Upper limit of grafting conversion and phase homogeneity: cellulose acetate/poly(styrene-*co*-maleic anhydride) grafting reaction system

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Reactive polymers each bearing large numbers of reactive groups are important for new compatibilized blends with the graft copolymers generated *in situ*. Potential of gelation and phase homogeneity are two important issues. A case study on cellulose acetate and poly(styrene-*co*-maleic anhydride) (SMA) was reported here to demonstrate the two issues. It was found that phase homogeneity appears when the grafting conversion of SMA exceeds around 50% for the dispersed SMA phase. There is a relatively narrow range of SMA grafting conversion for the formation of compatibilized ternary mixtures with a homogeneous phase size and a reasonable weight-average molecular weight. The study shows the importance of polydispersity in promoting phase homogeneity due to the weighting towards more grafting of higher-molecular-weight fraction of the reactive polymers.

(Keywords: solubilization; phase homogeneity; polymer blends)

INTRODUCTION

The presence of graft copolymers in immiscible blends can result in compatibilized blends. The graft copolymers can be produced *in situ* by solution grafting or reactive extrusion. Coupling two reactive polymers is one of the ways to synthesize graft copolymers to form a compatibilized blend. The availability of more and more functional polymers, whether they are made by copolymerization or chemical modification, provides new opportunities to make new alloys by coupling two reactive polymers[1-3]. A different approach has been graft polymerization, commonly by a free-radical process[4,5].

It happens that the numbers of reactive groups are numerous for a variety of reactive polymers. For a grafting system with these reactive polymers, the complexity of the graft copolymers grows as the grafting reaction continues, and gelation occurs when the extent of grafting reaction goes beyond a certain limit. It is therefore necessary to stop the grafting reaction at some point if gelation is not desirable. Another important issue is the phase size and phase homogeneity of the ternary blends. The materials properties, such as mechanical properties, transport properties, optical properties, etc., depend very much on phase size and phase homogeneity. The amount and the structure of the graft copolymers play a major role in that regard. One good example is the influence on the impact[6] and optical properties of rubber-modified polystyrene[7]. At high content of graft copolymers, phase homogeneity is a reflection of the solubility of ungrafted polymers into the corresponding chain segments of the graft copolymers.

It was concluded from early studies[8-13] that the homopolymer molecular weight must be less than or equal to that of the corresponding chain segment of the block copolymer for solubilization to occur, but a certain amount of solubilization occurs even at higher molecular weights of the homopolymers. Further studies[14] indicate that the power of solubilization of copolymers for homopolymers has the sequence diblock > triblock > four-arm block when the molecular weights of the block chains are close to each other. There was also a report on the solubilization behaviour with the so-called AB-cross-linked copolymers (ABCP)[15,16] of relatively complicated structure. Very limited solubilization of homopolymer into the microdomains of ABCP was observed. These studies point out the importance of the structures of the copolymers. Recent studies suggest that there are certain degrees of demixing between the chain segment of graft copolymers and the solubilized homopolymers within the microdomains, even with homogeneous solubilization[17-20].

At the same molecular weight of the chain segment, graft copolymers are often viewed as having less solubilizing ability for homopolymers than block copolymers. At low grafting conversion, i.e. <10 wt% graft copolymers in the products, the graft copolymers can function as a compatibilizer. The complexity of the structures of the graft copolymers grows as more and more graft copolymers are being produced during the grafting reaction. The net result is the reduction of the

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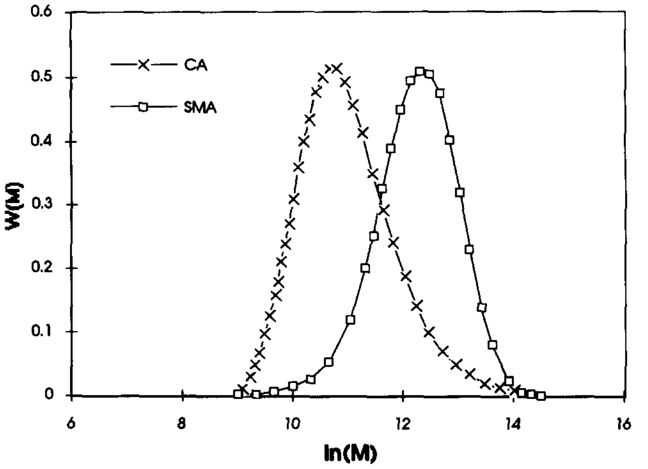

Figure 1 Molecular weight distributions of CA and SMA

effective chain length of the homopolymer chain segments of the graft copolymers. On the other hand, the reactive polymers are often highly polydisperse. It is important to look carefully at the effect of polydispersity in such grafting systems. Given the uncertainty in such a grafting system of the phase homogeneity due to the complexity of the graft copolymers, it is important to look at the change of phase size and homogeneity with the amount of graft copolymers produced in the grafting process, particularly at high content of graft copolymers.

In this paper we report on a practical grafting system of cellulose acetate–poly(styrene-*co*-maleic anhydride) (CA–SMA), our studies on the upper limit of grafting conversion of homopolymers to copolymers and the change of phase size and phase homogeneity with the amount of graft copolymers generated in the system. We would like to point out that there is a relatively narrow range of SMA grafting conversion for the formation of compatibilized blends with homogeneous phase size and a reasonable weight-average molecular weight. We would like to mention the importance of polydispersities of the reactive polymers in promoting a homogeneous phase size at high content of graft copolymers.

