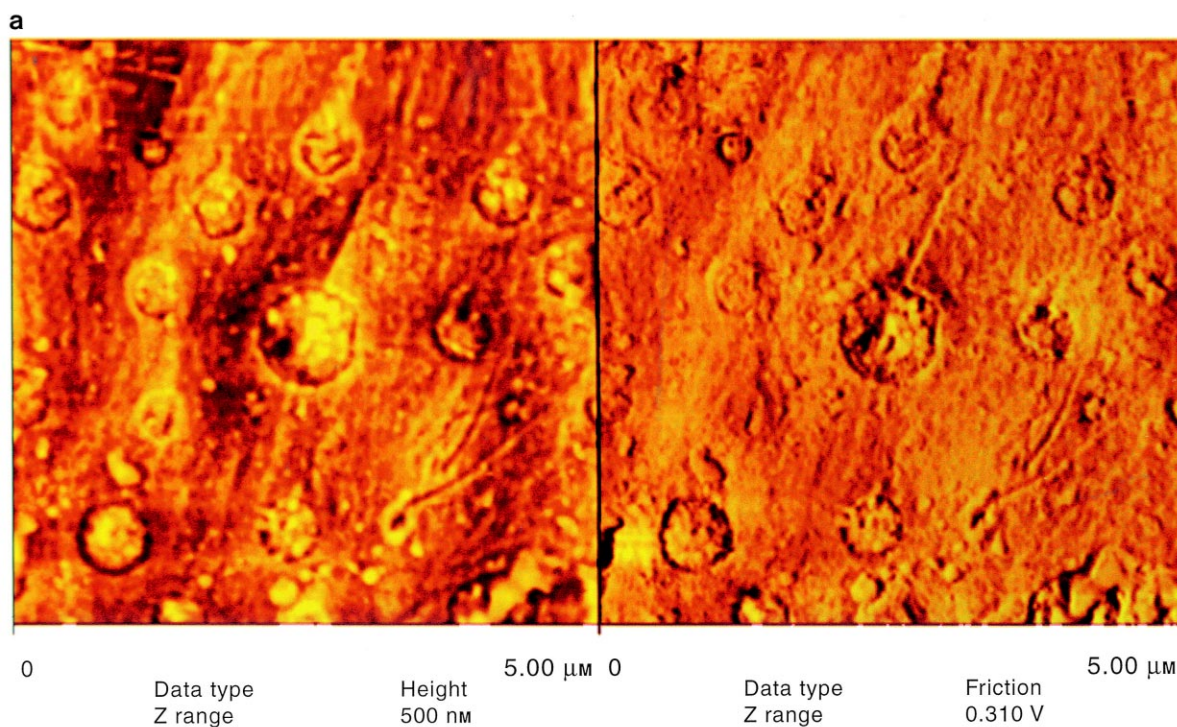


Fig. 1. AFM images of DCBA/PSU (15 wt% PSU) precured at 160°C : (a) contact mode images, topographical image (left) and lateral force image (right) $\lambda_1 = 5 \mu\text{m}$; (b) topographical image by Tapping mode $\lambda_2 = 15 \mu\text{m}$; (c) topographical 3D image by Tapping mode $\lambda_3 = 15 \mu\text{m}$.

