Grafting Cellulose Acetate with Styrene Maleic Anhydride Random Copolymers for Improved Dimensional Stability of Cellulose Acetate

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SYNOPSIS

Graft copolymers of cellulose acetate (CA, d.s.: 2.45) with styrene maleic anhydride random copolymers (SMAs) were synthesized by reacting the hydroxyls on CA backbone with the anhydride on SMA. The formation of graft copolymers leads to compatibilized blends with microscopic phase domains under appropriate conditions. The grafting reaction was studied in detail. The uniform dispersion of SMA in the CA matrix brings new properties to the grafting reaction products. Tests from acetone-cast films showed improved dimensional stability in comparison to cellulose acetate; i.e., in the presence of 50% SMA in the formulation, there is more than 50% reduction on the dimensional change as compared to CA. The dimensional stability of the grafting products is better or comparable to cellulose triacetate. There are, for the alloys, reduced moisture adsorption, improved tensile strength, tensile modulus, reduced elongation, as compared to cellulose acetate. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Grafting reaction provides a method for preparing new polymeric materials with improved and desirable properties.[1,2] The production of graft copolymers can be classified by two reaction schemes: (a) graft polymerization of monomers initiated by the active sites on the polymer backbone; (b) coupling of two reactive polymers. Graft polymerization proceeds by different mechanisms (free radical, anionic, cationic, ring opening, etc.), depending on the nature of active sites on the backbone and the type of monomer. Most people, both past and present, use free radical polymerization. Free radicals are generated on the polymer backbone by different methods: redox reaction, UV irradiation, high-energy radiation.[3-6] The radicals initiate the polymerization of monomers to form graft copolymers. Graft polymerization of vinyl monomers onto cellulose and its derivatives, nylons, poly(vinyl chloride), etc., has been studied extensively over the past decades. Most graft polymerization processes, irrespective of the initiation process, produced mixtures of graft copolymers, and homopolymers. One of the problems in radical polymerization has been on the control of the grafting process.[3] Recently, Kobayashi et al.[7] reported ring-opening graft polymerization of 2-oxazolines onto cellulose and cellulose diacetate, with the hydroxyls being tosylated. Narayan et al.[8,9] reported grafting of carboxyterminated polymers onto mesylated cellulose acetate and o-methyl cellulose by nucleophilic displacement of the methylate groups.

The availability of more and more functionalized and/or modified polymers[10] provides new opportunities for the production of graft copolymer and its alloys by coupling two reactive polymers. Maleic anhydride (MA)-modified polyolefins and random copolymers of maleic anhydride with some vinyl monomers are one family of reactive polymers. The reactivity is provided by the anhydrides. Extensive

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work have been done on the grafting reaction be-
tween the anhydride groups on one polymer and
amine groups on another polymer to form compa-
tibilized blends via reactive extrusion.[11–20] Hydroxyl-
bearing polymers are another family of reactive
polymers. Many natural polymers and its derivatives
(after chemical modification) are an important
source of hydroxyl-bearing reactive polymers. The
reaction between the anhydride and the hydroxyl is
another choice for the production of graft copoly-
mers to form compatibilized blends. One report uti-
lizing such reaction was given by Lambla et al.[21] on
the crosslinking of styrene maleic anhydride copol-
ymer with dihydroxyloligostyrene in the molten
state.

Cellulose acetate (CA, d.s.: 2.45) is one of the
many commercially important cellulose derivatives.
It is a tough material with excellent optical clarity.
Major applications are found in films, textile fibers,
and cigarette tow.[22] It is well known that cellulose
acetate has dimensional stability problem under high
humidity and elevated temperature. The other
shortcomings are its high cost, very limited com-
patibility with other synthetic polymers, and high
processing temperature.[23,24] So far, only poly(4-vinyl
pyridine)[25] and poly(styrenephosphonate ester)[26,27]
at certain degree of phosphorylation are reported to
be miscible with cellulose acetate. Styrene maleic
anhydride random copolymers (SMA) are commer-
cially available. Grafting reaction between cellulose
acetate and styrene maleic anhydride random co-

polymers will add new traits to cellulose acetate by
forming compatibilized blends. The incorporation
of hydrophobic SMA can help improve the dimen-
sional stability of CA, therefore, of better perfor-
mance in fibers and films applications when im-
proved dimensional stability is critically important.
In this study, we report the grafting reaction of CA
with SMA and the resultant products with improved
dimensional stability as compared to CA.

EXPERIMENTAL

Materials

Cellulose Acetate (CA, d.s.: 2.45, M_w: 103,000, M_n:
46,000) was provided by Courtaulds plc. Styrene
maleic anhydride random copolymers (SMA132:
4.75% maleic anhydride, M_w: 274,000, M_n: 136,000;
SMA232: 7.08 wt % maleic anhydride, M_w: 249,000,
M_n: 126,000; SMA332: 12.2% maleic anhydride, M_w:
193,000, M_n: 100,000) were provided by ARCO
Chemical Company. The contents of maleic anhy-
dride (MA) in SMAs were determined by back-ti-
tration. Gel permeation chromatography analysis for
the four samples were provided by Viscotek Corp.
The structural units of CA and SMA232 are shown
in Figure 1. 4-Dimethylaminopyridine (DMAP) and
anhydrous grade N,N-dimethylformamide (DMF,
99%) were purchased from Aldrich Chemical Com-
pany, Inc.
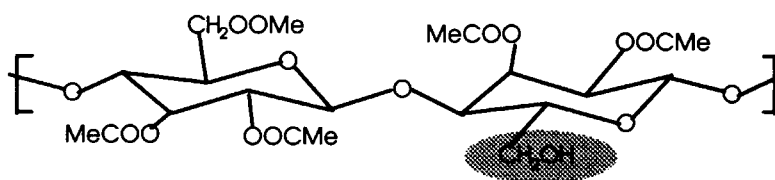
CA (not completely primary hydroxyl)
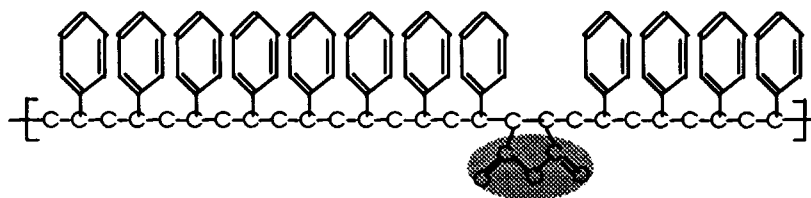

SMA (the distribution of MA is random)

Figure 1 Structures of CA and SMA.

Construction of Phase Diagram

The phase diagram was constructed by visual observation on the cloudy point with successive addition of small amount of solvent at fixed polymer composition. The tie line was determined by measuring the volume change after equilibrating the CA solution with SMA solution for three days. The SMA solution of lower density was carefully transferred on the surface of CA solution in the tube with volume indication. The tube was capped with serum stop and heated gradually to 110°C for equilibration (little head space, excess pressure from air was released with needle).

Grafting Reaction

Grafting reaction happens between the hydroxyl and anhydride to form a half ester only in the presence of catalysts. In the absence of water, the grafting reaction proceeds by
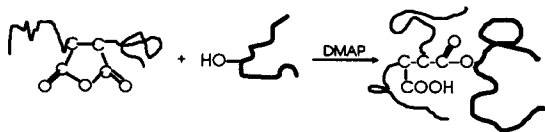
The complexity of graft copolymers keeps growing because of large numbers of reactive groups on the chain segments of the graft copolymers (85 hydroxyls of CA by number average, 90 anhydrides of SMA232 by number average). Above reaction leads to the formation of a simple graft copolymer.

Grafting reactions were carried out in DMF polymer solution at increased temperature with stirring. DMAP was used as a catalyst. Cellulose acetate was vacuum dried overnight at 90–100°C and kept under dry nitrogen before anhydrous DMF was transferred to the reactor through a transferring line; water was added to the reactor through a serum stop after transferring of DMF when looking at the effects of water. DMAP was added after the polymer solution reaches a stable temperature. The reaction temperature was controlled within 1°C. After reaction, the solutions were cooled immediately to room temperature and precipitated right away with three-time volume of water. Precipitate in the form of porous pulp (low grafting conversion) or porous string was washed with excess amount of hot water every 2 h for three times and soaked overnight with excess amount of water. It was washed further with methanol for three times. Extensive washing was for the removal of residual DMF and catalyst. The samples

were dried at room temperature, dried further at 50°C under full vacuum, and weighted under dry condition.