EXPERIMENTAL

Materials

CA (degree of substitution 2.45, M_w 102 000, M_n 46 000, PDI 2.21) was provided by Courtaulds plc. SMA (7.08 wt% maleic anhydride, M_w 249 000, M_n 126 000, PDI 1.97) was provided by ARCO Chemical Company. Both CA and SMA are commercially available. The molecular weight averages of CA and SMA were obtained from gel-permeation chromatography analysis provided by Viscotek Corp. There are on number-average 85 hydroxyls per CA chain and 90 anhydrides per SMA chain.

Grafting reaction

The grafting reactions were carried out in anhydrous dimethyl formamide (DMF) solutions at increased temperature with the aid of a catalyst and strong stirring. At a polymer concentration of 10 (wt%), the reaction solution is heterogeneous at the beginning, turning clear as more and more graft copolymers are formed. The reaction between the hydroxyls on the CA chain and the anhydrides on the SMA chain leads to the formation of graft copolymers. The reaction products were obtained by precipitating with water. Details on the grafting reaction will be shown elsewhere[21].

Characterization of grafting reaction products

The grafting conversion of SMA was obtained by Soxhlet extraction with toluene since the graft copolymers are not extracted. No appropriate solvent was found that extracts ungrafted CA only. The grafting reaction products were prepared at two CA–SMA compositions (CA:SMA = 1:1 and 3:1) with different grafting conversion of SMA. The grafting conversions of SMA and CA are related to each other by

$$f_{\mathrm{CA}}^{\mathrm{w}} = f_{\mathrm{SMA}}^{\mathrm{w}} \frac{1 - \int_0^\infty (1 - f_{\mathrm{ref}})^{\bar{M}/x} W_{\mathrm{CA}}(M)\,\mathrm{d}M}{1 - \int_0^\infty (1 - f_{\mathrm{ref}})^{\bar{M}} W_{\mathrm{SMA}}(M)\,\mathrm{d}M} \tag{1}$$

$$\bar{M} = M/\bar{M}_{\mathrm{n}}^{0} \tag{2}$$

where $W(M)$ is the weight fraction density function of molecular weight distribution, x is the molar ratio of CA/SMA, and f_{ref} is the grafting conversion of the reference SMA chains having a molecular weight of the number-average molecular weight of the starting SMA. Equation (1) is obtained under the assumption of homogeneous grafting reaction and large numbers of reactive groups on the reactive polymers. *Figure 1* shows the weight-fraction distribution function of CA and the weight-fraction distribution function of SMA using gel-permeation chromatography. *Figure 2* shows the relationship between the grafting conversion of CA and the grafting conversion of SMA at two compositions. It is important to note that the percentage conversion of CA is less than that of SMA. Heterogeneity at the early stage of grafting reaction will have some effect on equation (1), but it should not change the result of less percentage conversion of CA than of SMA.

Gel-permeation chromatography analyses were performed to obtain the molecular weight averages. The universal calibration method was used on the Viscotek 200. The column is a Plgel 20 μm mixed Å with a separation capacity of 1 k to 40 M. The standards for calibration are narrow molecular weight polystyrenes. Tetrahydrofuran (THF) was the carrier.

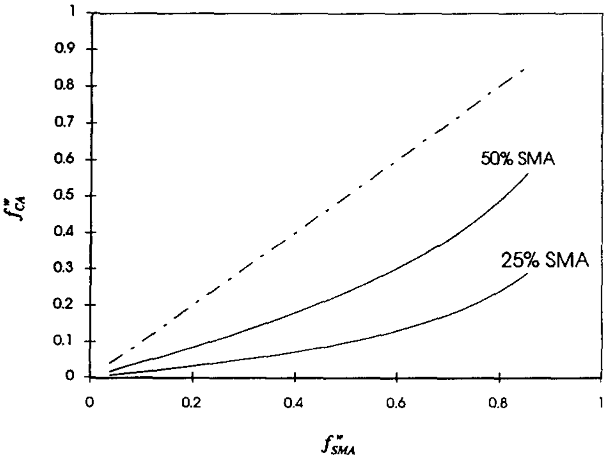

Figure 2 The grafting conversion of CA *versus* the grafting conversion of SMA

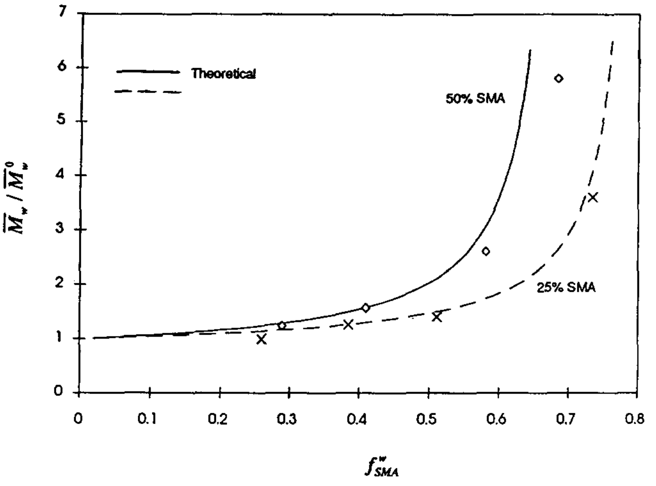

Figure 3 Reduced *WAMW versus* the grafting conversion of SMA

Sample preparation

Cast films for TEM study were prepared by fast evaporation of solvent at room temperature and 50–70°C (0.8–1.0 g/10 ml). The reaction products were dissolved in a near non-selective tetrahydrofuran–water mixture solvent and a strongly selective acetone–water mixture solvent. The solutions were stirred for 2 days before casting. A small amount of water is added to reduce the solution viscosity. Acetone and THF containing 4% water are good for reducing the solution viscosity.