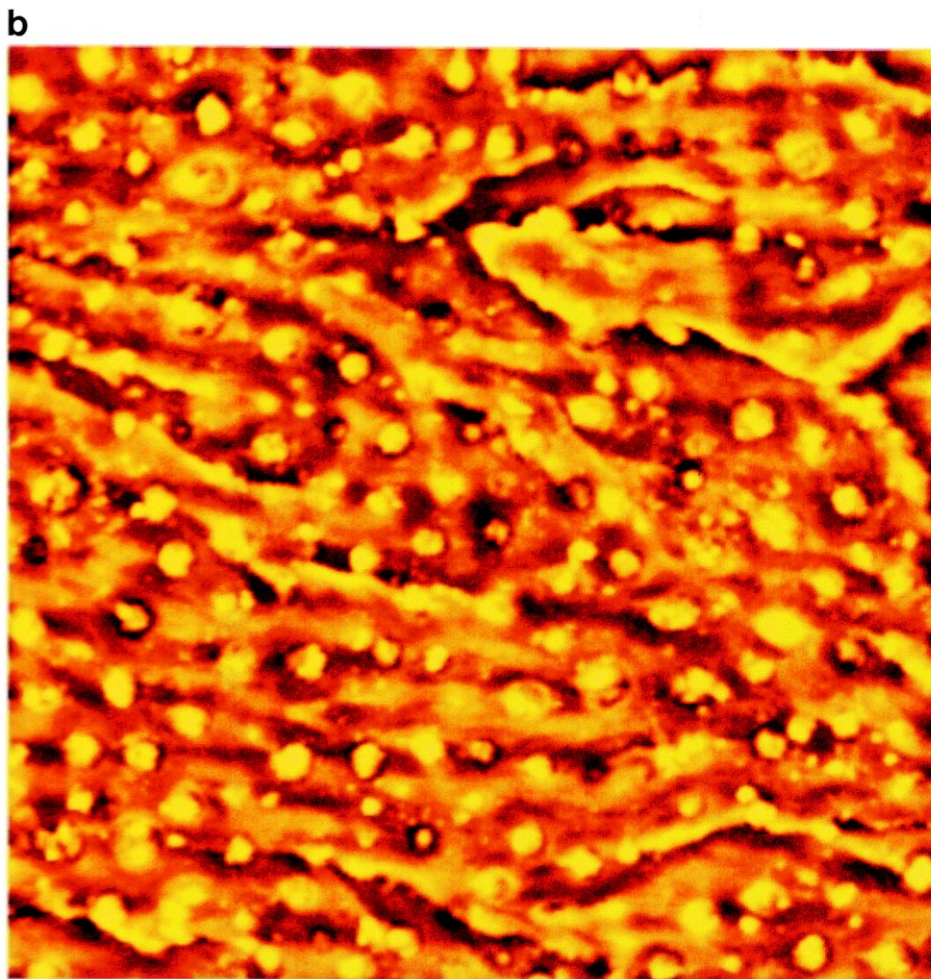


Fig. 1 (continued)

indicated that the increase of the molecular weight of the network-forming DCBA induced to phase separation phenomena giving different phase-separated microstructures as a function of curing temperature.

Firstly, the morphology of the bending broken mixture precured at 160°C was examined by AFM. This analysis was carried out using two modes of operation: contact and tapping in order to select the most suitable one for this mixture. No problems associated with friction, adhesion, electrostatic forces, and other difficulties that can plague contact mode were detected. Moreover, no differences in the images recorded by both modes were observed.

Fig. 1 shows the AFM images. In Fig. 1a the topographical and the lateral force images recorded at con-

tact mode are shown. Both images were recorded simultaneously in order to enhance the contrast of the phases. Fig. 1b and c shows a bigger view of the same sample recorded at tapping mode. Fig. 1c shows a 3D image, which allows having a spatial view of the mixture.

The images reveal that the morphology of the mixture precured at 160°C is a particulated microstructure, consisting of thermoplastic-rich particles into the continuous DCBA-rich matrix. These particles are not perfectly spherical and have different sizes. However, they are uniformly dispersed, and although the knowledge over the effect of the particle dispersion on toughening is still quite limited [16,17], in this case a rougher sur-

