

Electron microscopy of macroporous cellulose (acetate-co-butyrate)-polycarbonate semi-interpenetrating networks

B. Décamps¹ (✉), E. Leroy¹, J.L. Pastol², J. Laskar³, D. Teyssié³, N. Lacoudre⁴, V. Lalanne¹, S. Boileau⁴

¹ Laboratoire de Chimie Métallurgique des Terres Rares, UPR 209 du CNRS, 2-8 rue Henri Dunant, 94320 Thiais, France.

² Centre d'Etudes de Chimie Métallurgique, UPR 2801 du CNRS, 15 rue Georges Urbain, 94407 Vitry-sur-Seine, France.

³ Laboratoire de Recherche de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay-Lussac, Neuville sur Oise, 95031 Cergy-Pontoise Cedex, France.

⁴ Laboratoire de Recherche sur les Polymères, UMR 7581 du CNRS, 2-8 rue Henri Dunant, 94320 Thiais, France.

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Summary

Semi-interpenetrating polymer networks, s-IPNs, were prepared from cellulose acetate-co-butyrate (CAB), still containing 46% OH groups, and diethylene glycol bis allylcarbonate (CR39) which was crosslinked by free-radical polymerization initiated by benzoyl peroxide. Microstructure of s-IPNs (CAB/CR39) of relative weight proportions between 0.2/1 and 0.4/1 was examined by electron microscopy (TEM and SEM). Spheroidal compact objects of several μm diameter are randomly distributed within a microporous phase in which the pore connectivity was shown by density measurements. Such a microstructure is consistent with the formation of CAB polymer dispersed phase in a poly (CR39) network continuous phase.

Keywords:

Cellulose derivatives, polycarbonate, semi-interpenetrating networks (s-IPNs), macroporous structures, TEM, SEM.

Introduction.

Interpenetrating polymer networks, IPNs, are combinations of crosslinked polymers held together by permanent entanglements [1] [2]. Due to their interlocking configuration, the state of phase separation obtained at the end of their synthesis is frozen so that the miscibility of the polymers is increased compared to that of classical blends and a good dimensional stability of the resulting materials is observed. The aim for preparing such types of polymeric associations is to improve their mechanical properties and their resistance to degradation and eventually to obtain a synergy of the properties of both partners. The s-IPNs differ from the IPNs in that they are composed

of a non-crosslinked polymer embedded into another polymer network. Few s-IPNs based on CR39 are described. Poly(CR39)/PMMA IPNs were investigated [3], and phase separation was found to occur between the two polymers [4]. On the other hand, most of the described IPN type materials based on cellulose derivatives are hydrogels. Poly(CR39)/polysiloxane s-IPNs and IPNs were elaborated in order to obtain systems in which the drug delivery would be under chemical control, i.e. a pH-mediated hydrolysis, in view of preparing a therapeutic lens model [5] [6]. IPNs from "PAMAMOS" dendrimers and CAB networks were prepared in order to improve the mechanical properties of the dendrimer network without losing their metal salt complexing properties [7]. More recently, IPNs and s-IPNs based on CAB and poly(CR39) were synthesized and their mechanical properties were examined [8]. In the present work, the combination of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with density measurements was used to study the microstructure of CAB/poly(CR39) IPN type materials.

Experimental.

Network synthesis.

Single poly(CR39) network was prepared by free-radical polymerization of CR39 with benzoyl peroxide (BPO) as the initiator (5% by weight) at 60°C for 1h and 80°C for 2h followed by a 2h curing at 100°C. S-IPNs were obtained without any solvent, by dissolving from 0.1 to 0.4g CAB into 1g CR39 containing 5% by weight BPO with respect to CR39. The mixtures were allowed to polymerize as described for single CR39 network. IPNs were obtained according to a procedure described previously [8]. The samples are prepared directly in pyramidal preshaped polyethylene moulds (BEEM® capsules) especially designed for the preparation of TEM samples by ultramicrotomy.

