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Communications to the Editor

Bicontinuous Microfoams by Water-Induced Phase Separation in Poly(vinyl methyl ether)-*cross*-Polystyrene Semiinterpenetrating Networks

Introduction. Semiinterpenetrating (semi-IPN's) and interpenetrating (IPN's) polymer networks based on miscible polymer blends are receiving increasing attention.[1-7] Major points of interest are influences of cross-linking of one or both components on the phase diagram[1-5] and also the dynamics of phase separation. Another point is related to the orientational coupling between the two components in such a multicomponent material.[3] Cross-linking of one of the components allows the study of segmental orientation up to large deformations in uniaxial elongation. In addition, cross-linking provides a simple means to study the mechanical behavior in the glass-transition region over the whole composition range.[7] Other features of miscible semi-IPN's include the investigation of the relaxation of the free chains as a function of cross-link density and molecular weight of the free chain.

In the present communication we report the formation of bicontinuous microfoams starting from PVME-*cross*-PS semi-IPN's. Microfoam materials can show unconventional morphologies. The most recent work in the field has been developed by the groups of Keller[8] and Berghmans[9] by preparing glassy microfoams from PS solutions.

PVME-*cross*-PS semi-IPN's are prepared by reacting poly(styrene-*co*-maleic acid) copolymer P(S-*co*-MA) (about 4.8 mol % of MA units) with hexamethylenediamine (HMDA) in solution in the presence of PVME. A more detailed description of the synthesis is given elsewhere.[3,7] The synthesis of semi-IPN's starting from polymeric precursors rather than using cross-linking polymerization of styrene and divinylbenzene[2,10] has two major advantages.

S/DVB polymerization is known to result in heterogeneous networks; the formation of graft copolymer by radical abstraction of the tertiary hydrogen cannot be excluded. In addition, phase separation occurs at rather low levels of cross-linking.[2,6,10]

Experimental Section. Semi-IPN's of varying composition (0-90 wt % PVME) and cross-link density (1-4 mol % HMDA with respect to styrene repeating units) were prepared. Usually films of 0.1-0.3 mm thickness were prepared. After careful drying the samples were stored in a desiccator prior to use.

Swelling and Extraction. The swelling experiments in water were performed at 25 °C over a period of 4-5 mo, until no changes in the sample weight were detectable. Water was frequently exchanged to enhance the extraction rate by an osmotic pressure gradient.

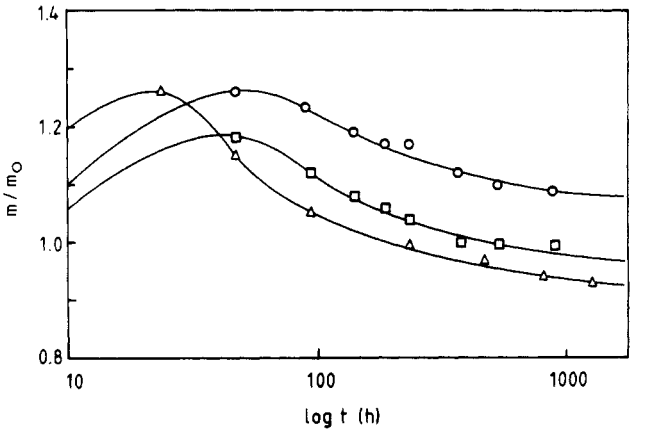

Figure 1. Change of the mass of PVME-*cross*-PS semi-IPN's with time upon swelling in water (T = 25 °C). Cross-link density: 4 mol % HMDA. The different symbols are related to different sample compositions. wt % PVME: ○, 60; △, 70; □, 80.

Electron Microscopy. The extracted samples were imbedded in EPON 812; ultrathin sections were obtained using a Reichert-Jung ultramicrotome (Ultracut E). A Zeiss 902 electron microscope, which allows element specific image analysis,[11] was used for the morphological studies. Both elastic bright field and element specific images from inelastically scattered electrons were made to cross-check the structural information.