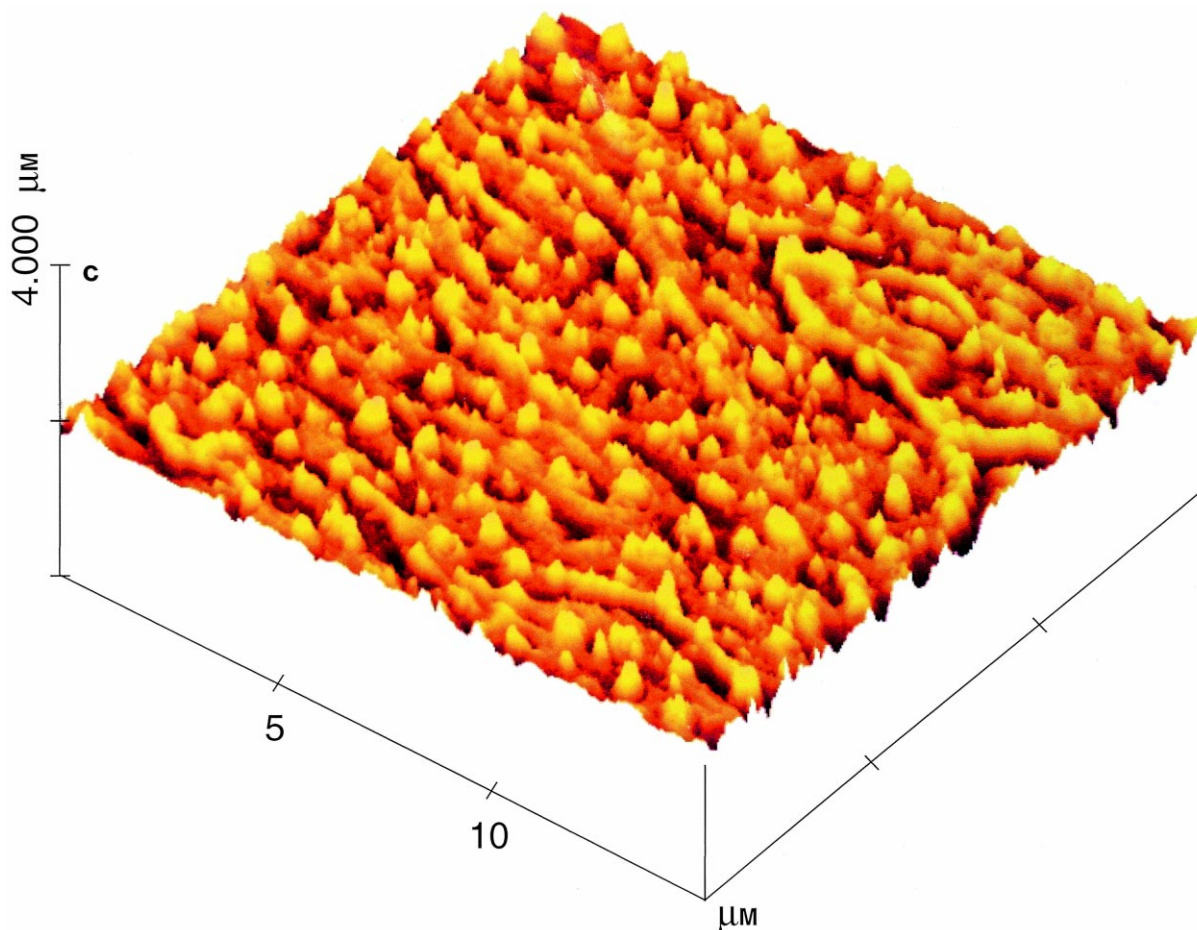


Fig. 1 (continued)

face is observed such as to become to fracture toughness.

Analysing one particle of around $0.80\ \mu\text{m}$ (Fig. 2), it can be seen that cavitation around the particle could progress to crack formation, this fact is also characteristic of toughened thermosets [18,19]. Another information from the analysis of the particle is that inside the thermoplastic domains there are spherical particles, which possibly are crosslinked DCBA. This means that a secondary phase separation in the already separated domains of thermoplastic can have taken place in a similar way to the morphologies reported by Oyangueren et al. for PSU-modified epoxy mixture [20]. This fact, together with the different size of the segregated particles, proves that phase separation occurred via a spinodal decomposition (SD) mechanism [21].

Subsequently, morphology of the bending broken

mixture precured at 180°C was examined. In this case, the images obtained by tapping had better resolution than the images obtained by contact. Thus, only the tapping images are shown in Fig. 3. Fig. 3a shows the topographical and the phase image also recorded simultaneously in order to have a good contrast of the phases. Fig. 3b shows a bigger view of the same sample and the 3D image is shown in Fig. 3c.