Electron microscopy

Phase size and phase homogeneity of the film samples were studied by transmission electron microscopy (TEM). Phase contrast develops after the ultrathin sections were exposed to the electron beam for a few seconds. Staining is not required for this system. Sections of silver colour (60–90 nm) were ultramicrotomed at room temperature. TEM studies were performed on a JEOL 100CX transmission electron microscope at 80 kV.

RESULTS AND DISCUSSION

Weight-average molecular weight (WAMW) *of the reaction products*

The simplest graft copolymers are statistical assemblies of graft copolymers with graft linkages from end-to-end block linkage to symmetric star linkage. The complexity of graft copolymers grows with grafting conversion. Gelation occurs when the grafting reaction goes beyond a certain limit. Theoretical analyses on the molecular characteristics of the grafting reaction products (in a broad sense) were given elsewhere[22]. The practical limit on the grafting conversion of SMA is seen from the weight-average molecular weight (control parameter on viscosity) of the reaction products. In the assumed homogeneous reaction system with no consideration of intramolecular reaction, the reduced weight-average molecular weight of the reaction product satisfies

$$\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{w}}^{0}}=\frac{1+x\dfrac{\bar{M}^{0}_{\mathrm{wCA}}}{\bar{M}^{0}_{\mathrm{wSMA}}}\dfrac{\bar{M}^{0}_{\mathrm{nCA}}}{\bar{M}^{0}_{\mathrm{nSMA}}}+2E\dfrac{\bar{M}^{0}_{\mathrm{wSCA}}}{\bar{M}^{0}_{\mathrm{nSMA}}}}{\left(1+x\dfrac{\bar{M}^{0}_{\mathrm{wCA}}}{\bar{M}^{0}_{\mathrm{wSMA}}}\dfrac{\bar{M}^{0}_{\mathrm{nCA}}}{\bar{M}^{0}_{\mathrm{nSMA}}}\right)\left(1-\dfrac{E^{2}}{x}\dfrac{\bar{M}^{0}_{\mathrm{wSMA}}}{\bar{M}^{0}_{\mathrm{nSMA}}}\dfrac{\bar{M}^{0}_{\mathrm{wCA}}}{\bar{M}^{0}_{\mathrm{nCA}}}\right)}\qquad(3)$$

$$E=-\ln(1-f_{\mathrm{ref}})\qquad(4)$$

$$f^{\mathrm{W}}_{\mathrm{SMA}}=1-\int_{0}^{\infty}(1-f_{\mathrm{ref}})^{\bar{M}}W_{\mathrm{SMA}}(M)\,\mathrm{d}M\qquad(5)$$

Figure 3 shows the theoretical prediction and experimental prediction and experimental results at two compositions. *WAMW* rises quickly after the grafting conversion of SMA goes beyond a certain limit: ~60% for a half amount of SMA and ~70% for a quarter amount of SMA. There is, therefore, a practical limit on the grafting conversion of SMA in order to avoid too high a *WAMW* for the system.

Greater grafting conversion of high-molecular-weight chain fraction of the reactive polymers

The formation of complex graft copolymers of such a grafting reaction system has the net effect of reducing the effective chain length of the grafted chain segments. On the other hand, the grafting reaction happens with more grafting conversion of higher-molecular-weight chain fraction of the reactive polymers. In a homogeneous state, the grafting conversions between two chain fractions having molecular weights of M_i and M_j (CA or SMA) satisfy

$$1-f_{M_i}=(1-f_{M_j})^{M_i/M_j}\qquad(6)$$

This is because the numbers of reactive groups on the chain are proportional to the chain length. We can look at the effect of polydispersity in increasing the effective chain length of the graft copolymers by comparing the number-average molecular weight of the free chains to that of the chains on the graft copolymers, both CA and SMA. The number-average molecular weights for the free SMA and the grafted SMA are calculated by

$$(\bar{M}^{\mathrm{f}}_{\mathrm{n}})_{\mathrm{SMA}}=\frac{\int_0^\infty(1-f_{\mathrm{ref}})^{\bar{M}}W(M)\,\mathrm{d}M}{\int_0^\infty(1-f_{\mathrm{ref}})^{\bar{M}}W(M)/M\,\mathrm{d}M}\qquad(7)$$

$$(\bar{M}^{\mathrm{g}}_{\mathrm{n}})_{\mathrm{SMA}}=\frac{\int_0^\infty[1-(1-f_{\mathrm{ref}})^{\bar{M}}]W(M)\,\mathrm{d}M}{\int_0^\infty[1-(1-f_{\mathrm{ref}})^{\bar{M}}]W(M)/M\,\mathrm{d}M}\qquad(8)$$

The ratio of the number-average molecular weights of the grafted SMA chains to the free SMA chains is defined as

$$R=\frac{(\bar{M}^{\mathrm{g}}_{\mathrm{n}})_{\mathrm{SMA}}}{(\bar{M}^{\mathrm{f}}_{\mathrm{n}})_{\mathrm{SMA}}}\qquad(9)$$

Figure 4 shows the changes of the number-average

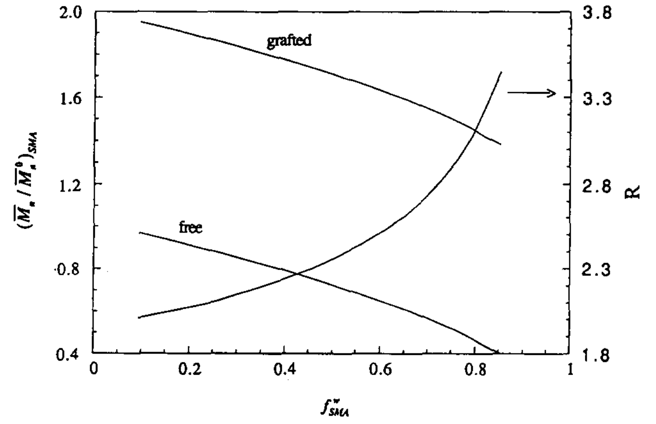

Figure 4 Change of the number-average molecular weights for the grafted and ungrafted SMA chains as well as the ratio of the two with grafting conversion