Extraction

Information on grafting conversion of SMA (wt %) was obtained by soxhlet extraction with toluene for 2 days. Elemental analysis for the extractable (CHN analysis, very accurate because of big difference in carbon content between CA and SMA) showed less than 2% of CA in the extractable; therefore, only free SMA was extracted. Percentage conversion of SMA was obtained from mass balance. Precipitates of simple blends at two compositions (10% SMA, 50% SMA) gave 100% extraction of SMA.

Differential Scanning Calorimetry (DSC)

The glass transition temperature of samples were studied by DSC at a heating rate of 10°C/min. The glass transition temperature was reported as the midpoint of a step transition.

Sample Preparation and Test Methods

Test samples for dimensional stability, moisture adsorption, and mechanical properties were cast from a acetone:water (96:4) mixture solvent with a film applicator and dried at 80°C for 15 min. The presence of water helped reduce the solution viscosity. For tests of dimensional stability, the films were soaked in water at several temperatures for 30 h. The dimensional changes of films were measured after the film samples were dried naturally for 1 day. The initial dimensions of the films were taken as the dimensions cut from the glass plates. All samples had dimension of $8 \times 2''$. The changes in length were reported as measure of dimensional stability. The moisture adsorptions of cast films were tested according to ASTM D570–81 under a relative humidity of 95%. Tensile properties of cast films were tested according to ASTM D882–83. The tests were performed on a United tensile tester with a crosshead movement at a testing speed of 2%/min. The test samples were cut into dimensions of $4 \times 5/16''$ with a thickness around 0.04''. The thickness of the samples were measured individually with a caliper having a precision of 0.0005''. Before testing, the samples were dried overnight at 60°C and conditioned at room temperature and a relative humidity of 60%. All test samples were free of bubbles. The test results were reported by averaging 10 useful samples.

RESULTS AND DISCUSSION

Grafting Reaction

Phase Diagram of the Ternary Mixture

CA is immiscible with SMA resins. Phase separation happens in solution even though the presence of solvent dilutes greatly the unfavorable interaction between CA and SMA. Phase diagram can be constructed according to the Flory-Higgins theory if the three phenomenological interaction parameters were available. Scott's[28] analysis shows semiquantitatively the important feature of phase behavior in ternary solution. For CA and SMA dissolved in DMF, no interaction parameters are available. Figure 2 shows the phase diagram of DMF-CA-SMA at 110°C on a weight percentage basis from cloudy-point observations.

Three things are noted to be important for grafting reaction from the phase diagram. (1) The shape of phase separation curve is very flat. There is little solubilization of one polymer into the phase containing another polymer whence the weight fraction of polymers in solution falls below the tie line. The rate of grafting reaction depends on the contact area of the two phases when there is no mutual solubilization of the two polymers. (2) DMF partitions more in the CA phase than in the SMA phase. The SMA phase will be a dispersed phase if the amount of SMA is less than CA. (3) The unfavorable interaction between CA and SMA decreases with the content of maleic anhydride in SMA resins.

To have a better appreciation of the presence of solvent in diluting the unfavorable contact and the content of maleic anhydride of SMA resins in reducing the immiscibility between CA and SMA, we can do a qualitative analysis for the free energy of mixing of the ternary mixture. According to Flory-Higgins's theory, the free energy of mixing in a assumed homogeneous state satisfies

$$\frac{\Delta G_m}{RTV} = \frac{\phi_{DMF}}{V_{DMF}} \ln \phi_{DMF} + \phi_{DMF}\phi_{SMA} B_{DMF\text{-}SMA}$$
$$+ \phi_{DMF}\phi_{CA} B_{DMF\text{-}CA} + \phi_{CA}\phi_{SMA} B_{CA\text{-}SMA} \quad (2)$$

where the combinatorial entropies of CA and SMA were neglected. B_{ij} is the binary interaction energy density, for nonpolar or slightly polar system it is related to solubility parameters by

$$B_{ij} = \frac{1}{RT} (\delta_i - \delta_j)^2 \quad (3)$$

Because DMF is a good solvent for both CA and SMA, the driving force for a phase separation comes from the unfavorable interaction between CA and SMA [last term of Eq. (2)]. Let Φ'_{CA} be the volume fraction of CA in the absence of solvent, Φ'_{SMA} be the volume fraction of SMA in the absence of solvent ($\Phi'_{CA} + \Phi'_{SMA} = 1$), we have for the last term of Eq. (2)

$$\phi_{CA}\phi_{SMA} B_{CA\text{-}SMA}$$
$$= \phi'_{CA}\phi'_{SMA} B_{CA\text{-}SMA} (1 - \phi_{DMF})^2 \quad (4)$$
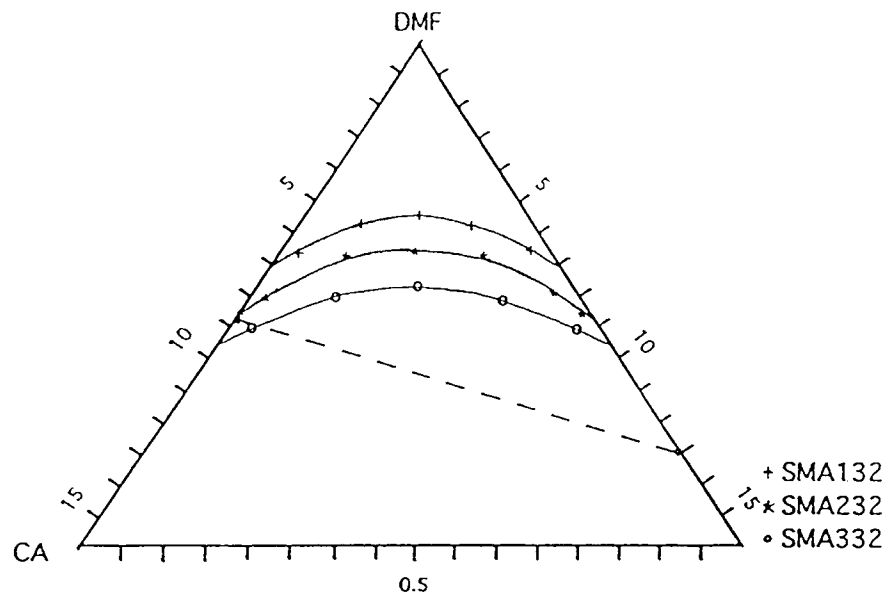
Figure 2   Phase diagram of DMF-CA-SMA at 110°C (weight-percentage basis).

We can see from Eq. (4) that the dilution of unfavorable interaction is quite sensitive to the amount of solvent in solution, especially at a low polymer concentration. The polymer solution is often prepared at a concentration of less than 20 wt % polymers to avoid too high a solution viscosity. At this low end of polymer concentration, the reduction on the unfavorable interaction between CA and SMA is very sensitive to the changes in polymer concentrations. As a result, the grafting process is expected to be much affected by the changes in polymer concentrations.

SMA resins are commercially available with several maleic anhydride (MA) contents. We can look at the effect of maleic anhydride content in SMA on the CA-SMA binary interaction energy density by decomposing the interaction between CA and SMA into the interaction among CA and the monomer units of SMA. Let Φ''_{ma} be the volume fraction of maleic anhydride in SMA, Φ''_{sty} be the volume fraction of styrene in SMA ($\Phi''_{ma} + \Phi''_{sty} = 1$), the binary interaction energy density between CA and SMA, following Paul and Barlow's generalization[29], becomes

$$
\begin{aligned}
B_{CA\text{-}SMA} &= B_{sty\text{-}CA}\phi''_{sty} + B_{ma\text{-}CA}\phi''ma - B_{sty\text{-}ma}\phi''_{sty}\phi''_{ma} \\
&= B_{sty\text{-}CA}(1 - \phi''_{ma}) + B_{ma\text{-}CA}\phi''_{ma} \\
&\quad - B_{sty\text{-}ma}(1 - \phi''_{ma})\phi''_{ma} \quad (5)
\end{aligned}
$$

The presence of a minus term is due to the unfavorable interaction within the structural units of SMA. It is the presence of such unfavorable interaction within the copolymer itself that opens miscibility windows in some polymer blends involving random copolymers. To fix the idea, let us assume that the binary interaction energy density of $B_{ma\text{-}CA}$ is close to zero (it is supposedly to have a small negative value for the possible weak hydrogen bonding between the hydroxyl of CA and the anhydride), and $B_{sty\text{-}CA}$ equals to $B_{sty\text{-}ma}$ ($\delta = 9.3$, $\delta_{CA} = 12.7$, $\delta_{ma} = 13.6$, $\delta_{sa} = 15.4$, $(cal/cm^3)^{0.5}$, sa stands for succinic anhydride).[30] It is conservative to have

$$
B_{CA\text{-}SMA} = B_{sty\text{-}CA}(1 - \phi''_{ma})^2 \quad (6)
$$

We see from Eq. (6) that the unfavorable interaction between CA and SMA reduces with increasing MA content in SMA. This explains the shift of phase diagram as MA content in SMA changes. However, the sensitivity of MA content in reducing the unfavorable interactions is less than solvent because

the important commercial resins have MA contents of less than 25%.