Results. Homogeneous, single-phase networks are obtained at low levels of cross-linking (1 and 2 mol % of crosslinker).[7] Two glass transitions are observed for networks with a higher degree of cross-linking (3 and 4 mol %).[12] This clearly demonstrates the significant influence of cross-linking on the phase behavior. A more detailed study of these phenomena will be given elsewhere.[12]

Water easily penetrates into the PVME-*cross*-PS semi-IPN's due to the hydrophilicity of PVME and the low glass transition (despite for materials with a high PS content). The transparent semi-IPN's become opaque, indicating phase separation.

The overall process to be considered upon immersing the semi-IPN's in water includes swelling, phase separation (or further phase separation in the higher cross-linked samples), and extraction of free PVME chains.

While the observed turbidity clearly proves water-in-

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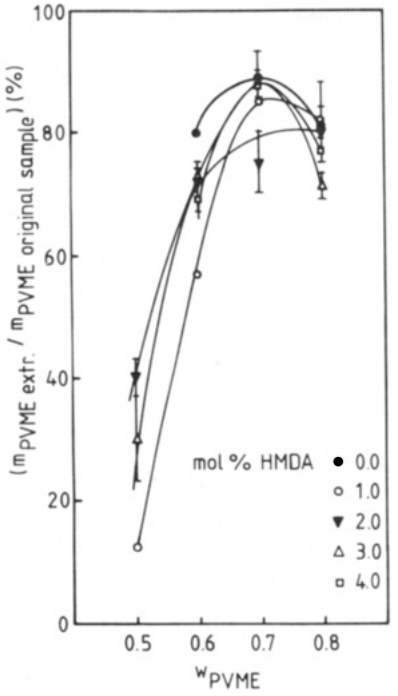

Figure 2. Fraction of PVME extractable from PVME-*cross*-PS semi-IPN's as function of original semi-IPN composition for different cross-link densities (mol % HMDA): ●, 0%; ○, 1%; ▽, 2%; △, 3%; □, 4%.

duced phase separation, the overall weight change of the sample is governed by two opposing effects. Swelling increases the sample mass, while diffusive extraction of free PVME chains reduces the hydrophilicity. As a consequence the overall mass (network + PVME + water) decreases. A typical result for 4% cross-linked material is shown in Figure 1, where the mass of samples with varying composition is plotted as a function of the exposure time (log t). A swelling maximum is observed after a relatively short time. Then the overall mass decreases and finally can be considerably lower than the mass of the starting material. These materials still contain large amounts of water, but the major part of PVME is extracted. Thus the hydrophilicity decreases, and the overall mass becomes lower than that of the starting material. Because of the similar densities of the components, the observed decrease in swelling must be related to a partial collapse of the network. The degree of this collapse depends on the initial composition and cross-link density. When the proper conditions are chosen, the final material may have the same dimensions as the original network. In Figure 2 the amount of PVME extractable from the semi-IPN's is shown as a function of the initial composition and cross-link density. At low PVME content (<40%) only a very small fraction of the PVME can be extracted from the network within a period of 4 mo, probably due to the fact that these materials are glassy at room temperature. Extraction at higher temperatures will be complicated by the LCST behavior of the PVME/water system. At higher PVME contents, the amount of extractable PVME strongly increases. For an initial PVME fraction of 70 wt %, about 80% of the PVME can be extracted from the network. For networks containing more PVME the extractable fraction slightly decreases. Structural differences in the formed phase-separated materials might be responsible for the observation of this maximum. After drying and subsequent annealing of the phase-separated networks at higher temperatures, only a single glass transition is observed. The final compositions either obtained by mass balance or estimated from the T_g/composition relation are in reasonable agreement.