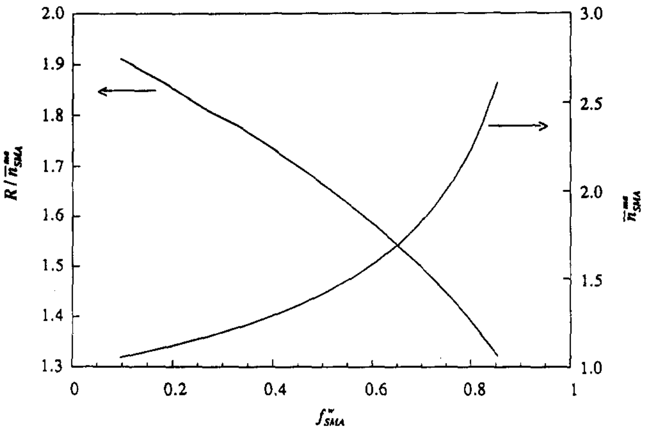

Figure 5 Change of the ratio of the effective number-average molecular weight of the grafted SMA chains to that of the free SMA chains with the grafting conversion of SMA

molecular weights of the free SMA chains and the grafted SMA chains, as well as the ratio of the two averages, with the grafting conversion of SMA (in reduced form). We can see that the number-average molecular weight of the grafted SMA chains is more than twice that of the free chains. The ratio R increases with the grafting conversion. The selectivity of the grafting process is quite substantial. If we divide R by the average numbers of linkages per grafted SMA chain we have a sense of the effective chain length for the grafted chains and the free chains. The average number of graft linkages per grafted SMA chain is defined as

$$\bar{n}_{\mathrm{SMA}}^{\mathrm{ma}}=\frac{C_{\mathrm{MA}}^{0}f_{\mathrm{ma}}}{C_{\mathrm{SMA}}^{0}f_{\mathrm{SMA}}} \tag{10}$$

It is related to the molecular weight distribution and the grafting conversion of the reference chain by

$$\bar{n}_{\mathrm{SMA}}^{\mathrm{ma}}=\frac{-\ln(1-f_{\mathrm{ref}})}{1-\bar{M}_{n}^{0}\int_{0}^{\infty}(1-f_{\mathrm{ref}})^{\bar{M}}W(M)/M\,\mathrm{d}M} \tag{11}$$

Figure 5 shows the ratio of the effective molecular weight of the grafted chains to the average molecular weight of the free chains ($R/\bar{n}_{\mathrm{SMA}}^{\mathrm{ma}}$). We can see that this ratio decreases with grafting conversion but is still greater than unity (the actual ratio would be smaller since graft linkage reduces the effective chain length as compared with block linkage). Polydispersity, therefore, would have a significant effect on the solubilization of free chains into the domains of the graft copolymers, particularly at high grafting conversion of SMA.

Phase homogeneity

Figures 6 and *7* show two sets of micrographs of the reaction products at different grafting conversions of SMA. SMA is the dispersed phase. The films were cast from an acetone–water mixture solvent (SMA is swelled only in this mixture solvent). The matrix phase looked homogeneous. The overall features of the two sets of micrographs are very similar. Homogeneous solubilization occurs when the grafting conversion of SMA is above a value of around 50%. The composition of SMA has a minor effect. At low grafting conversions (26, 39 and 51% in *Figure 6*, 30 and 45% in *Figure 7*), macrophase separation and microphase separation coexist. Films with such phase heterogeneity are not transparent while the others are transparent but with a blue tint. A close inspection of the phase size at lower SMA conversions shows a distribution from small to large. There is no clear division into two sizes with an order of magnitude difference. The presence of such characteristics cannot be explained simply by the insolubilization of free SMA chains into the SMA chain segments of the graft copolymers.

Figures 8 and *9* show two sets of micrographs of the corresponding reaction products cast from THF–water mixture solvent. The THF–water mixture solvent is close to being non-selective. The SMA phase becomes continuous except for the case of 26% SMA conversion (*Figure 8*). At higher grafting conversion of SMA, the phase structures become homogeneous and co-continuous phases are observed. The SMA phase in its matrix state is homogeneous at lower grafting conversion compared with the case of the dispersed state. There is no separated microphase of SMA. The dispersed CA phase appeared less homogeneous. This is because the grafting conversion of CA is less than the grafting conversion of SMA. Apparently, solubilization of SMA free chains by the SMA chain segments of the graft copolymers happens at the lowest grafting conversion. It seems to suggest that there is no solubilization limit when SMA is in the matrix state.