Description of the Rate of SMA Grafting Conversion

Grafting reaction will happen in the diffusive interface when each phase contains only one polymer (SMA is meant for SMA232 in rest of the discussion unless specified). The phase sizes will decrease with the grafting conversion of SMA. This is due to the dispersing power of the graft copolymers once they are formed in the reaction system. Experimentally, we observed that the clarity of the reaction solution changed gradually from opaque to clear. To understand the grafting process, we need to relate the grafting reaction to the percentage conversion of SMA, the only information we can obtain from extraction. The percentage grafting conversion of SMA is defined as

$$
\begin{aligned}
f^w_{sma} &= 1 - \left(\frac{\int MdC}{\int MdC^0} \right)_{sma} \\
&= 1 - \left(\frac{\int MdC}{\bar{M}^0_n C^0} \right)_{sma} \quad (7)
\end{aligned}
$$

The rate of disappearance for the concentration of free (ungrafted) SMA chain of a certain molecular weight satisfies

$$
-\left(\frac{dC_i}{dt} \right)_{sma} = \left(\frac{\alpha_p M_i C_i}{\sum M_i C^0_i - (1 - \alpha_p) \sum M_i C_i} \right)_{sma} \delta n \bar{S} r_{ma} \quad (8)
$$

where r_{ma} is the rate of MA consumption. $\alpha_p M_i C_i / (\sum M_i C^0_i - (1 - \alpha_P) \sum M_i C_i)$ is the statistical weight of the reaction used for the consumption of chain species of that particular molecular weight (the numbers of MA reacted on the graft copolymers were neglected in the statistical weight due to the large numbers of MA on the SMA chains). α_P is the fraction of ungrafted SMA chains that have the same chance of collision for reaction as the grafted chains. It is a function of phase size and phase size distribution. Its value should increase with grafting conversion if there were no blocking effect by the graft

copolymers. δ is the equivalent interfacial penetration depth for reaction. It should be relatively constant under given conditions. n is the total number of dispersed SMA phases per unit volume. $\bar{S}$ is the number-average interfacial area of the two phases for the given size distribution of the dispersed SMA. By multiplying both side of Eq. (8) by M_i and summing for all the i, we have

$$-\left(\frac{\sum M_i dC_i}{dt}\right)_{\text{sma}}$$

$$= \left(\frac{\alpha_p \sum M_i^2 C_i}{\sum M_i C_i^0 - (1 - \alpha_p) \sum M_i C_i}\right)_{\text{sma}} \delta n \bar{S} r_{\text{ma}} \quad (9)$$

By substituting Eq. 7 into Eq. (9) and rearranging, we have

$$\frac{df^{\,w}_{\text{sma}}}{dt} = (1 - f^{\,w}_{\text{sma}})\left(\frac{\bar{M}^f_w}{\bar{M}^0_w}\frac{\text{PDI}}{C^0}\right)_{\text{sma}}$$

$$\times \frac{1}{1 + f^{\,w}_{\text{sma}}(1/\alpha_p - 1)} \delta n \bar{S} r_{\text{ma}} \quad (10)$$

$\bar{M}^f_w/\bar{M}^0_w$ is the reduced weight-average molecular weight of free SMA. *PDI* is the polydispersity index of SMA as received.

Among several parameters of Eq. (10), only r_{ma} does not change with grafting conversion because the numbers of reactive groups consumed are negligible when the grafting conversion of SMA is less than 80%. The phase size and distribution are difficult to quantify for a number of factors: the extent of immiscibility (interfacial tension) between CA and SMA; the change of phase size and distribution with grafting reaction; and stirring strength. As a result, the initial values and the change of α_P, n, and $\bar{S}$ with grafting reaction are hardly available. Actual modeling of the rate of SMA grafting conversion is not attempted in looking at some parameters of Eq. (10).

Effect of Polydispersity on the Change of $\bar{M}^f_w/\bar{M}^0_w$ with Grafting Conversion

The change of $\bar{M}^f_w/\bar{M}^0_w$ in Eq. (9) depends on the molecular weight distribution of the starting SMA. It satisfies

$$\frac{\bar{M}^f_w}{\bar{M}^0_w} = \frac{\displaystyle\int M/\bar{M}^0_w(1 - f_{\bar{M}^0_w})^{M/\bar{M}^0_w}W(M)\,dM}{\displaystyle\int (1 - f_{\bar{M}^0_w})^{M/\bar{M}^0_w}W(M)\,dM} \quad (11)$$

where $f_{\bar{M}^0_w}$ is the grafting conversion of a reference SMA chain, which has a molecular weight of the
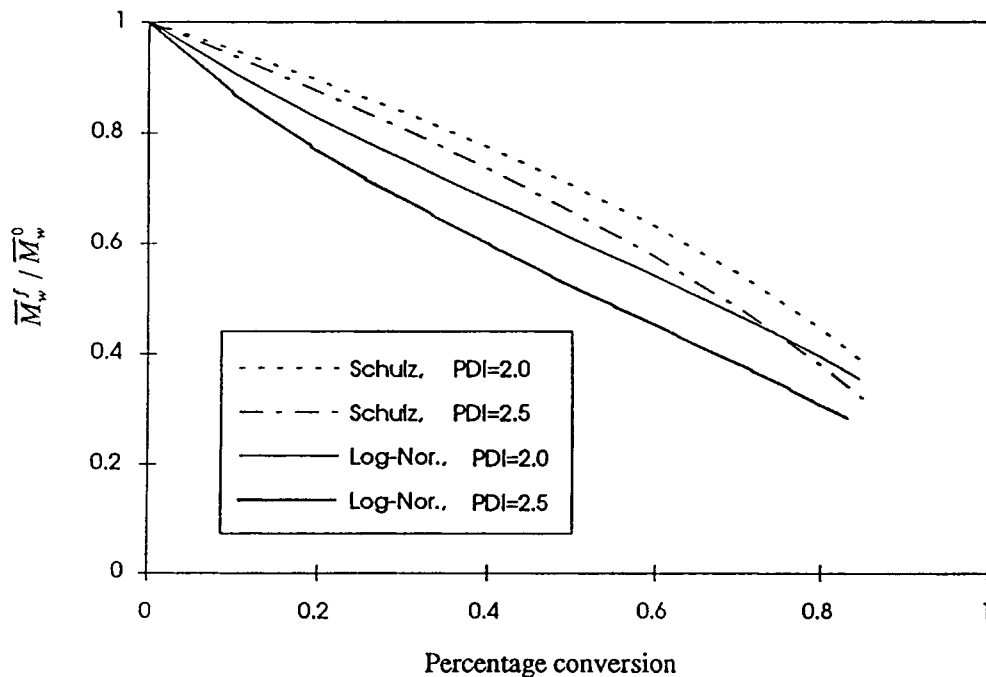