The images reveal a dual-phase morphology. This means that two microstructures coexist: a particulated microstructure where the thermoplastic-rich phase form small spherical particles in a continuous DCBA-rich matrix, and a co-continuous microstructure where the DCBA phase appears as discrete particles in a continuous thermoplastic-rich phase. These DCBA particles of around $0.20\ \mu\text{m}$ are bigger than the particles of DCBA observed inside the spherical domains of

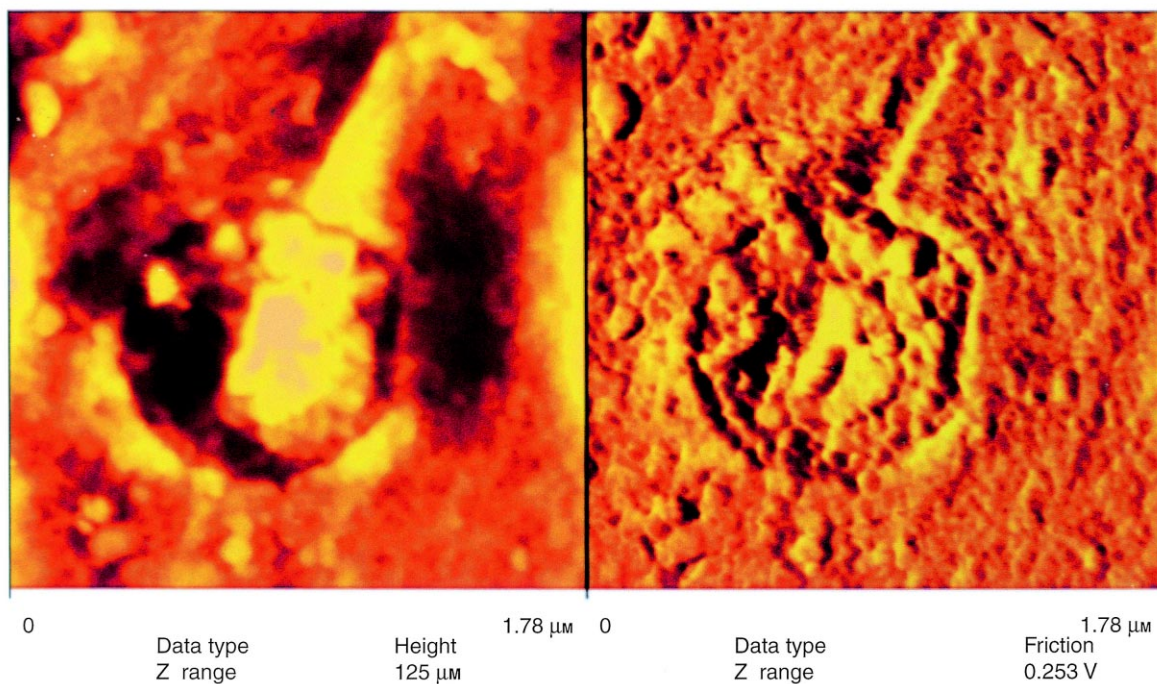


Fig. 2. Contact mode AFM images of DCBA/PSU (15 wt% PSU) precured at 160°C, topographical image (left) and lateral force mode image (right) $\lambda_1 = 1.78 \mu\text{m}$.