From the four sets of micrographs, we found that phase size homogeneity increases with grafting conversion. The homogeneity of SMA is observed at lower conversion in the continuous state than in the dispersed state. The formation of more and more complex graft copolymers causes a net reduction of block length of graft copolymers, as was discussed earlier. However, such a reduction of the block length of the graft copolymers does not reverse the phase homogeneity with the grafting conversion of SMA. The desirable feature of this grafting reaction system is explained by the grafting conversion of more high-molecular-weight chain fractions of the reactive polymers. To illustrate the importance of the selectivity of grafting reaction, the free SMA in one reaction product (*Figure 7d*) was extracted and the remainder was mixed with the SMA without going through the grafting reaction (the SMA was treated the same way as the reaction product except for the absence of CA) to arrive at the same composition. The cast film from acetone–water mixture solvent at the same condition (*Figure 7d*) was no longer transparent. Insolubilization or less solubilization of the high-molecular-weight free chain is seen from such a test. This simple test shows the importance of the effective chain length of the free chains and chain segments of the graft copolymers. It also demonstrates that adding a small amount of reaction products with high copolymer content to the blend of CA/SMA may not provide the same kind of compatibilizing effect of the graft copolymers as the graft copolymers produced *in situ* by a reactive extrusion process.

Homogeneous solubilization happened at relatively high grafting conversion. There is therefore at equal amounts of CA and SMA only a narrow range of SMA grafting conversion from a practical point of view so that a homogeneous phase size is obtained while the *WAMW* of the reaction product is still kept at a reasonable value.

The appearance of macrophase separation from visual observation of optical clarity and electron microscopy is often used as evidence of insolubilization of homopolymer or evidence of a solubility limit on the amount of homopolymer that can be solubilized if the homopolymer

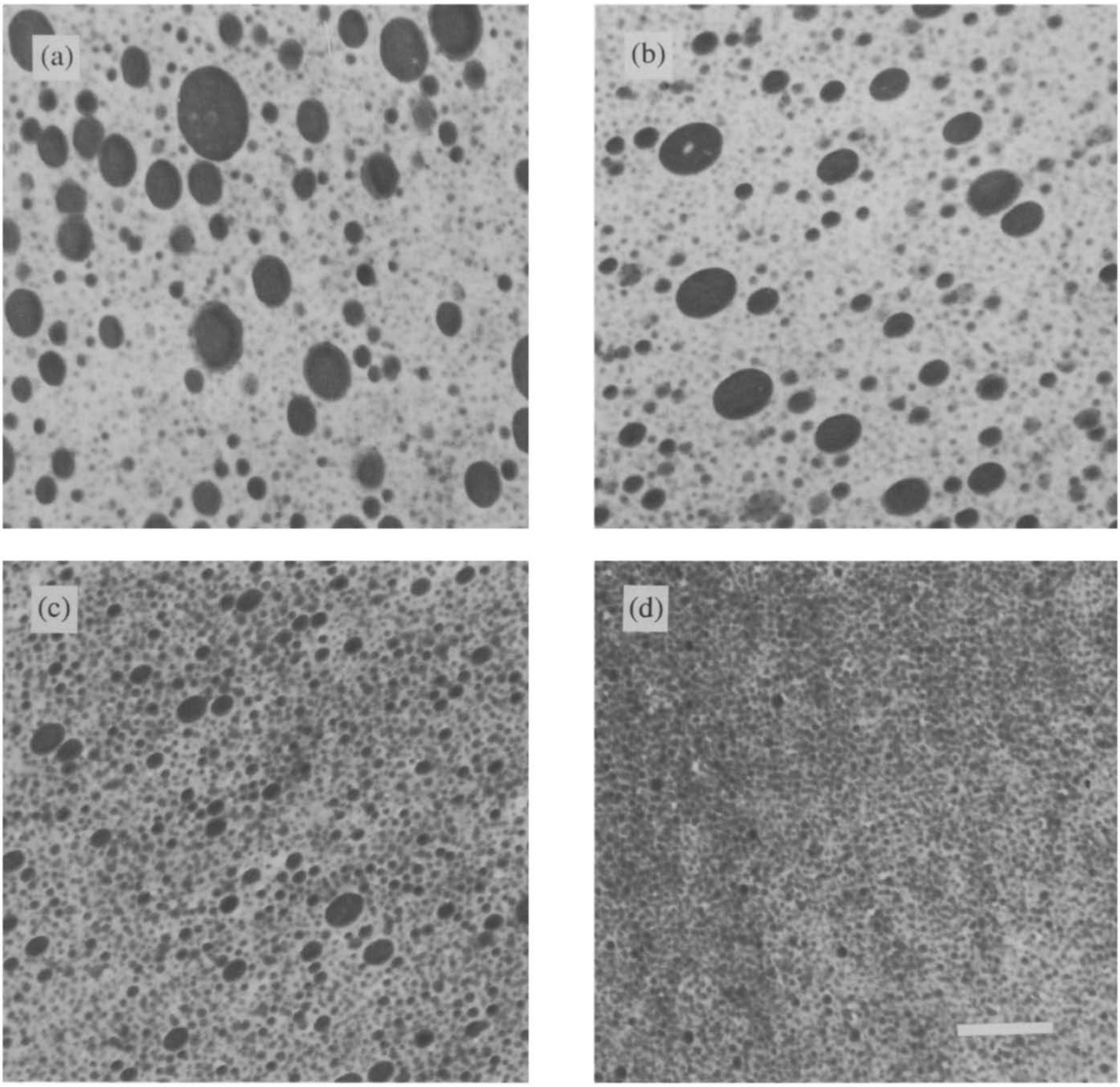

Figure 6 TEM micrographs of the films cast from acetone–water mixture solvent (96:4) at 70°C with 25% SMA in the alloys. f^{w}_{SMA}: (a) 0.26, (b) 0.39, (c) 0.51, (d) 0.74. Bar length: 1 μm

is initially solubilized. Theoretical analyses by Meier[23], and Helfand and Wasserman[24] show the importance of the conformational entropy of the confined chain on phase size and morphologies of pure block copolymer. The driving force for homopolymer solubilization has to do with the conformational entropy of both confined chains and free chains. It is the relaxation of the confined chains that results in homopolymer solubilization. The homopolymer chain has to be disturbed at the same time. It has, therefore, less degree of freedom compared with its unperturbed state. The system takes the form of a uniform phase size so to have a free energy minimum if the reduction of free energy is more than linear to the amount of solubilized homopolymer. However, the reduction of free energy may not necessarily be more than linear since the relaxation comes from both phases. Therefore heterogeneous phase size is not necessarily an indication of insolubilization. On the other hand, as more and more homopolymers are solubilized into the domains of graft copolymers, the driving force for solubilization may become so small from a relaxation point of view that dynamic force can easily distort the equilibrium phase structure.

