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Synthesis and Characterization of Graft-type MCS Resin

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MCS resin, formed from methyl methacrylate (MMA), styrene (St), chlorinated polyethylene (CPE), was synthesized by suspension swelling graft-copolymerization. In this paper, the synthesis conditions of MCS, the effect of different synthesis conditions on graft efficiency, the mechanical properties, rheological behavior and morphology were investigated. The graft efficiency increased with increasing CPE content. The apparent viscosity of melt increased with increasing the content of CPE. The copolymer composition was analyzed by FTS-40 Fourier transform infrared spectrometer and PE-2400 element analyzer. The fractured surface morphology of MCS resin was observed by SEM and X-ray energy dispersive spectroscopy.

Keywords: Graftcopolymerization; Methyl methacrylate (MMA); Styrene (St); Chlorinated polyethylene (CPE); Rheological property

INTRODUCTION

ABS resin, which formed from acrylonitrile (AN), butadiene (B), and styrene (St), is one of the best and widely used construction engineering plastic. ABS resin possesses many superior properties, such as high mechanical strength, dimensional stability, chemical resistance, electrostatic deposition of dust and so on. But there are unsaturated bonds in the ABS molecular, so its weather fastness is poor [1]. The application of ABS is restricted by this weak point. Thus, studies

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about its replacement products are becoming active. The replacement products should possess high application value. MCS resin is a methyl methacrylate (MMA), styrene (St), and chlorinated polyethylene (CPE) terpolymer, which possess fire resistance, weather fastness and some transparency. Recently, there appeared some reports on the synthesis of MCS resin [2–4]. Blending and graft copolymerization are the two main synthesis methods. The blending of copolymer (PMS) formed from MMA and St with CPE, can not produce uniform phase because CPE possessed high melt viscosity. It not only affects the mechanical properties of the material, but also makes processing difficult. The MCS resin, which formed from graft copolymerization, overcomes the shortcoming of blending MCS resin. However, there are no reports on the relationships between graft efficiency and the synthesis condition, the effect of different components on the rheological behavior and morphology.

In this paper, the synthesis conditions of suspension graft copolymerization, the relationships between the components of the copolymer and rheological behavior, mechanical property, morphology were investigated. This work supplied the basis of the synthesis and application for MCS.

EXPERIMENTAL

Materials

The monomers, methyl methacrylate (MMA) and styrene (St), were supplied by Beijing Chemical Reagent Co.. Benzoyl peroxide (BPO), sodium dodecylsulfate (SDS), potassium persulfate ($K_2S_2O_8$), $Al_2(SO_4)_3 \cdot 18H_2O$ and Na_3PO_4 were all of analytically pure grade, and were supplied by Tianjin chemical reagent Co.. Polyvinyl alcohol (PVA), chlorinated polyethylene (CPE, degree of chlorination 35%), tribasic lead sulphate (TLS), dibasic lead phosphite (DLP), barium stearate (BS) and paraffin wax were all commercial grade.

Synthesis and Characterization of PMS

The copolymers of methyl methacrylate with styrene were synthesized by emulsion polymerization. The monomers, MMA and St, were freshly distilled. Sodium dodecylsulfate was used as an emulsifier, and

potassium persulfate was used as initiator. Distilled deionized water (DIW) was used in all polymerizations. All components were purged under N₂ for 20 min. The SDS and DIW were charged into a four-necked glass flask. Then the reaction vessel was heated to 80°C and the mixture stirred. The monomer mixture and initiator (K₂S₂O₈) were added over the course of 1.5 h under a nitrogen atmosphere. At the same time, Na₃PO₄ was added as the pH adjusting agent. The reaction was held at 85°C for additional 3 h. The copolymer was precipitate by the Al₂(SO₄)₃ solution and purified by washing with warm DIW, then it was dried in vacuum. The monomer conversion was usually over 98 percent. The molar mass was determined by gel permeation chromatography (GPC). The composition of copolymer was analyzed by FTS-40 Fourier transform infrared spectrometer and PE-2400 element analyzer [5].

Graft-type MCS Resin Synthesis

CPE was swelled by a mixture of BPO, St and MMA for 12 h. It was then put into a four necked-glass flask which was charged with 0.4 percent PVA solution. The four-necked glass flask, which was equipped with a stirrer, a thermometer and a reflux condenser, was heated to 80°C in N₂ atmosphere. The reaction was held at 80°C for 3 h, and then it was held at 90°C for additional 3 h. The product was purified by warm DIW, and then the product was dried in vacuum. The monomer conversion was usually over 98 percent.