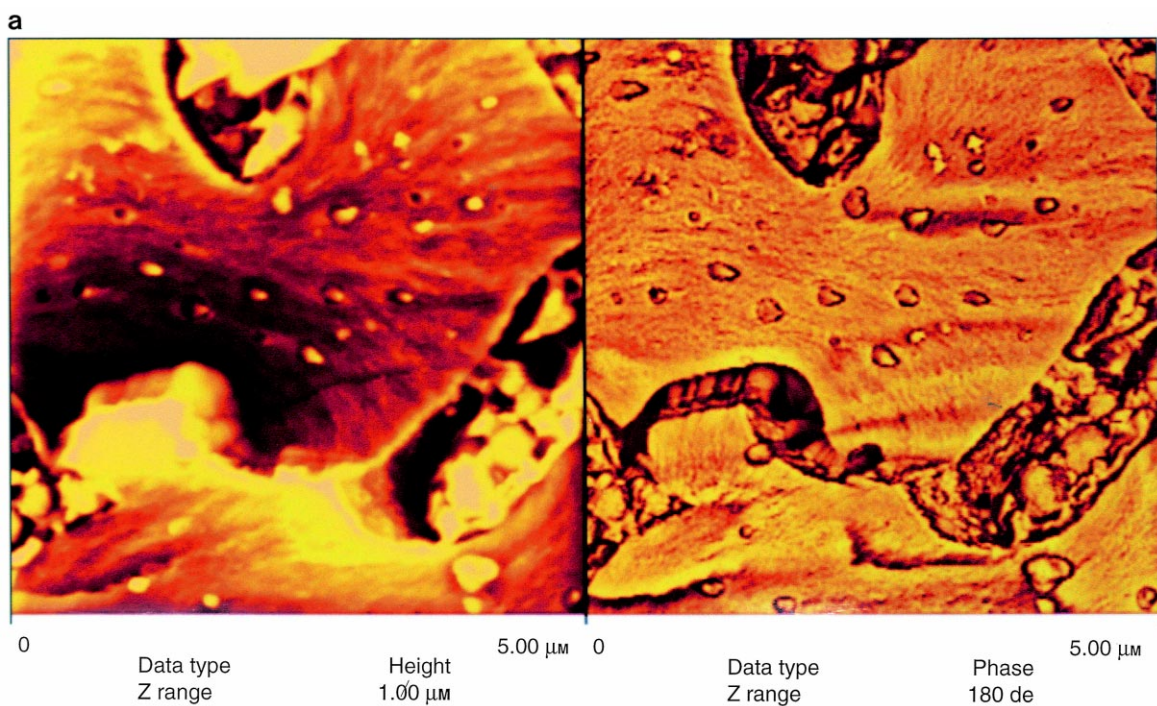


Fig. 3. AFM images of DCBA/PSU (15 wt% PSU) precured at 180°C: (a) tapping mode images, topographical image (left) and phase image (right) $\lambda_1 = 5 \mu\text{m}$; (b) topographical image by Tapping mode $\lambda_2 = 15 \mu\text{m}$; (c) topographical 3D image by Tapping mode $\lambda_3 = 15 \mu\text{m}$.