For morphological studies the water in the swollen networks was exchanged with a water-soluble curable resin (EPON), which is frequently used for preparation of biological samples. After curing ultrathin sections were obtained. In Figure 3 electron micrographs are shown for two networks containing originally 70 wt % of PVME at two different cross-link densities (1 and 4 mol % HMDA).

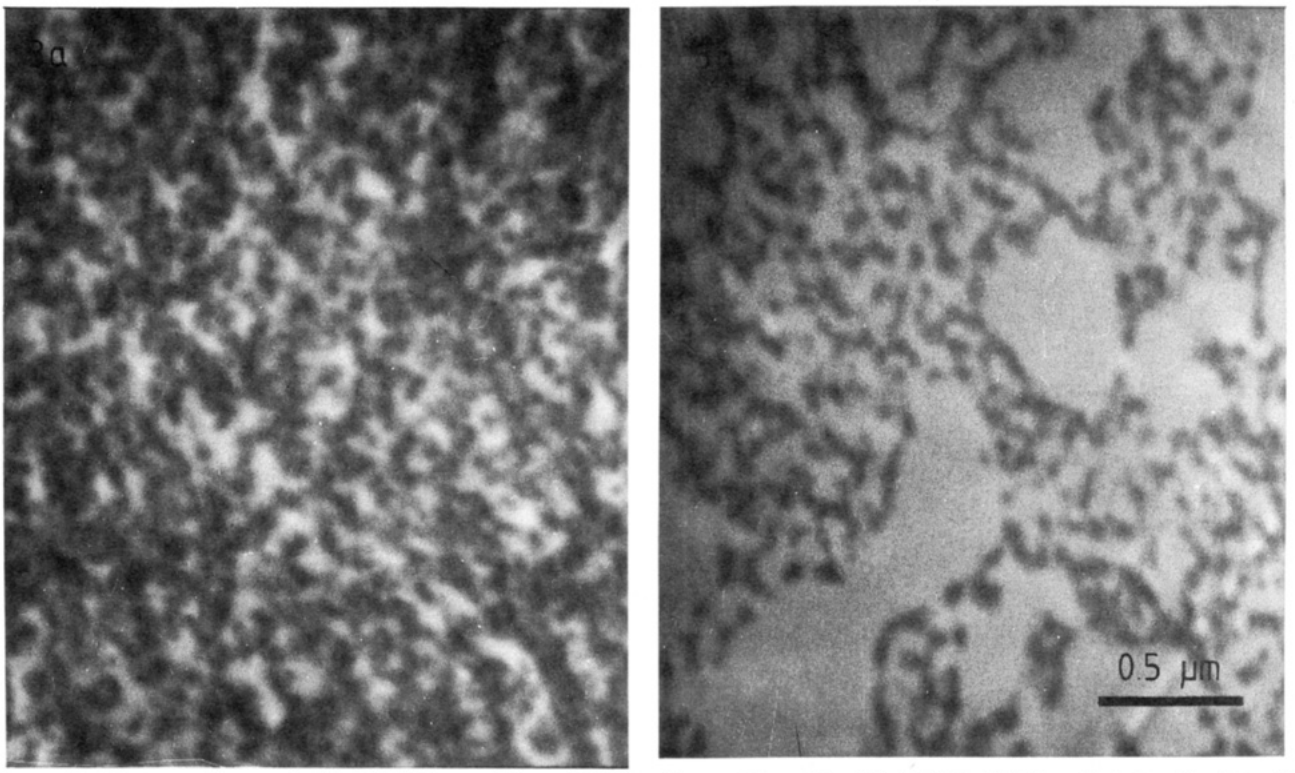

Figure 3. Electron micrographs for PVME-*cross*-PS semi-IPN's. Composition: 70 wt % PVME. (a) Cross-link density: 1 mol %. (b) Cross-link density: 4 mol %.