Measurement for Graft Efficiency of Monomers

Graft-type MCS resin and PMS were extracted by Soxhlet Extractor [6], using acetone and tetrahydrofuran mixture (3 : 1 in volume) as the volatile extraction solvent. After extracting 36 h, the PMS was fully dissolved by the extraction solvent, and the bipolymer in the MCS was extracted. Graft copolymer of MCS resin remained after the extraction. The extracted and non-extracted MCS resin were analyzed by FTS-40 Fourier transform infrared spectrometer. Graft efficiency was calculated by:

$$\text{graft efficiency (GE)} = \left(1 - \frac{W_0 - W_1}{M} \right) \times 100\%$$

where W_0 is the weight of MCS resin, W_1 is the weight of graft copolymer, and M is the weight of monomers.

The Rheological Behavior

Lubricant (BS 0.2 parts, wax 0.1 parts) and stabilizer (TLS 2 parts, DLP 1 parts) were added to graft-type MCS resin (100 parts). All components were first mixed in a mixer and then milled on laboratory two-roll mill at a temperature of 180°C for 10 min. Five millimeter-thick plaques were pressed at temperature of 170–190°C. After being cooled in a cooling press, the plaques were tempered at 60°C for 10 h. The rheological behavior of graft-type MCS resin was investigated at 180°C by a Shimadzu koka flow tester [7]. The apparent viscosity η_a of MCS resin was estimated at different loads and constant temperature of 180°C. The flow activation energy was calculated by estimating the apparent viscosity η_a of MCS resin at several temperatures and fixed load of 100 kg/cm². The nozzle diameter was 1 mm, and the nozzle length was 10 mm. The weight of each specimen was 1.3 g.

The Mechanical Properties and Morphology of MCS

The MCS resin was shaped into various experimental samples. The tensile tests were performed using an electronic tensile tester. Tests were conducted at an extension rate of 12.0 mm · min⁻¹ at 25°C and 50% relative humidity. The notch impact tests were carried out using an XCJ-40 impact tester. The fractured surfaces of the tensile and impact specimen were observed by scanning electron microscopy using the method of Zelinger [8]. A combination of SEM and X-ray energy dispersive spectroscopy was used to observe the CPE distribution in MCS resin [9, 10].

RESULTS AND DISCUSSION

Molar Mass and Characterization

The number average molar mass (\bar{M}_n), weight average molar mass (\bar{M}_w) and the width index Q of molar mass distribution ($Q = \bar{M}_w/\bar{M}_n$) were determined by GPC. The results are shown in Table I.

TABLE I Molar mass and distribution in different composition

Weight ratio	$\bar{M}_n, 10^5$	$\bar{M}_w, 10^5$	Q
MMA:St = 1:1	1.25	3.82	3.05
MMA:St = 1.5:1	1.21	2.96	2.43
MMA:St = 2.2:1	0.80	2.11	2.12

As seen from Table I, the \bar{M}_n of MMA/St copolymer is in the range of $0.80 - 1.25 \times 10^5$ g/mol, \bar{M}_n decreased as the content of MMA increasing. The \bar{M}_w is in the range of $2.11 - 3.82 \times 10^5$ g/mol, but \bar{M}_w and Q decrease as the content of MMA increasing.

The composition of copolymer was analyzed by FTS-40 Fourier transform infrared spectrometer and PE-2400 element analyzer.

As shown in Figure 1a, the characteristic absorption peak of ester group in the MMA is 1725 cm^{-1} , and benzene ring in St is 760 and 700 cm^{-1} .

The analytical results as seen from Table II show that the composition of bipolymer is similar to the recipe of the monomer feed.

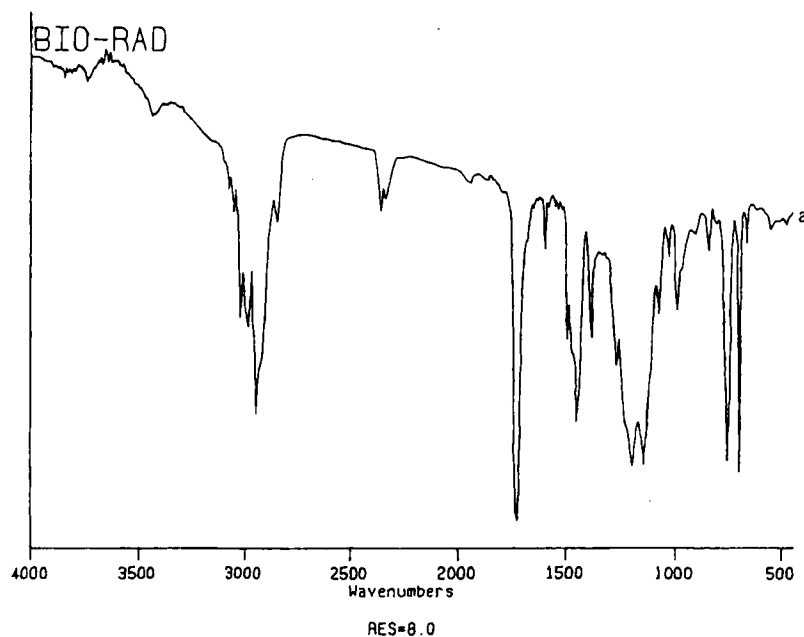


FIGURE 1 Infrared spectrometer PMS (a) and MCS resin (b,c).