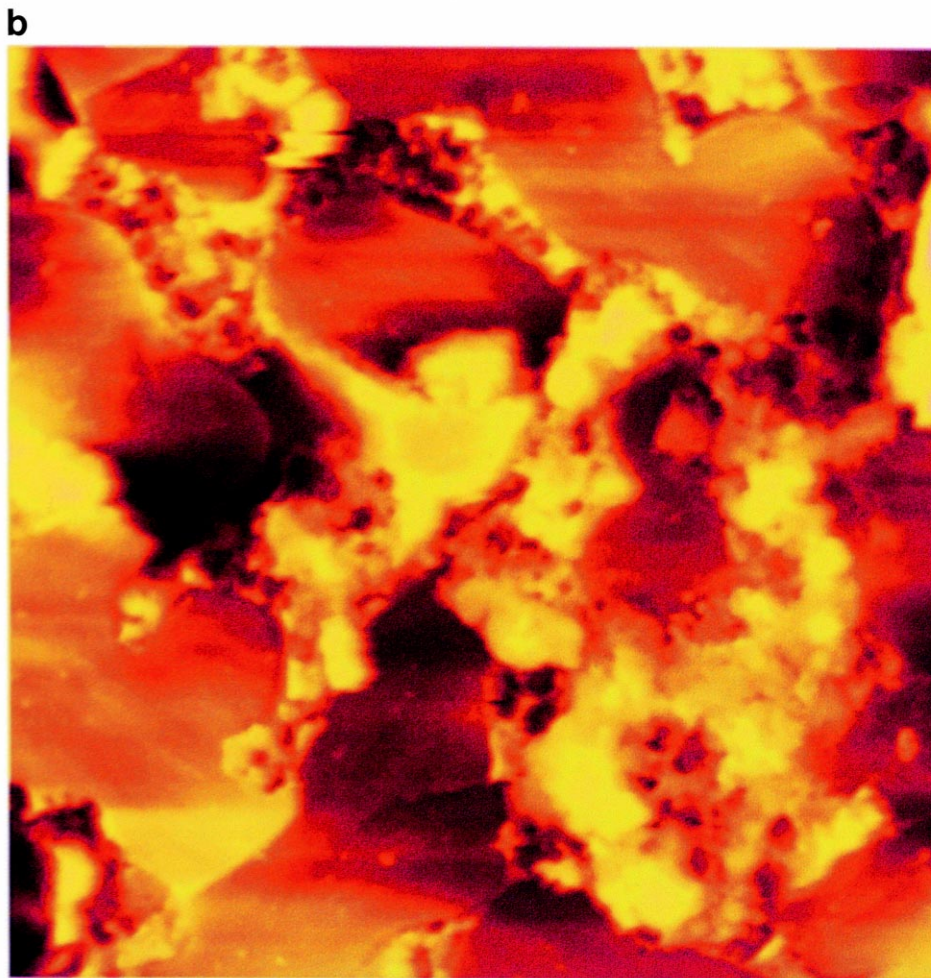


Fig. 3 (continued)

PSU in the mixture precured at 160°C (around 0.10 μm).

These differences observed on the morphology of the mixtures precured at different temperatures can be explained by supposing that phase separation occurred through a spinodal decomposition (SD) mechanism as a consequence of the increase on the molecular weight of the resin through curing. The mixture precured at 160°C had enough time to overcome the co-continuous microstructure before gelating, developing spherical particles. On the contrary, the microstructure for the mixture precured at 180°C was earlier fixed so not overcoming the co-continuous stage. Furthermore, the DCBA had less

time to disperse in the thermoplastic-rich matrix, so conducting, by a spinodal mechanism occurring in the PSU-rich phase, to bigger spherical particles than the spherical particles found in the PSU-rich phase in the particulated microstructure of the mixture precured at 160°C.

In view of the above images, it can be expected that the mixture precured at 180°C results in higher fracture toughness than the mixture precured at 160°C, according to several investigators who claim that a co-continuous structure results in higher fracture toughness [17]. However, we can not make any statement without having the mechanical analysis, which will be presented in future publications.