Let us take a look at the dispersed spheres (chain A) in the case of slow relaxation of the confined chains with low content of graft copolymers. Let $\bar{V}_A$ be the volume of the confined A chain in its compact state and $\bar{S}_A$ be the interfacial area per confined chain. We have from material balance

$$\frac{1}{6}\pi d^3 = \frac{n_c \bar{V}_A}{f_A^w} \qquad (12)$$

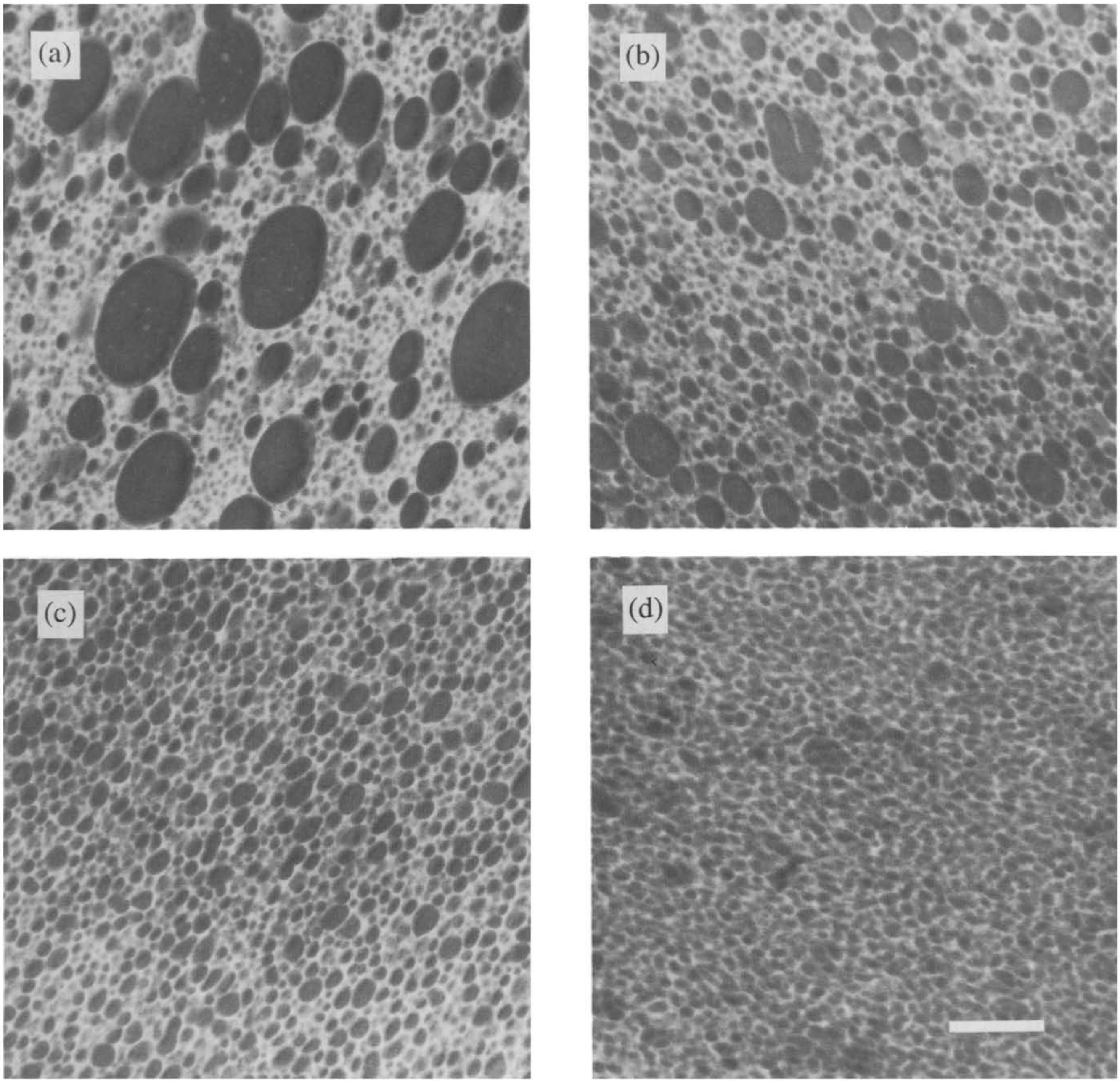

Figure 7 TEM micrographs of the films cast from acetone–water mixture solvent (96:4) at 70°C with 50% SMA in the alloys. $f^{\mathrm{w}}_{\mathrm{SMA}}$: (a) 0.30, (b) 0.45, (c) 0.56, (d) 0.66. Bar length: 1 μm

The surface area of the sphere becomes:

$$\pi d^2 = n_c \bar{S}_A \qquad (13)$$

Dividing equation (12) by equation (13) gives

$$d = \frac{6}{f^{\mathrm{w}}_{\mathrm{A}}} \frac{\bar{V}_A}{\bar{S}_A} \qquad (14)$$

If the interfacial area per confined chain $\bar{S}_A$ does not change with the solubilization of homopolymers, a reasonable assumption at relatively low content of graft copolymers, the diameter is inversely proportional to the fraction of the copolymer. *Figure 10* shows the size of the sphere as the content of copolymer decreases. It is important to point out that the change of phase size is the most drastic at low copolymer content. Therefore phase heterogeneity on the order of a few fold differences in size does not necessarily mean that the homopolymer is not solubilized in the copolymers at relatively low content of the graft copolymers. It could mean that the driving force for solubilization is weak if there is no solubility limit for the given system at low graft copolymer content. This seems to explain why discussion of homogeneous solubilization is more meaningful at high content of graft or block copolymers from an experimental point of view.