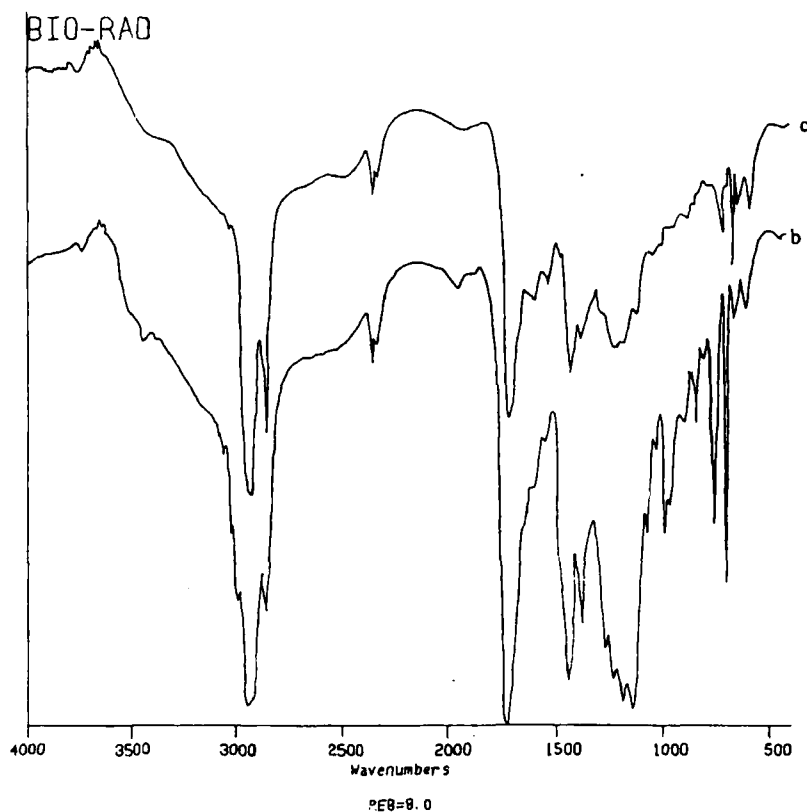


FIGURE I (Continued).

TABLE II The components of bipolymer

Samples		C, %	H, %	O, %
MMA:St = 1:1	T_v	76.11	7.84	15.98
	E_d	75.68	7.90	15.92
MMA:St = 1.5:1	T_v	72.88	7.95	19.16
	E_d	72.44	8.01	19.05

Where T_v is theoretical value, E_d is experimental data.

The infrared spectra of non-extracted and extracted graft-type MCS resin were shown in Figure 1b and Figure 1c, respectively. As seen from Figure 1c, extracted MCS resin possesses a characteristic absorption peak of ester group in MMA is 1725 cm^{-1} , benzene ring in St

is 760 and 700 cm^{-1} , Cl element in CPE is 662 and 618 cm^{-1} . The result shows that graft copolymerization must take place. CPE was not lost at the experimental condition, so the composition of the terpolymer was identical with the recipe used in the experimental section.

Effect of Concentration of BPO and Content of CPE on Graft Efficiency

When the content ratio of MMA, St, CPE was 2:2:1 (in Wt.) and other conditions were not changed, the graft efficiency was estimated at different concentrations of benzoyl peroxide. When the BPO concentration were 0.5%, 1.0%, 1.5%, the graft efficiencies were 2.19%, 3.61%, 5.01%, respectively. The graft efficiency increased with increasing concentration of benzoyl peroxide because as the radical concentration increased, and reaction rate increased and the numbers of graft point increased at the same time.

When the content ratio of MMA, St was 1:1 (in Wt.), 0.5 percent BPO was fixed, the graft efficiency was estimated at different contents of CPE. The data are shown in Table III.

The result shows that the graft efficiency increased with increasing content of CPE. Monomer absorb and penetrate into the CPE particle surface when it is swelled in the mixture of monomer. When reaction took place, the reaction field was mostly on the surface of CPE. The higher the content of CPE, the higher was the absorption ratio on the surface of CPE. The monomers which took part in the reaction easily reached to CPE chains, and graft polymerization easily took place, so that the graft efficiency increased.