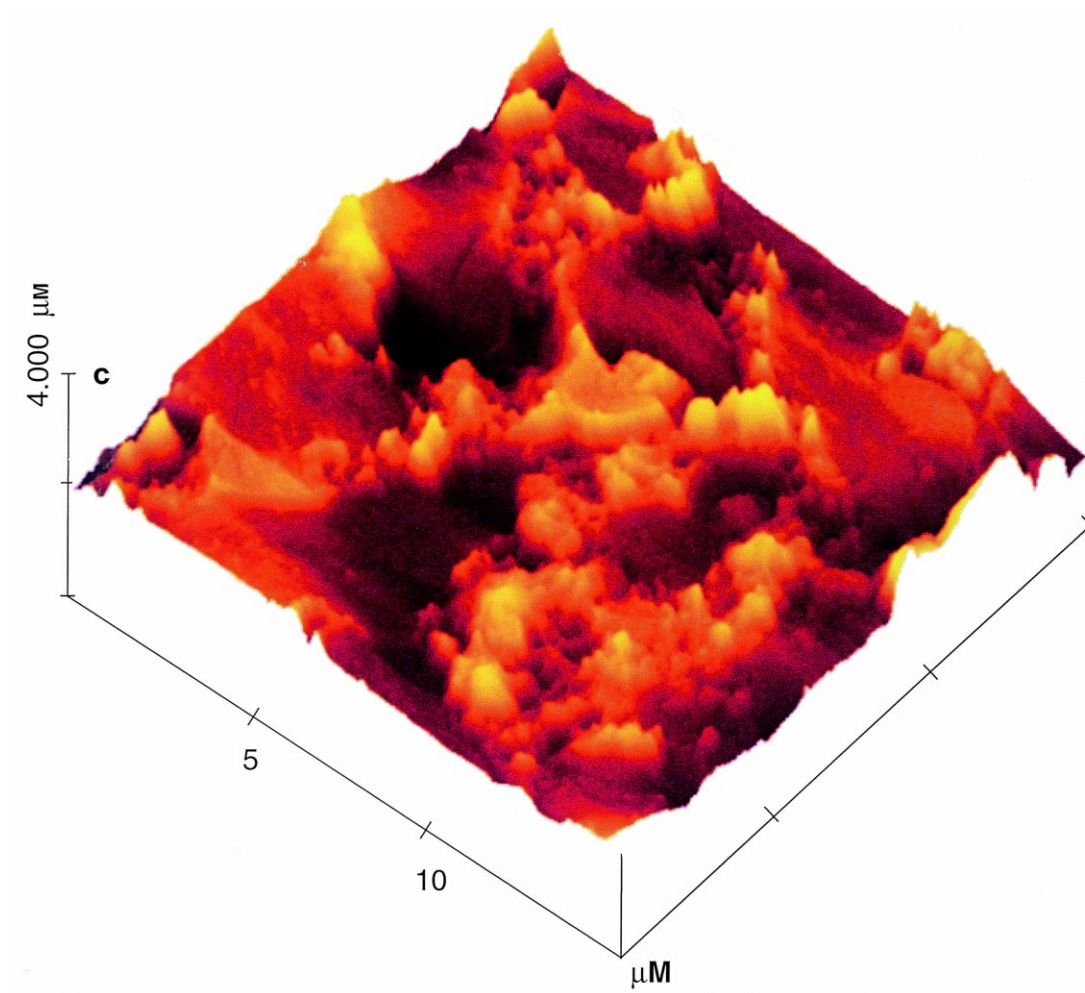


Fig. 3 (continued)

3.2. Advantages of AFM in the characterisation of polymer surfaces

Traditionally, the Electron Scanning Microscope has been one of the most used techniques to examine morphology of polymers. In the development of the present work SEM was also used to characterise the morphology.

Fig. 4 shows a SEM image of the mixture precured at 160°C. The morphology of the mixture cured at 160°C is a particulated microstructure, such as was observed in the images obtained by AFM (Fig. 1). The similarity of the images can prove the AFM as an available microscopic technique. Some advantages over SEM even can be mentioned: no chemical or physical changes occur during the visualisation, no specific

treatments are needed and AFM has the ability to differentiate materials by several techniques developed as extension to the basic SPM.

4. Conclusions

In this study, the effect of the cure temperature on the morphology of a cyanate resin modified with a 15 wt% PSU has been studied by AFM and SEM. Results of this investigation can be summarised in the following.

- Phase separation started from spinodal decomposition induced by the molecular weight increase of the cyanate matrix during curing.