Figure 3 Reduced weight-average molecular weight of free chains vs. grafting conversion at two values of PDI for two types of distribution.
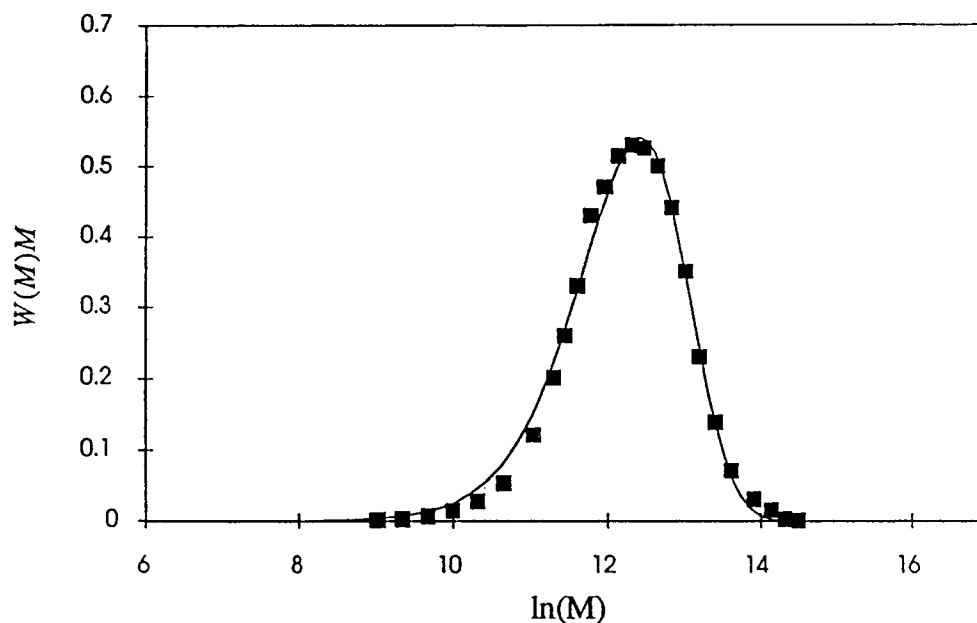
Figure 4   Molecular weight distribution of SMA fitted with Schulz function.

weight-average molecular weight of SMA as received. In case of Schulz distribution we have

$$(\bar{M}_w^f/\bar{M}_w^0)_{sma} = (1 - f_{sma}^w)^{1/b+2} \qquad (12)$$

b is the model parameter characterizing the polydispersity of the sample. Figure 3 shows the change of $\bar{M}_w^f/\bar{M}_w^0$ with the grafting conversion of a polymer at two values of polydispersity for two typical distributions: Schulz and log-normal. We can see from Figure 3 that the effect of polydispersity on the change of $\bar{M}_w^f/\bar{M}_w^0$ is quite substantial. The reduction of $\bar{M}_w^f/\bar{M}_w^0$ is nearly linear with the percentage conversion of a polymer.

SMA has a PDI of 1.98 from GPC analysis. Its molecular weight distribution can be fitted closely by the Schulz function. Figure 4 shows the close fitting for the molecular weight distribution of SMA by Schulz function.

Effect of Stirring Speed on Grafting Reaction

The complexity involved in α_P and $n\bar{S}$ comes from both the extent of mixing and the dispersing power of the graft copolymers. The polymer solution is very viscous at a concentration of around 10 wt %. The dispersing force from the stirrer caused viscous shear. The low interfacial tension (diluted in the presence of solvent) at the diffusive interface will result in micron/submicron dispersion for the dispersed SMA phase. The high solution viscosity will slow down the merging of the dispersed phase to

form a dispersion of larger sizes. The formation of graft copolymers during the reaction provides a dispersing force to the dispersed phase to stabilize the dispersion (similar to the role of surfactant). The low interfacial tension, high solution viscosity, plus the stabilizing force from the graft copolymers formed more and more during the reaction, will reduce the effect of stirring intensity on the grafting reaction. Table I shows the effect of stirring speed on the rate of grafting reaction. It can be seen that the grafting reaction rate increased slightly as the stirring speed increased from 200 rpm to 600 rpm. Therefore, the speed of stirring in that range is not particular important for the grafting reaction. A stirring speed of 400 rpm was selected in the rest of the studies.

Effect of Polymer Concentration

Studies on the effect of polymer concentration on the rate of SMA conversion were conducted at three

Table I   Effect of Stirring Speed on the Grafting Conversion of SMA*

Speed (rpm)	200	425	600
f_{SMA}^w	0.41	0.43	0.44

* CA : SMA = 1 : 1, 14 g polymers/100 mL DMF, 0.5 g cat./ 100 mL DMF, 2 h, 110°C.

Table II f_{SMA}^w vs. Reaction Time at Three Polymer Concentrations*

8 g/100 mL DMF		11 g/100 mL DMF		14 g /100 mL DMF	
Time (h)	f_{SMA}^w	Time (h)	f_{SMA}^w	Time (h)	f_{SMA}^w
0.5	0.27	0.5	0.30	1.0	0.33
1.0	0.40	1.0	0.45	2.0	0.46
1.5	0.51	1.5	0.56	3.0	0.54
2.0	0.58	2.0	0.66	4.5	0.63
2.5	0.64	2.5	0.74	5.9	0.72
3.0	0.69				

* CA : SMA = 1 : 1, 0.5 g DMAP/100 mL DMF, 110°C.

concentrations (Table II). We can see from Table II that the grafting conversions of SMA are very sensitive to polymer concentrations. At a concentration of 8 g/100 mL DMF, the grafting process is very close to be homogeneous (the solution turned to clear in less than 10 min). A plot of $2[1/(1 - f_{SMA}^w)^{0.5} - 1]$ vs. time is shown in Figure 5. The factor 2 is the value of denominator of the power term in Eq. (12) because b equals to zero for a polydispersity of 2. Constant reaction rate r_{ma} is seen from the linear curve fitting.

We can probe somewhat into the effect of phase separation on the grafting process by plotting $-\ln(1 - f_{SMA}^w)$ vs. reaction time (see Fig. 6). It happened that at a concentration of 11 g (CA+SMA)/100 mL DMF, the curve is nearly linear. The production of graft copolymer, therefore, helps disperse the homopolymers so to give more reaction area. There is

about onefold increase in the reaction area from the beginning to the SMA grafting conversion of 75% because the reduction of $\bar{M}_w^f/\bar{M}_w^0$ in Eq. (10) is close to half at that conversion. However, such dispersion power from the graft copolymers seems to disappear at higher polymer concentration. There is an obvious deviation from the linear relationship at a concentration of 14 g/100 mL. The grafting reaction solution never turned clear. The α_P factor in Eq. (10) could be responsible for such behavior. The explanation might be that the graft copolymers present at the interface may block somehow the chance of homopolymers to react. Such blocking action should increase with polymer concentration. As a result, more reaction is given to the graft copolymers at the same grafting conversion of SMA as compared to the situation of lower polymer concentration.

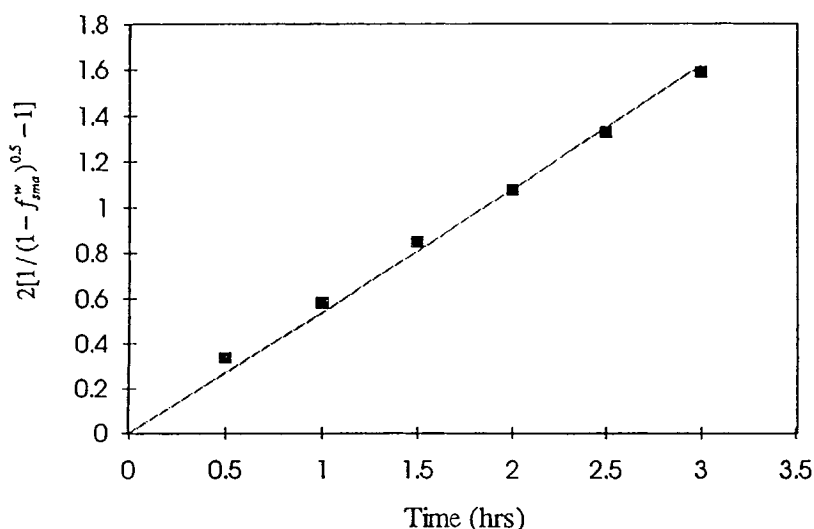It is to point out here that the presence of blocking