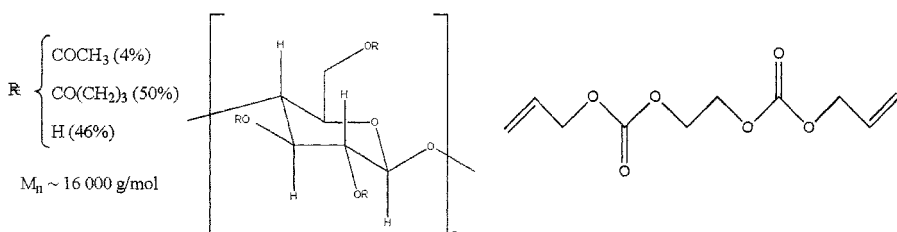


Figure 1. Formula of the precursors cellulose acetate-co-butylate (left) and diethylene glycol bis allylcarbonate (right).

Sample preparation for electron microscopy.

The samples were prepared at room temperature with a Reichert Om U2 ultramicrotome using a 35° diamond knife. The cuts are taken from the water surface and deposited on a 400 mesh copper grid. The thickness of the samples thus prepared was around 150 nm. For SEM observations, the samples are coated with a Pd/Pt conductive layer prior to the observation.

Electron Microscopy measurements.

The samples were observed by transmission electron microscopy using a JEOL 2000FX apparatus at 200 kV, and by scanning electron microscopy on a LEO 1530 apparatus at 3 kV. No staining treatment was applied prior to the TEM observation. The same samples were observed by both techniques.

Density measurements.

Density measurements were performed by pycnometry with helium pressure, using a Micromeritics apparatus. The results are given in Table 1.

CAB content (Per g of CR39)	% CAB/CR39 (w/w)	Maximal spheroid size (μm)	Density (25°C) (measured)	Density (25°C) (calculated*)
0.2	16	4	1.295	1.298
0.3	23	3	1.281	1.291
0.4	28	2	1.279	1.285

Table 1: Characteristics of samples. * calculated from the non-crosslinked CAB (1.208) and CR39 single network (1.316) densities.

Results and discussion.

Single networks as well as IPNs are transparent whereas all the s-IPNs are opaque. As expected, continuous films exhibiting a uniform contrast are observed by TEM for single networks. The observations are similar for true IPNs, which could arise from the deliberate absence of specific staining agent and/or a very small size of the domains. This prompted us to focus our attention on s-IPNs in which the size of the domains is higher than 150nm.

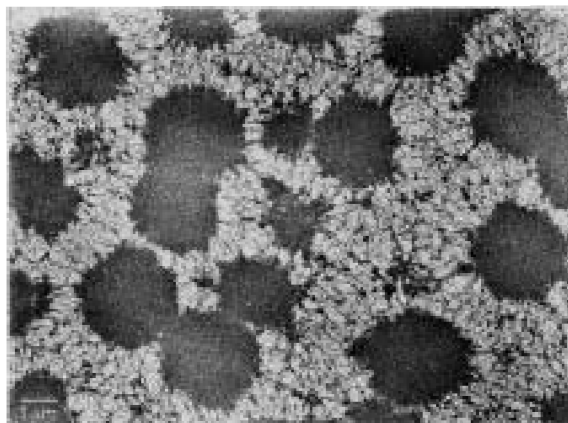


Figure 2. TEM micrograph of s-IPN CAB/CR39 0.3/1.

The TEM observations for all compositions (only micrographs of CAB/CR39 0.3/1 and 0.4/1 s-IPNs are displayed in this paper) reveal some contrast despite the fact that the samples are not stained as shown in figures 2 and 3. The samples are composed of

