

PI-*b*-PMMA diblock copolymers: Nanostructure development in thin films and nanostructuring of epoxy thermosetting systems

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A diblock copolymer is a polymer which consists of two sequences of monomer units of different chemical composition covalently bonded. Due to the thermodynamic incompatibility between the blocks, they can self-assemble in a wide variety of nanostructures because the connectivity of the blocks by covalent linkage prevents the phase separation to take place at macroscopic scale [1-2].

For nanostructuring thin films of block copolymers different techniques, such as thermal or solvent vapour annealing, graphoepitaxy or epitaxial growth, etc, can be used.

On the other hand, many research studies on the formation of ordered nanostructures in epoxy thermosets containing diblock and triblock copolymers can be found in the literature [3, 4]. Interesting properties are expected in the case of composite materials based on matrices nanostructured with block copolymers that can be used for selective placement of different nanoparticles or for the generation of templates or nanopatterns.

The aim of this work is, from one side, to obtain nanostructured thin films of PI-*b*-PMMA diblock copolymers (specified in Table 1) by both thermal and solvent vapour annealing, analyzing different morphologies obtained for different copolymer compositions and annealing methods. On the other side, the second aim is to nanostructure an epoxy thermosetting system with different Pi-*b*-PMMA amounts, analyzing its effect on obtained morphologies and dynamic-mechanical properties.

Table 1. Diblock copolymer specification

	M_{nPI}	M_{nPMMA}	M_{ntot}	M_w	f_{PI}	I
A	17000	60500	77500	93000	22	1.2
B	31800	48000	79800	86200	52	1.08

Figure 1 shows morphologies obtained for copolymer A and B thin films after thermal annealing as obtained by atomic force microscopy (AFM). Copolymer A does not assemble into nanoordered morphology, microseparating into a worm-like nanostructure, without any ordered orientation. For copolymer B, a lamellar nanostructure can be observed.



Figure 1. AFM phase images of copolymer A and B thin films after thermal annealing

On the other hand, for solvent vapour annealing treatment, acetone has been used as selective solvent for PMMA block. Figure 2 shows morphologies obtained for copolymer A and B thin films after solvent vapour annealing as obtained by AFM.

A cylindrical morphology oriented perpendicularly to the substrate can be observed for copolymer A, where the cylinders are packed hexagonally. For copolymer B, a cylindrical nanostructure has been also

observed. If this structure is compared to the hexagonally packing structure of the copolymer A the difference is the diameter of cylinders that increases with PI content.

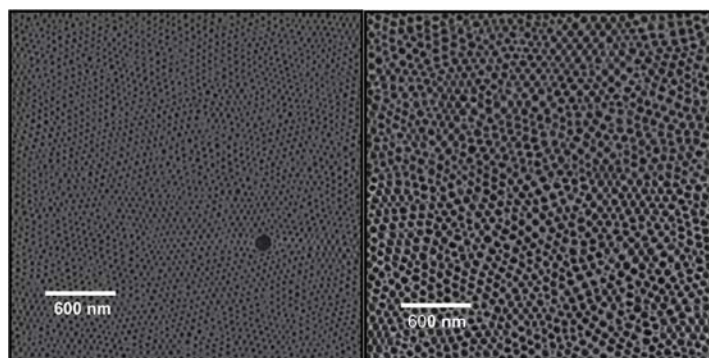


Figure 2. AFM phase images of copolymer A and B thin films after solvent vapour annealing

On the other hand, A copolymer has also been used for nanostructuring a DGEBA/MCDEA thermosetting system. In Figure 3, morphologies obtained after curing can be seen, for different copolymer amounts.

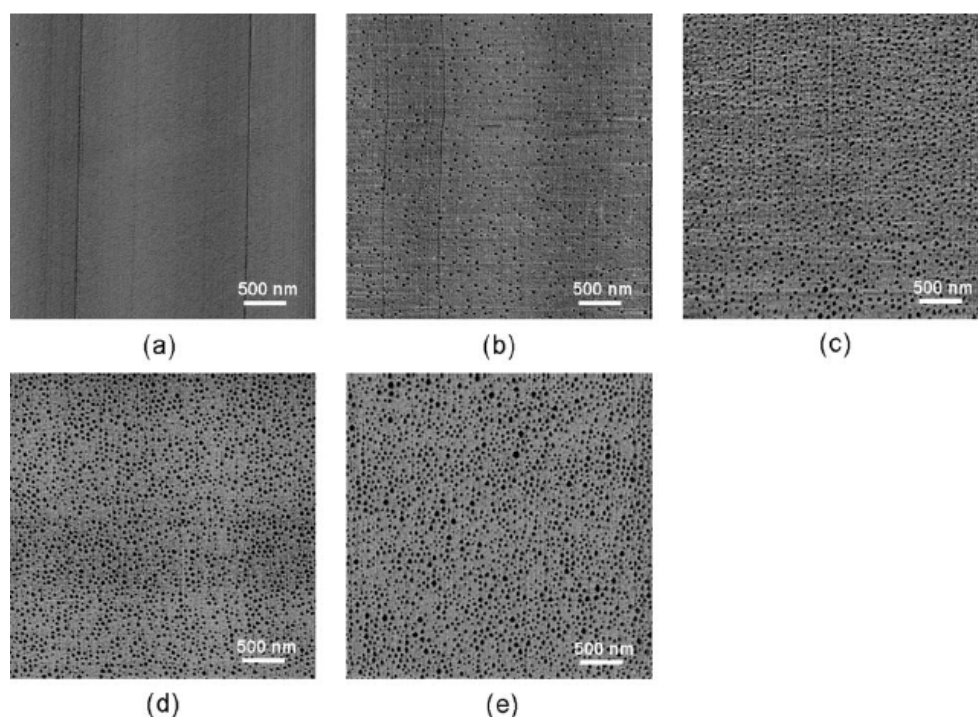


Figure 3. Morphologies obtained for DGEBA/MCDEA systems modified with different amounts of A copolymer: (a) 0, (b) 5 wt%, (c) 10 wt%, (d) 20 wt% and (e) 30 wt%.

PI-*b*-PMMA forms microphase-separated domains dispersed in a continuous crosslinked epoxy matrix where PMMA subchains remain miscible. The spherical-shaped micelle nanodomains are ascribed to PI chains. It has to be noted that the number and the size of spherical nanodomains, and consequently the volume fraction of the separated phase increases with increasing PI-*b*-PMMA content but the nanostructure does not shift from spherical micelles to any other morphology.

References

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