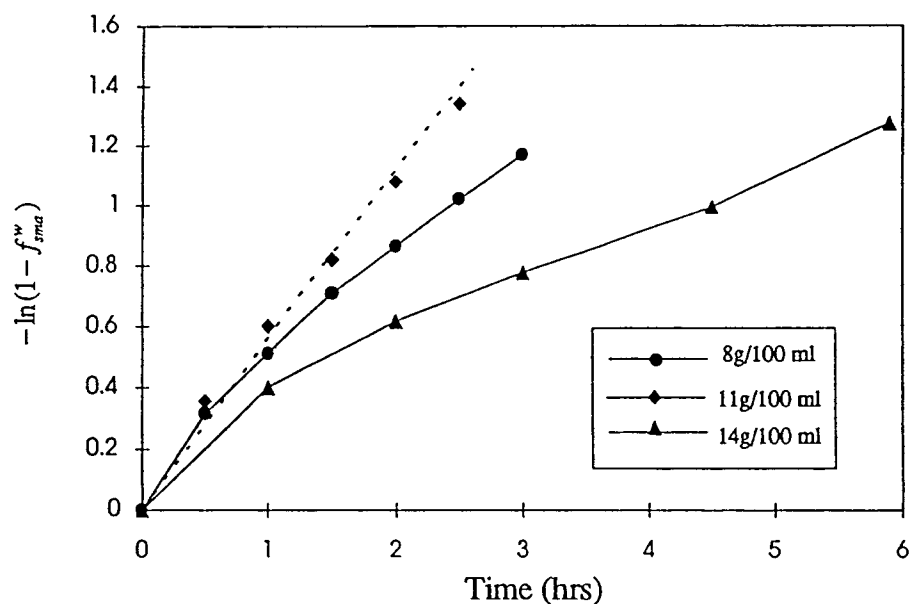**Figure 5**   Linear fitting for homogeneous grafting reaction showing constant reaction rate.

Figure 6 Change of with reaction time at three concentrations.

effect by the graft copolymers is unfavorable for free chain solubilization because the effective chain length of the graft copolymers will be reduced. As a result, there will be a reduction on the solubilization ability of graft copolymers for the free polymers. Tests of free SMA solubilization by comparing the optical clarity of cast film from acetone–water mixture solvent (96% acetone) are shown in Table III. The transparency of the films comes from the homogeneous solubilization of free SMA into the domains of grafted SMA, and domain size is well below the wavelength of visible light (see details in another publication).[31] We can see from Table III that the solubilization power of the graft copolymers produced at the highest polymer concentration is less than the other two. Too high a polymer concentration, therefore, is not favorable for producing compatibilized blends with homogeneous phase size.

Effect of Catalyst Concentration

Changing the concentration of the catalyst has little effect on the phase separation of CA and SMA. At a polymer concentration of 11 g/100 mL DMF, the increase of SMA grafting conversion is very close to be first order with the concentration of free SMA. We can use the same kind of plot as in Figure 6 to see the dependence of reaction rate on the concentration of the catalyst. Figure 7 shows a first-order dependence of reaction rate on the concentration of DMAP. The reaction rate, therefore, is directly proportional to the concentration of the catalyst.

Effect of Reaction Temperature

The effect of temperature on grafting reaction comes from two factors: reaction kinetics and phase heterogeneity. The change of grafting conversion with

Table III Film Clarity of Reaction Products Prepared at Three Polymer Concentrations*

8 g/100 mL	f_{SMA}^{w}	0.27	0.040	0.51	0.58
	clarity	opaque	translucent	transparent	transparent
11 g/100 mL					
	f_{SMA}^{w}	0.30	0.45	0.56	0.66
	clarity	opaque	translucent	transparent	transparent
14 g/100 mL					
	f_{SMA}^{w}	0.33	0.46	0.54	0.63
	clarity	opaque	opaque	translucent	transparent

* Films cast onto glass plate at 80°C, all transparent films have blue tint.
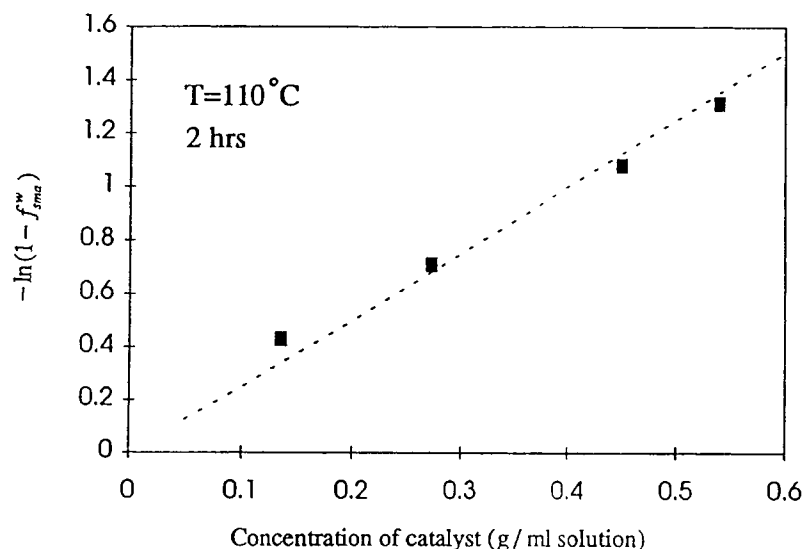
Figure 7   First order dependence of reaction rate on the concentration of DMAP.

temperature is shown in Table IV for a polymer concentration of 11 g/100 mL DMF. There is quite an influence of reaction temperatures on the rate of SMA grafting conversion.

Effect of MA Content in SMA on the Rate of Grafting Reaction

Immiscibility between CA and SMA reduces with the content of MA in SMA resins. The grafting reaction between CA and SMA132/SMA332 can be analyzed the same way as in CA and SMA232. The overall features shall be the same, except in case of CA-SMA132, the concentration dependence will shift to lower polymer concentration, and in case of CA-SMA332, the concentration dependence will shift to higher polymer concentration. Increased MA content in SMA and the resultant reduction on the immiscibility between CA and SMA will lead to increased rate of grafting reaction. Table V shows the grafting conversion of CA with three SMAs at the same polymer concentration. The rate of SMA332 grafting conversion is much faster than SMA232, so is SMA232 than SMA132.

Table IV   Effect of Reaction Temperature on the Grafting Conversion of SMA*

Temp. (°C)	91	100	110	125
f_{SMA}^{w}	0.43	0.58	0.66	0.73

* CA : SMA = 1 : 1, reaction time = 2.0 (h), 05. g DMAP/100 mL DMF.

Effect of Water on the Grafting Reaction

Water is an important factor in this grafting reaction system. The presence of water can result in the hydrolysis of anhydride and the ester groups of cellulose acetate. It will also limit the equilibrium grafting conversion. Table VI shows the loss of the total amount of polymers at three water levels. Both hydrolysis of anhydride and hydrolysis of CA are seen from material balance. The partial hydrolysis of anhydride causes a slight gain in weight for the polymers (compared to anhydrous case). The hydrolysis of CA results in the loss of polymer mass, it is severe at water/MA molar ratio of 12. Table VII shows the weight loss of CA at two degrees of substitution, remember there is only a half amount of CA for the polymer composition shown in Table VI. So only a small amount of water can be tolerated in this grafting reaction system.

Table VIII shows the effect of a small amount of water on the grafting conversion of SMA. The addition of a small amount of water causes steady increase on the grafting conversion of SMA. It is, therefore, necessary to control the amount of water in the reaction system even though it is only a small amount. The highest water amount in Table VIII corresponds to a water content of 0.45 wt % in DMF.

Properties of Reaction Products

The properties of the grafting products depend on the phase size and phase arrangement of CA and SMA in the final products. The inclusion of SMA is meant to improve the performance of CA. It is,

Table V   Effect of MA Level on the Grafting Conversion of SMA*

Sample	MA wt %	(g) DMAP/100 mL DMF	Reaction Time (h)	Grafting Conversion
SMA132	4.74%	0.5/100	2.0	0.56
SMA232	7.08%	0.5/100	2.0	0.66
SMA332	12.20%	0.2/100	1.0	0.61

* CA : SMA = 1 : 1, T = 110°C, 11 g (CA + SMA)/100 mL DMF.

therefore, necessary to disperse the SMA into CA and to have a fine dispersion. Acetone is the most common solvent used for CA in film casting and fiber spinning. It is fortunate that SMA is also soluble in acetone. Films cast from a acetone–water mixture solvent gave a desirable matrix phase for CA, a fine and uniform solubilization of ungrafted SMA into the domain of grafted SMA chain segments is obtained when the grafting conversion of SMA is above a value of around 50%.[31] Under such conditions, cast films retain optical clarity (with blue tint) because the domain size of the SMA phase is well below 0.1 micron. Property evaluations in the form of cast film were done with such prerequirements.