CONCLUSIONS

Graft coupling of two reactive polymers having large numbers of reactive groups for the purpose of forming compatibilized blends and alloys is an interesting system.

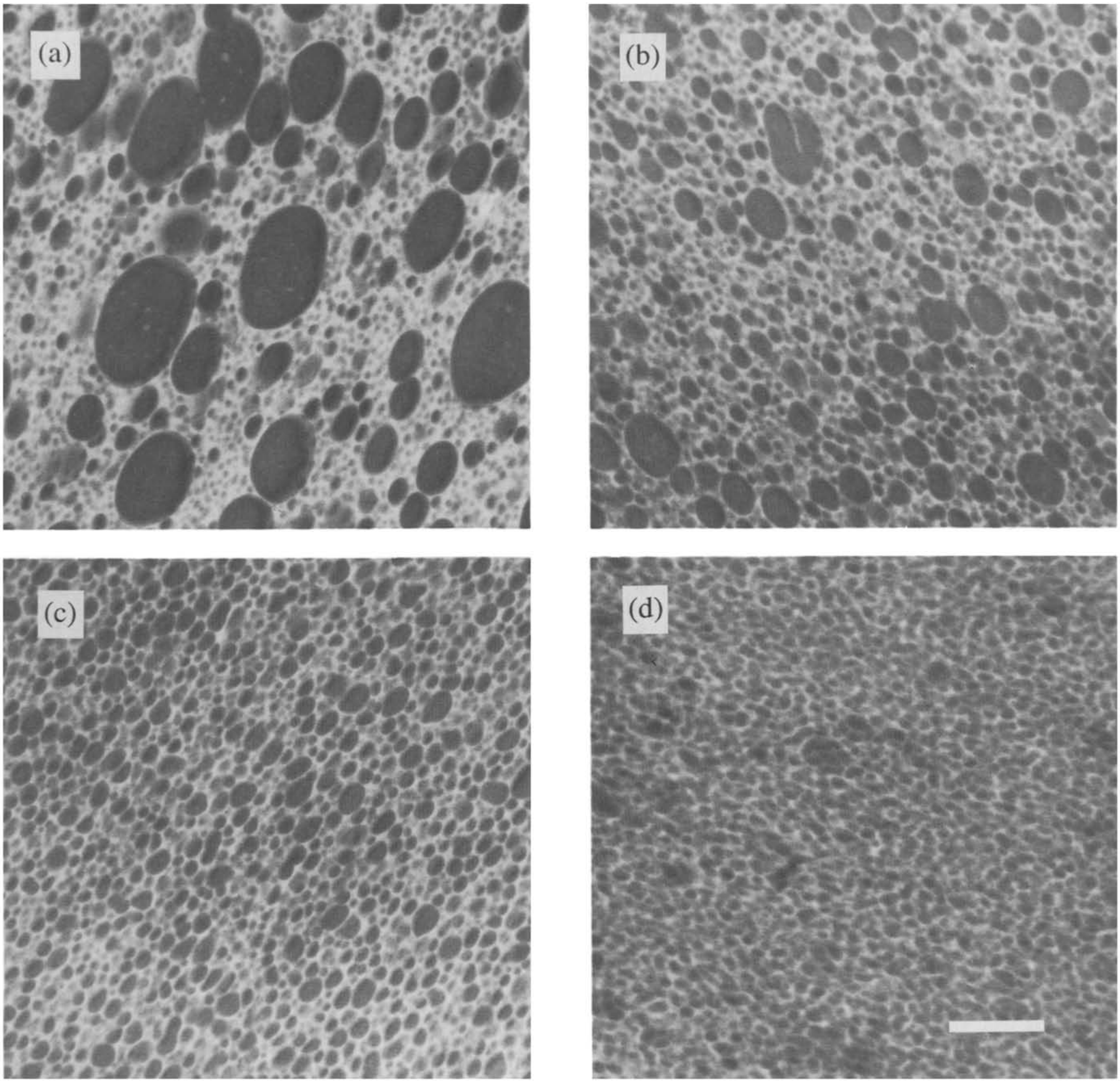

Figure 8 TEM micrographs of the films cast from THF–water mixture solvent (96:4) at room temperature with 25% SMA in the alloys. f_{10}^{w}: (a) 0.26, (b) 0.39, (c) 0.51, (d) 0.74. Bar length: 1 μm

On one hand, the amount of graft copolymers that can be formed is limited by the problem of gelation. On the other hand, there is a need for enough graft copolymers to be produced for a homogeneous microphase size. A case study on the CA–SMA grafting reaction shows that homogeneous phase structures appeared in the grafting reaction product of CA–SMA as grafting conversion of SMA increases. Substantial solubilization of the free chains into the domains of graft copolymers were found. There is a narrow range of SMA grafting conversion for a homogeneous phase size while keeping the *WAMW* of the reaction products in a reasonable range.