two phases: one phase exhibiting a dark and uniform gray level surrounded by a second non-uniform phase. Figure 2 reveals clearly the porosity of the continuous phase. In figure 3 left, two scratches caused by the cutting process can be observed. The shape of the uniform phase is roughly circular while the interstitial phase appears to have a constantly changing shape and density. Since the samples are consisting of a uniform cut of randomly distributed objects, the two-dimensional observation can be extrapolated to the three-dimensional shape distribution of the objects. Thus, we can assume that the uniform phase is made of spheroids. An evolution of the uniform phase upon the composition is observed: by increasing the CAB content the size decreases and the circularity is less marked. The maximum size of the spheroids is reported in table 1. It is noteworthy that the size regularly decreases with the increase of CAB content. In TEM, image contrast between phases is generally poor in unstained polymers because the low atomic number elements involved in polymers produce little electron scattering. In our case, the origin of the contrast may be explained by the difference of the material density in the different regions of the sample as ultramicrotomy cuts are of equal thickness as mentioned above. We can expect that the uniform phase will be a compact phase and the non-uniform phase a porous material.

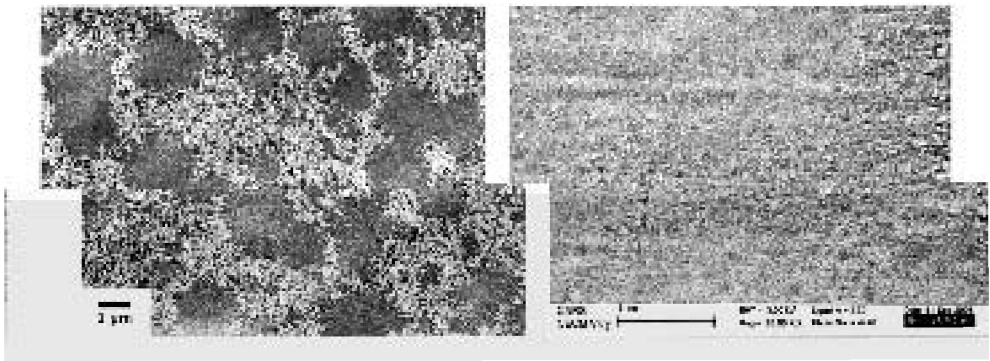


Figure 3. TEM micrograph of s-IPN CAB/CR39 0.4/1 (left). SEM micrograph of s-IPN CAB/CR39 0.3/1 (right).

To validate our hypothesis, SEM experiments were performed to have access to the sample roughness. The secondary electron images recorded for the different samples confirm the porous character of the continuous phase. An example is given in figure 3 right. The pore mean size is lower than 150 nm, which is the thickness of the TEM specimens. This fact proves that the pores do not extend throughout the entire foil, so in the porous region, the sample is composed of a random mixture of matter and pores. This explains perfectly the observed TEM contrasts of the porous phase and the torn region. From these two experiments, no conclusions can be drawn concerning the connectivity of the pores. This is why density measurements were performed.

Concerning the density measurements, it may be noticed that they present an excellent agreement with the calculated values. This fact proves the connectivity of the pores for all compositions. Otherwise, the measured density of the macroporous material would be much lower as the helium (used for the measurements) would stay outside of the pores.

Such structures could be explained by the fact that although the CAB/ CR39 starting

mixture is homogeneous, a phase separation is observed during the polycarbonate network formation. The CAB tends to form spheres in which the coiled macromolecules are held together by hydrogen bonds. The size of those spheres, the maximum diameter of which is of a few micrometers, is large enough to explain the opacity of the final material. The polycarbonate network elaboration occurs with some shrinkage, which could lead to microvoid formation responsible for the observed microporous structure. Indeed, the synthesis method of s-IPNs should lead to a poly(CR39) network continuous phase with a CAB polymer dispersed phase. Moreover, the thermomechanical properties of those s-IPNs are in good agreement with such a representation [8].

Conclusions.

In conclusion, a peculiar microstructure composed of spheroidal compact objects, the maximum diameter of which is of a few micrometers, randomly distributed within a macroporous phase has been evidenced by TEM, without the need for staining, on s-IPNs prepared from CAB and poly(CR39). In addition the pore connectivity in the macroporous phase has been shown by density measurements. Such microstructures are consistent with the formation of a CAB polymer dispersed phase in a poly(CR39) network continuous phase, assumed from the used synthesis method. A similar behavior is observed apparently for other s-IPNs systems based on CAB. More detailed results in this field will be published in the near future.

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