Diethyl Phthalate as Plasticizer

Diethyl phthalate (DEP) is a good plasticizer for CA. The presence of DEP help increase the toughness of CA films or molding parts. In this CA-SMA system, DEP was found to be a good plasticizer for both CA and SMA. The effect of DEP is, therefore, also considered in property evaluations. Table IX shows the reduction of the glass transition temperature (T_g) of SMA with DEP.

Figure 8 shows the DSC scan of CA films with different amount of DEP cast at room temperature. There is no obvious glass transition for CA under such casting conditions. In the presence of DEP, the melting temperature of CA decreases with increasing amount of plasticizer. The crystallinity of CA is

completely suppressed at a DEP level of 0.4/1.0 (DEP/CA). Figure 9 shows the DSC scans of CA films with different amount of DEP cast at 80°C. Under such casting conditions, there is no time for CA to crystallize. It is interesting to notice the appearance of glass transition temperature of CA. Figure 10 shows the DSC scan of CA-SMA (1:1) grafting products at different amount of DEP cast at 80°C. The glass transition temperature of SMA is much reduced in the presence of DEP. There is quite an amount of DEP partitioned in the SMA phase.

Tensile Properties

Tensile properties of reaction products (CA:SMA = 1:1) in the form of cast films were measured with the SMA grafting conversions of 56% and 66% at equal amount of CA and SMA. Cast films of CA were tested for comparison. Table X shows the test results with/without DEP plasticizer. There is basically no difference in tensile properties for the two alloy films at two SMA grafting conversion; therefore, there is no reason to pursue higher grafting conversion from the point of view of mechanical properties whence the films exhibit a uniform and microscopic phase size. The alloy films showed slightly increased tensile strength in contrast to the most dramatic drop in simple blends under such composition, much increased tensile modulus, but of reduced elongation at break. The difference in those properties between alloy films and CA widens with increasing amount of DEP. The most likely explanation is that DEP partitioned more into the

Table VI   Weight Change of Reaction Product with Reaction Time at Three Water Levels*

Total Weight Change (%)		1 h	2 h	4 h
H₂O/MA (mol/mol)	0	−1.0	−1.1	−1.1
	6	−0.71	−0.73	−0.80
	12	−1.9	−3.7	−7.7

* T = 100°C, (SMA + CA + DMAP)/DMF = (5 + 5 + 0.5)/100 (g/mL).

Table VII   Weight Change of CA at Two Degrees of Substitutions

D.S.	Unit Weight*	Unit Wt. Change
1.0	202	−23.8%
2.0	244	−7.9%
2.5	265	basis

* Modified anhydroglucose.

Table VIII   Effect of Small Amount of Water on the Grafting Conversion of SMA*

H₂O/MA (Molar)	0.0	4.0	6.0
f^w_{SMA} (1 h)	0.45	0.48	0.50
f^w_{SMA} (2 h)	0.66	0.70	0.71

* $T = 110°C$, 5.5 + 5.5 + 0.5 (CA + SMA + DMAP)/100 mL DMF.

Table IX   Glass Transition Temperature of SMA in the Presence of DEP

DEP/SMA (g/g)	0.0/1.0	0.1/1.0	0.2/1.0	0.3/1.0	0.4/1.0
T_g (°C)	118	86	65	56	51

SMA phase than the CA phase. This seems to be supported by the results of moisture adsorption. Increased tensile modulus and decreased elongation at break are both good for improving the dimensional stabilities of the new materials.

Moisture Adsorption

CA is moisture sensitive. Substantial amount of moisture adsorption causes dimensional stability problems in films and fibers. Figure 11 shows the moisture adsorption of CA, cellulose triacetate (CTA), and one reaction product containing 50% SMA at different amount of DEP. The moisture adsorption of CTA was measured for comparison. As we can see the presence of 50% SMA in the new product reduces the moisture adsorption nearly by

half, even lower than CTA. However, there is no synergistic effect on the reduction of moisture adsorption, this is expected because SMA is immiscible with CA. In all cases, the presence of DEP helps reduce further the amount of moisture adsorption.

Dimensional Stability

The dimensional stability of CA is seen from its dimensional change (contraction) in contact with water. In case of film sample, uneven exposure of film surface to water, i.e., water drop on the surface, can destroy the smoothness of the film after the evaporation of the water drops. Changes in the dimensions of film samples under water soaking condition of various temperatures can be used as a measure of the dimensional stability of the new materials. Figures 12–15 show the percentage contractions of film samples with different amount of DEP under several water soaking temperatures. The
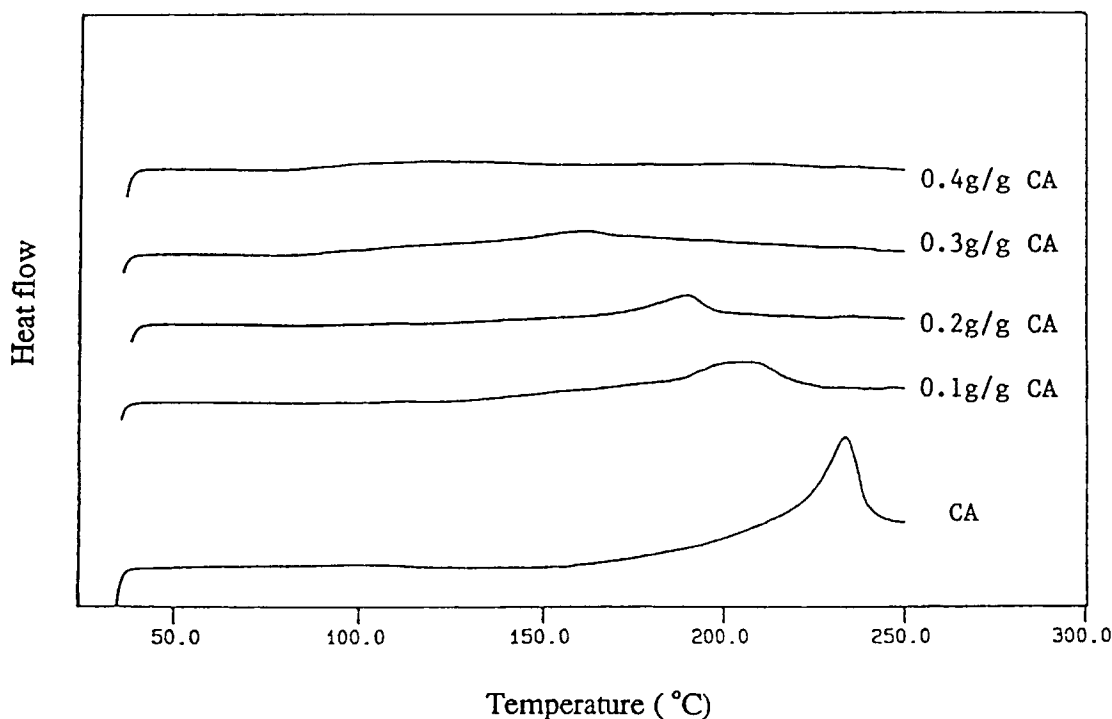
Figure 8   DSC scan of CA films with different amount of DEP cast at room temperature.
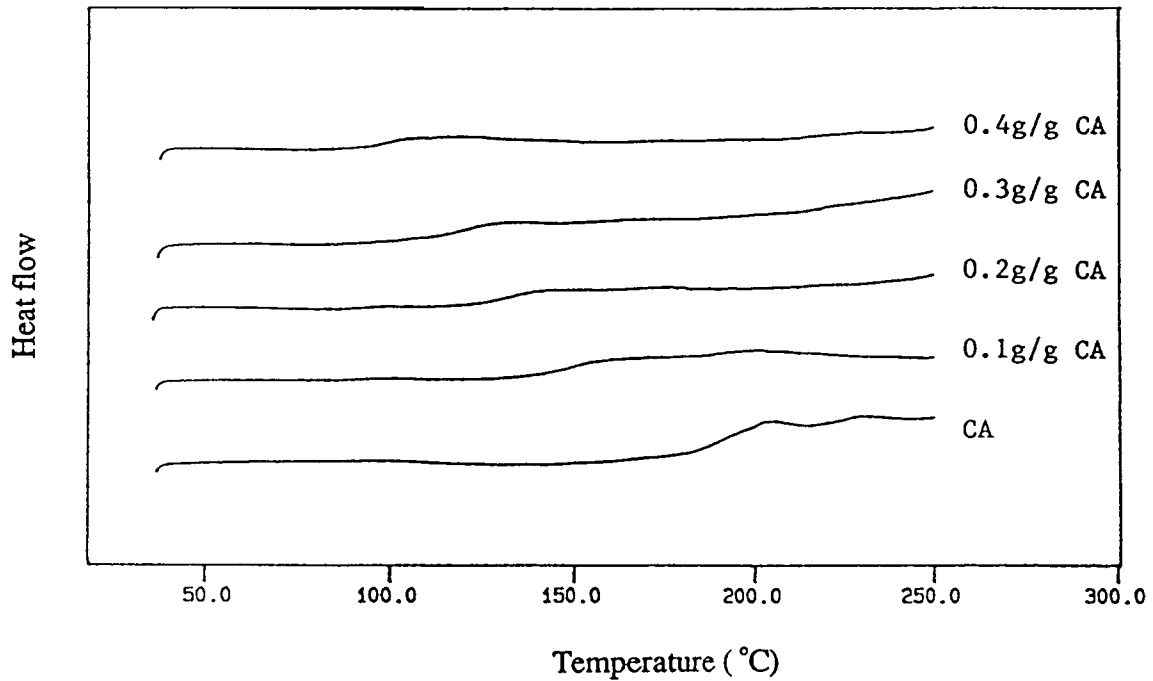
Figure 9   DSC scan of CA films with different amount of DEP cast at 80°C.