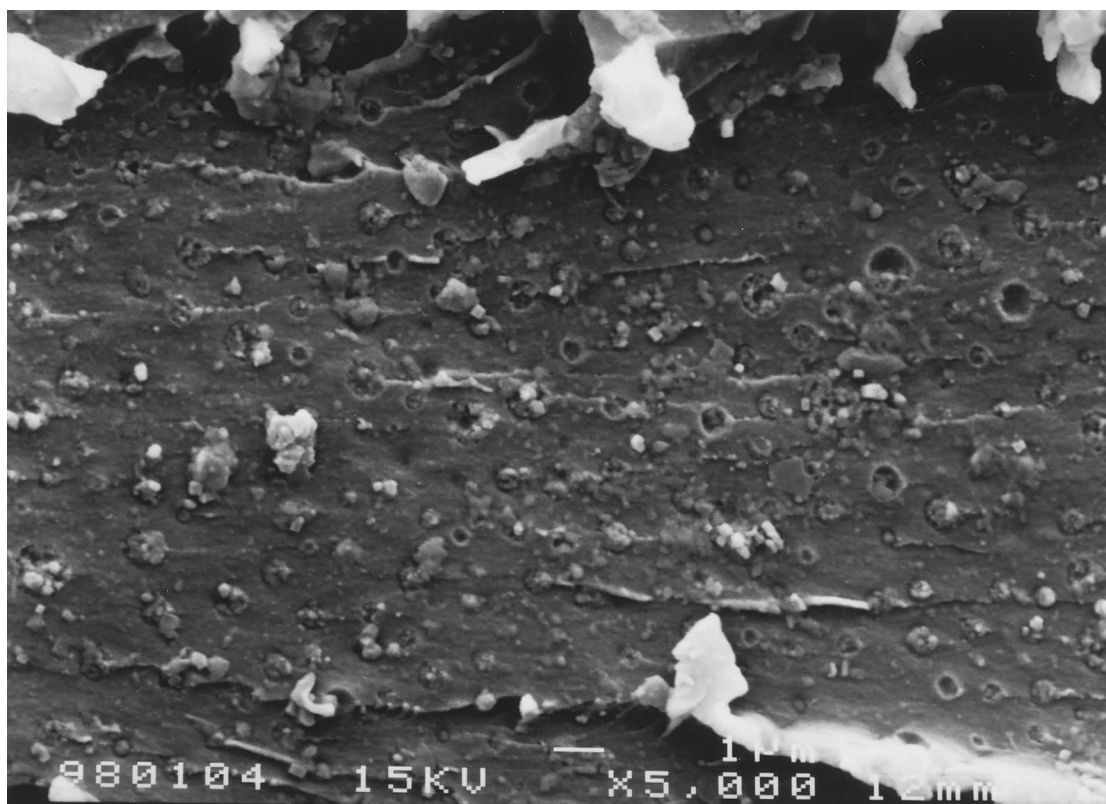


Fig. 4. SEM micrograph of DCBA/PSU (15 wt% PSU) precured at 160°C.

- The final morphology of these thermosetting mixtures is clearly influenced by the precured temperature: at 160°C the microstructure is a particulated microstructure while at 180°C a dual-phase morphology is observed.
- AFM has proved to be a powerful and simple tool for the characterisation of polymer mixture morphology. Besides, this technique allows selecting the appropriate modes to suit the material under examination and the properties of interest. The resolution obtained with AFM technique can be superior to that observed in SEM.

Acknowledgements

The authors would like to acknowledge the Diputación Foral de Gipuzkoa and CICYT MAT95-0701 for their generous support for the development of this work.

References

- [1] Hamerton I. Chemistry and technology of cyanate ester resins. Glasgow, UK: Blackie Academic, 1994.
- [2] Lee BK, Kim SC. *Polym Adv Tech* 1995;6:402.
- [3] Hedrick JC, Hedrick JL, Cecere JA, Liptak SC, McGrath JE. *ACS (PMSE)* 1990;63:190.
- [4] Pearson RA, Yee AF. *ACS (PMSE)* 1990;63:311.
- [5] Mondragon I, Remiro PM, Martin MD, Valea A, Franco M, Bellenger V. *Polym Int* 1998;47:152.
- [6] Fang T, Shimp DA. *Prog Polym Sci* 1995;20:61.
- [7] McEvoy RL, Krame S, Wu P. *Polymer* 1998;39:5223.
- [8] Huang Y, Yang YQ, Petermann J. *Polymer* 1998;39:5301.
- [9] Hobbs JK, McMaster TJ, Miles MJ, Barham PJ. *Polymer* 1998;39:2437.
- [10] Stocker W, Schumacher M, Graff S, Thierry A, Wittmann JC, Lotz B. *Macromolecules* 1998;31:807.
- [11] Kelley TW, Schorr PA, Johnson KD, Tirrell M, Frisbie CD. *Macromolecules* 1998;31:4297.
- [12] Ivanov DA, Jonas AM. *Macromolecules* 1998;31:4546.
- [13] Harismendy I, Gomez C, Ormaetxea M, Martin MD, Eceiza A, Mondragon I. *J Polym Mater* 1997;14:317.

- [14] Bashford D. Thermoplastics directory and databook. London, UK: Chapman and Hall, 1997.
- [15] MultiMode[®] Scanning probe microscope instruction manual. Digital Instruments 1997.
- [16] Sue HJ, Garcia-Meitin EI, Pickelman DM, Yang PC. In: Riew CK, Kinloch AJ, editors. Toughened plastic, ACS Series 233, 1993. p. 259.
- [17] Quian JY, Pearson RA, Dimonie VL, Shaffer OL, El-Aasser MS. *Polymer* 1997;38:21.
- [18] Kinloch AJ, Shaw SJ, Tod DA, Hunston DL. *Polymer* 1983;24:1341.
- [19] Huang Y, Hunston DL, Kinloch AJ, Riew CK. In: Riew CK, Kinloch AJ, editors. Toughened plastic, ACS Series 233, 1993. p. 259.
- [20] Oyanguren PA, Riccardi CC, Williams RJJ, Mondragon I. *J Polym Sci: Part B: Polym Phys* 1998;36:1349.
- [21] Inoue T. *Prog Polym Sci* 1995;20:119.