At high vacuum and by the action of the electron beam, the epoxy resin is degraded, giving rise to the observed contrast without additional staining. The PS is black while the original holes of the microfoam are light. For the weakly cross-linked network the starting material was homogeneous, while the semi-IPN with higher cross-link density already was phase separated. In the first case a finely dispersed bicontinuous structure with average dimensions of about 50 nm is observed, while in the case of the phase-separated starting material larger holes on the order of 500–1000 nm as well as the finely dispersed structure is observed. Dynamic mechanical analysis of the phase-separated semi-IPN shows a sharp loss maximum, which corresponds to "pure" PVME and a broad second relaxation maximum arising from the PS-rich phase but still contains considerable amounts of PVME.[12] Extraction of the PVME in these phase-separated systems is only possible if the phase-separated structure already is bicontinuous (on the large length scale) or if the PS-rich phase undergoes spinodal-like phase separation, providing the necessary channels for material transport. According to the morphological picture given in Figure 3b, both situations may occur simultaneously. The morphological features give strong support to spinodal-like phase separation induced by the interaction of water with homogeneous semi-IPN's. Preliminary permeation studies show that such bicontinuous microfoams may have interesting properties as barrier materials. The generation of microfoams via solvent-induced phase separation of miscible polymer system provides unique possibilities for structural control in such materials.

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Registry No. (S)(MA)(HMDA) (copolymer), 41497-14-7; PVME, 9003-09-2.

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Structural Changes of Native Cellulose Crystals Induced by Annealing in Aqueous Alkaline and Acidic Solutions at High Temperatures

In the previous paper[1] we have reported on the basis of cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR analyses that native cellulose crystals, which may be roughly classified into cotton–ramie type (cellulose I_a) and bacterial–valonia type (cellulose I_b),[2,3] are transformed into a new type of crystals by annealing above 260 °C with saturated steam. Since the CP/MAS ^{13}C NMR spectrum of the new type of crystals is very close to that of cellulose I_a, we refer to these crystals as cellulose I_a'. Although the same crystal transformation was also observed for the cases of the regenerations from cellulose triacetate I[4] and cellulose III_1,[5] the degree of crystallinity significantly decreases and the morphology of the microfibrils seems to undergo appreciable changes in these two cases. In contrast, the annealing with saturated steam induces almost no change in crystallinity[1] and the preliminary electron microscopic observation has also revealed no significant change in the morphological structure of the microfibrils. Therefore, the examination of the transformation process induced by this annealing will lead to better understanding of the crystal structure of native cellulose. In particular, the detailed comparison of the crystal structures of intact and annealed valonia celluloses seems to provide an important clue to solve the controversial problems[3] related to a new proposal that native cellulose crystals are a composite of two allomorphs,[6,7] because both samples are highly crystalline and the ordering in crystals is also very high.

In this annealing, we used glass fiber sheets to put each sample between them and to anneal it in the vapor phase without the contact with the liquid phase.[1] However, the glass fiber sheets have been found to play an unexpected important role in preventing the decomposition of the cellulose samples, because the vigorous decomposition of cellulose occurs without them at high temperatures. Since the dissociation of H_2O is greatly enhanced at high temperatures,[8] the increase of H ions, which may promote the decomposition reaction, will be suppressed by the glass fiber sheets. In order to find better annealing conditions, we have investigated annealing effects of native cellulose samples in different aqueous alkaline and acidic solutions at high temperatures. In this paper we report that the same transformation of valonia and cotton cellulose crystals as previously reported is reproduced by annealing in 0.1 N NaOH aqueous solution above 260 °C without the decomposition. The annealing effect of tunicate cellulose is also reported for comparison.

Valonia macrophysa, cotton, and tunicate celluloses, which were purified by the conventional method, were subjected to annealing in different aqueous NaOH or HCl solutions at 220–280 °C for 30 min. After it was washed with deionized water, each sample was packed in a MAS rotor with an O-ring seal together with an appropriate amount of deionized water. CP/MAS ^{13}C NMR mea-

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