grafting products show greatly improved dimensional stability, i.e., at 50% SMA content the reduction of dimensional change is more than 50% in comparison to CA. The dimensional stabilities of the alloys are better or comparable to CTA at various conditions. Further work on the dimensional stabilities of the grafting reaction products in the form of spun fiber is being attempted.
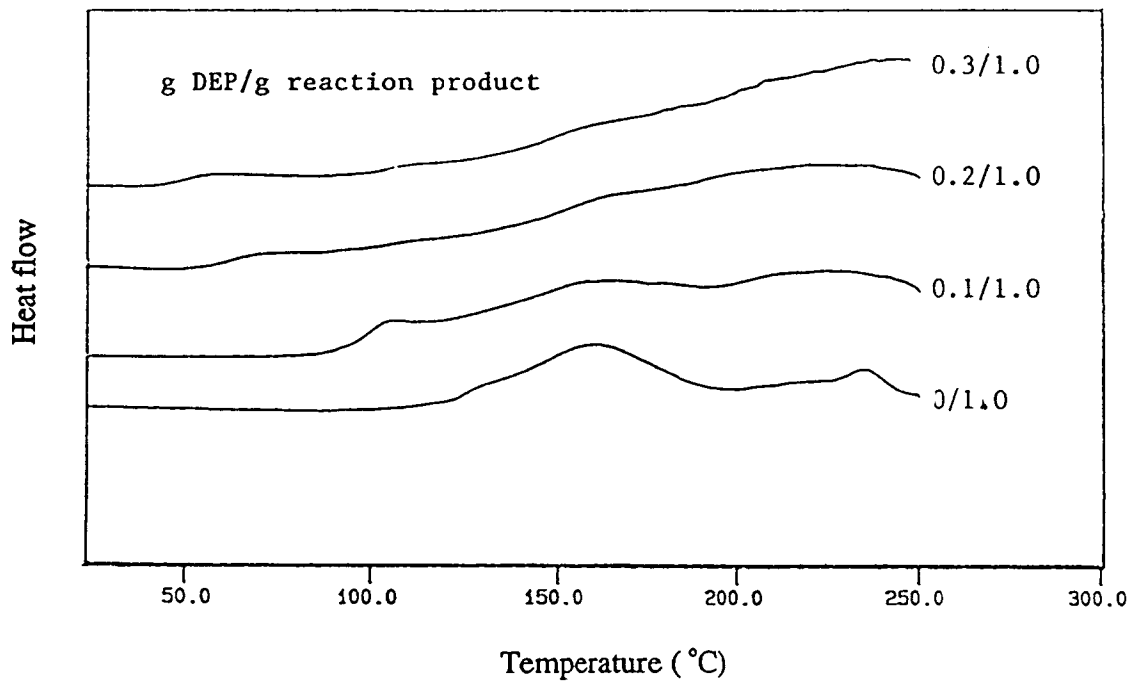

Figure 10   DSC scan of CA-SMA grafting product with different amount of DEP cast at 80°C.

**Table X   Tensile Properties of Cast Films with/without DEP**

Sample	DEP/Sample (g/g)	Tensile Break × 10³ psi	Tensile Modu. × 10³ psi	Elon. % Break	S.D.% Tensile	S.D.% Modu.	S.D.% Elon.
CA : SMA	0.0	7.5	0.39	3.1	8.6	3.6	15.2
(1 : 1)	0.1	6.1	0.36	3.2	7.8	3.2	12.6
$f_{SMA}^w = 0.56$	0.2	5.4	0.34	3.5	7.1	3.3	9.6
CA : SMA	0.0	7.7	0.38	3.3	9.2	3.4	14.4
(1 : 1)	0.1	6.2	0.35	3.5	6.3	3.3	13.3
$f_{SMA}^w = 0.66$	0.2	5.7	0.34	3.9	7.6	4.1	10.6
CA	0.0	7.1	0.35	5.4	6.0	3.0	11.3
	0.1	6.3	0.29	8.7	4.8	2.9	10.8
	0.2	6.1	0.27	10.1	5.1	2.3	13.1

CONCLUSIONS

Grafting reactions of cellulose acetate with styrene maleic anhydride random copolymers are successfully carried out in solution with the aid of DMAP catalyst. The grafting reaction was studied in detail. The phase diagram of the CA-SMA-DMF ternary mixture was constructed first. The dilution of unfavorable contact between CA and SMA is very sensitive to the concentration of polymers dissolved. Increasing the MA level in SMA reduces the im-miscibility between CA and SMA. Analysis on the free energy of mixing by a mean field approach shows qualitatively the order of sensitivity.

The rate of grafting conversion can be described by taking into account the effect of phase separation and the effect of polydispersity of the reactive polymers. Although the effect of polydispersity on the rate of SMA grafting conversion can be analyzed exactly, the rate of SMA grafting conversion cannot be described in a simple manner because information on the phase size and phase size distribution is not
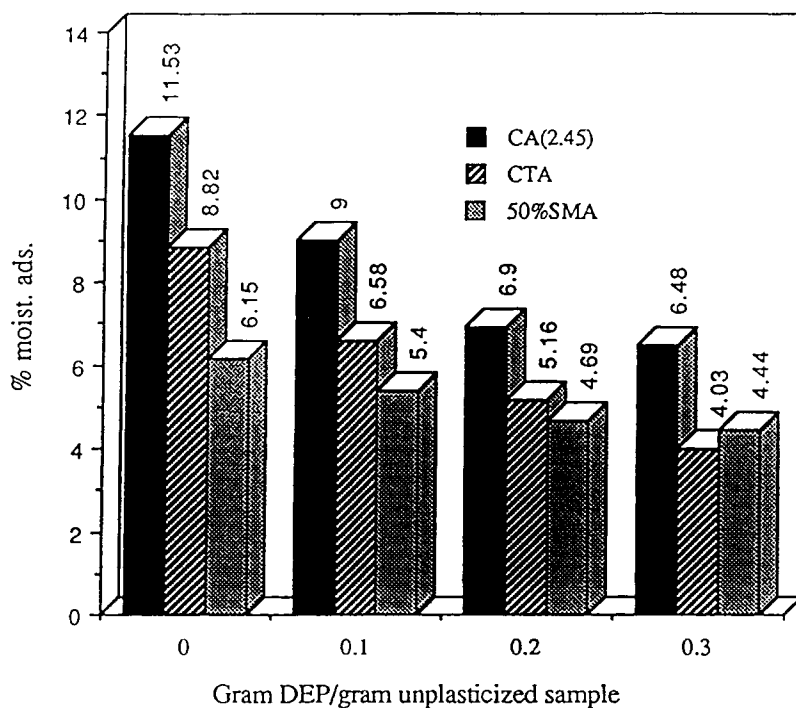
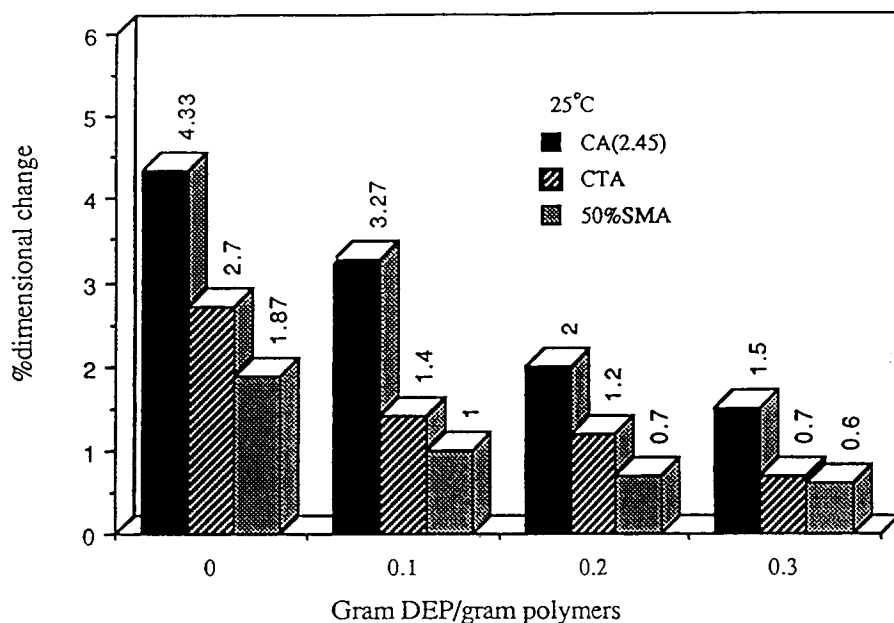**Figure 11**   Comparison of moisture adsorption for CA, CTA, and alloy.