The formation of the complex graft copolymers at high grafting conversion of SMA does not lead to the insolubilization of the free SMA chains. Such a desirable property is explained by the grafting conversion of more high-molecular-weight chain fractions of the reactive polymers, a unique feature for synthesizing the graft copolymers in such grafting systems. The study shows the importance of the polydispersities of the reactive polymers in promoting homogeneous phase size in the defined grafting reaction system.

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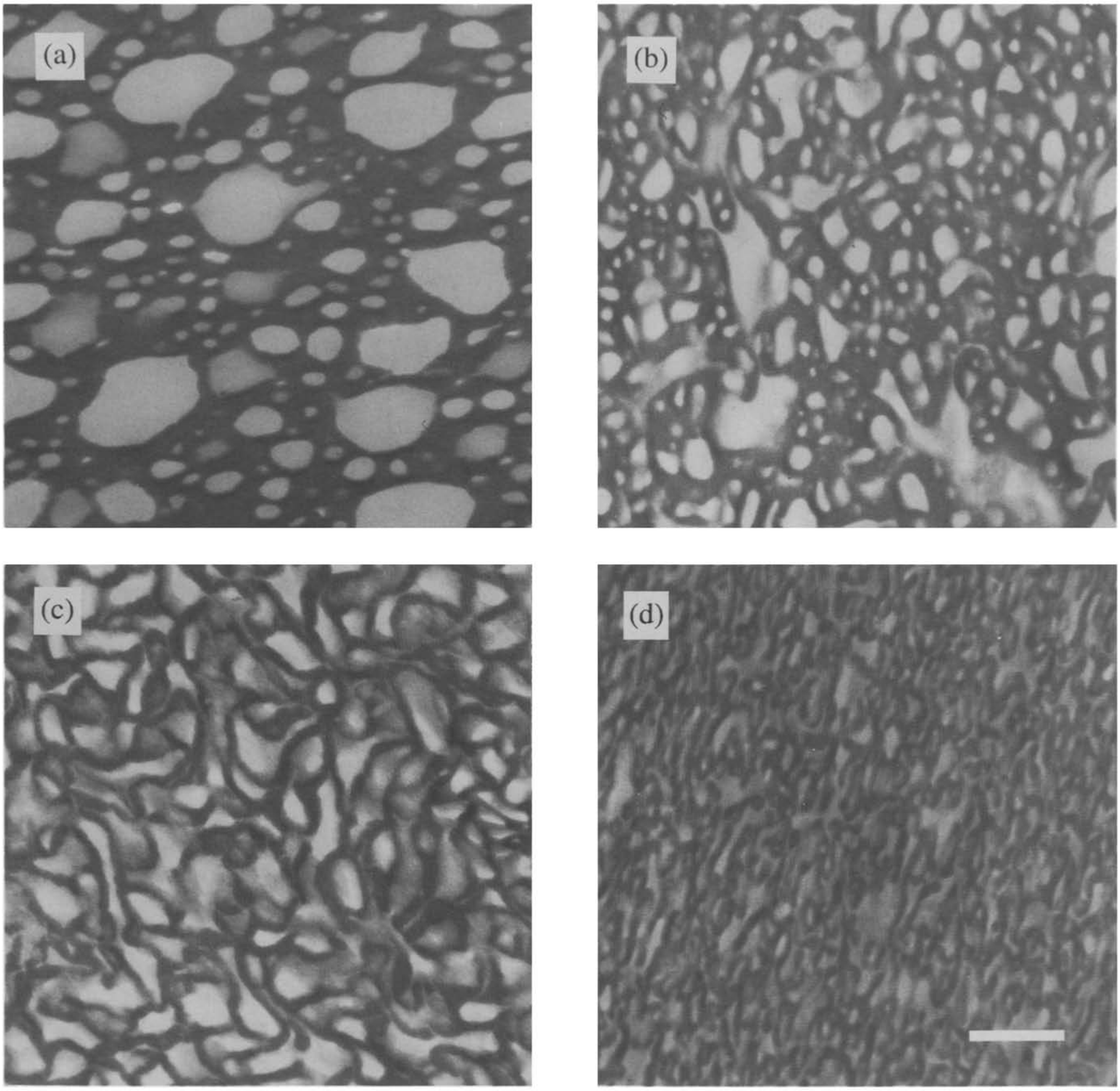

Figure 9 TEM micrographs of the films cast from THF–water mixture solvent (96:4) at room temperature with 50% SMA in the alloys. f^{w}_{SMA}: (a) 0.30, (b) 0.45, (c) 0.56, (d) 0.66. Bar length: 1 μm

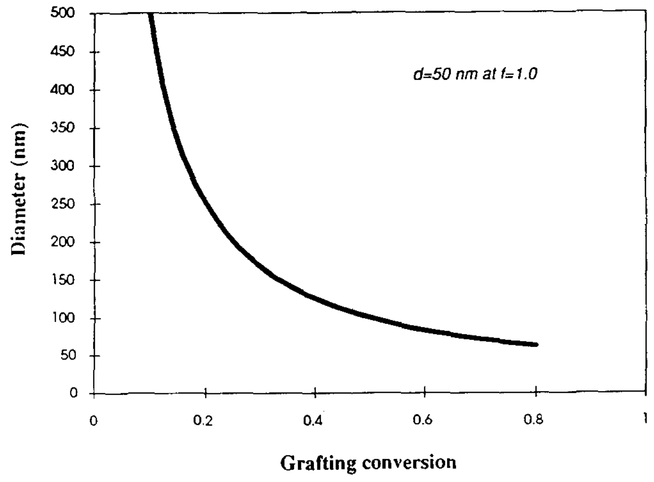

Figure 10 Change of domain size with grafting conversion

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