Figure 12 Comparison of dimensional changes at 25°C.

readily available. The complexity of the grafting process is also shown by the dispersion power of the graft copolymers whence they are produced in the course of grafting reaction.

Several parameters affecting the grafting conversion of SMA were looked at separately. The stirring intensity indicated by the stirring speed in the range of 200–600 (rpm) has little effect on the rate of SMA grafting conversion. This is explained by

the low interfacial tension and high solution viscosity; these two important factors tend to smear out the effect of mixing intensity. The grafting reaction is very sensitive to the concentration of polymers in a solution. The concentration of polymers in a solution is limited in order to avoid the reduction of compatibilizing ability of the graft copolymers. There is a first-order relationship on the intrinsic kinetics between the reaction rate and the concen-
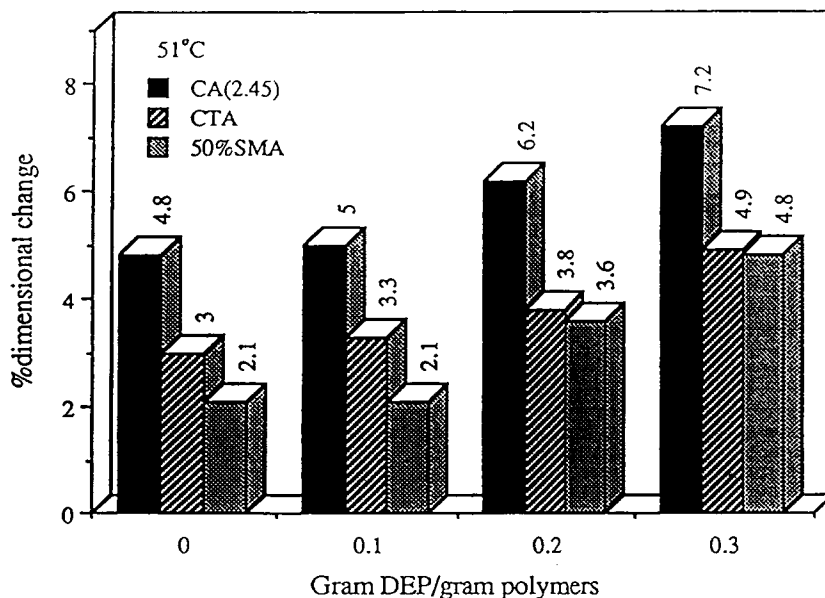

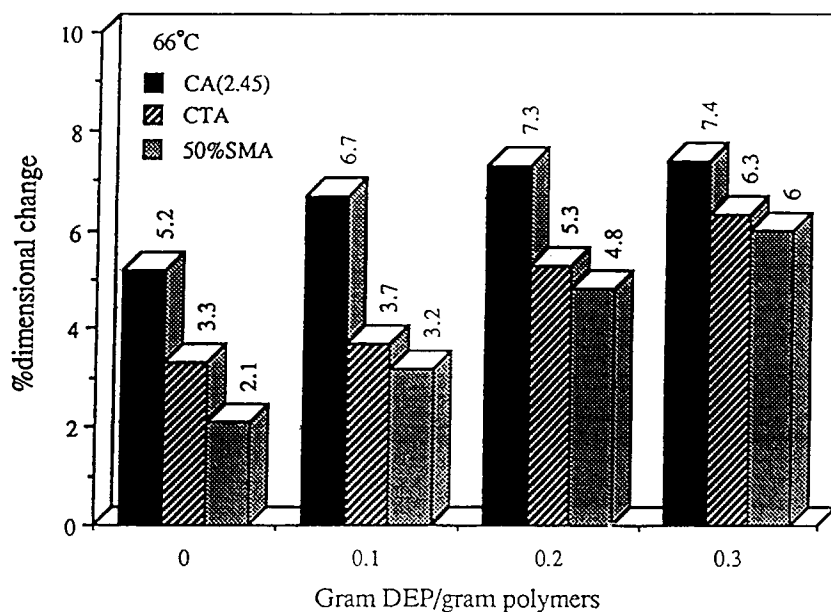**Figure 13** Comparison of dimensional changes at 51°C.

Figure 14 Comparison of dimensional changes at 66°C.

tration of the catalyst. The grafting reaction is quite sensitive to reaction temperatures, so is the MA level in SMA. Only a small amount of water is allowed in this grafting reaction system to avoid excess hydrolysis of CA; however, the presence of a small amount of water promotes grafting reaction.

Tensile properties, moisture adsorption, and the dimensional stability of some grafting reaction products in the form of cast films were measured. The film alloys show slightly improved tensile strength, much increased tensile modulus, and much reduced elongation at break in comparison to CA, with/without the plasticizer. Such tensile properties, together with reduced moisture adsorptions, are good for improving the dimensional stabilities of the grafting products, i.e., in the presence of 50% SMA
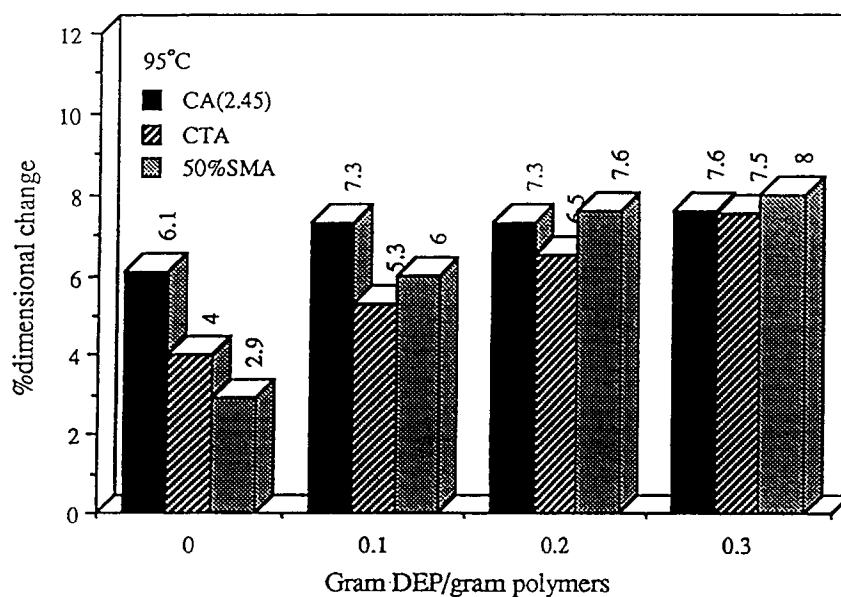

Figure 15 Comparison of dimensional changes at 95°C.

in the alloys, there is more than a 50% reduction on the dimensional changes in comparison to CA with samples tested in the form of cast film under various water soaking conditions. The dimensional stabilities of the film alloys are better or comparable to CTA.

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