Rheological Behavior of MCS Resin

The rheological behavior of MCS was investigated by a KOKA Flow Tester. The experimental temperature was fixed at 180°C, with experimental loads of 100, 110, 120, 130 kg/cm^2 , respectively. The

TABLE III Graft efficiency and content of CPE

CPE content	15%	20%	25%	30%
GE	1.17	2.19	5.48	12.4

weight ratio St : MMA was 1 : 1, and benzoyl peroxide was 0.5 percent (in monomer Wt.), the content of CPE was 10%, 15%, 20%, 25%, 30%, the experiments were carried out, and the samples were numbered as A, B, C, D and E, respectively.

The apparent shear rate $\dot{\gamma}_w$ and apparent viscosity η_a were calculated using the three following equations. Effective shear stress at the wall of the nozzle:

$$\tau_w = \frac{P \cdot r}{2L} \quad (1)$$

where P is applied pressure (Kg/cm²), r is nozzle radius (cm), L is nozzle length (cm).

The efflux rate is given by:

$$Q = \frac{h \cdot S}{t} \text{ (cm}^3\text{/s)} \quad (2)$$

where h is downward displacement of plunger (cm), S is area of plunger (cm²), t is effluent time of melt(s).

The apparent shear rate at the wall of the nozzle was calculated by:

$$\dot{\gamma}_w = \frac{4Q}{\pi r^3} \text{ (s}^{-1}\text{)} \quad (3)$$

According to Ostwald-de Waele Power-law equation [11]:

$$\tau = k\dot{\gamma}^n \quad (4)$$

The non-Newtonian parameter-flow power n can be obtained from the plot of $\ln \tau_w$ versus $\ln \dot{\gamma}_w$.

According to Ref. [12], $\dot{\gamma}_w$ was obtained for non-Newtonian from the following equation:

$$\dot{\gamma}_w' = \frac{3n + 1}{4n} \dot{\gamma}_w \quad (5)$$

The apparent viscosity is given by:

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \cdot 9.8 \times 10^5 \text{ (poise)} \quad (6)$$

Figure 2 is a plot of $\ln \eta_a$ versus $\ln \dot{\gamma}_w'$.

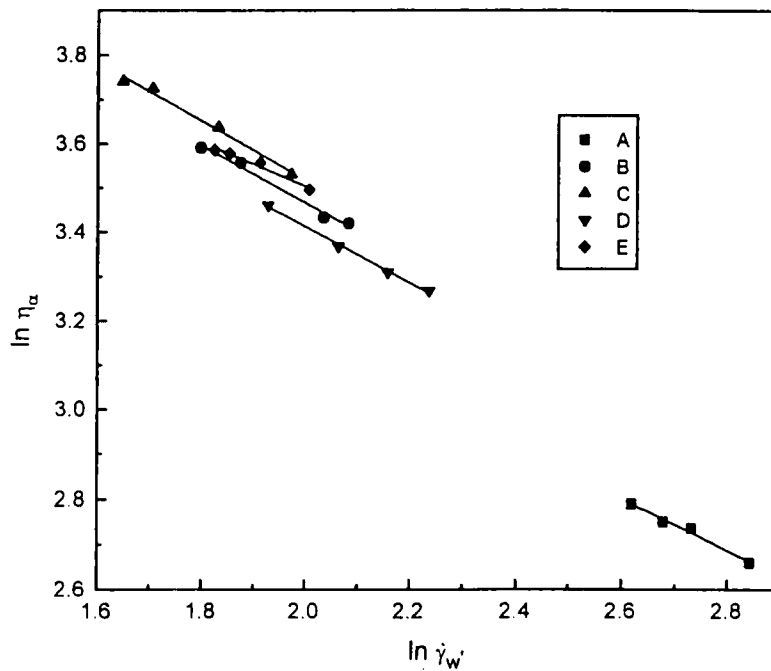


FIGURE 2 Relationship between apparent viscosity of graft-type MCS resin and content of CPE in melt with shear at 180°C. (specimens: A, B, C, D, E).

It was found that the flow behavior of MCS resin in the melt reflects the behavior of a pseudoplastic liquid. The apparent viscosity (η_a) reaches the highest point when the content of CPE is 20%. At this point, the melt flow is the slowest. It may be explained that at this point the system compatibility is the best. CPE, as the rubber phase, is distributed in the continuous phase plastic. When CPE content grows over 20%, phase separation took place, and the apparent viscosity decreased.

The experimental load was fixed 100 kg, and the experimental temperature were, 180, 185, 190, 200°C, respectively. The activation energy for flow was obtained from $\eta_a = A \cdot e^{(E_a/RT)}$ [11]. The plots of $\ln \eta_a$ versus $1/T$ are given in Figure 3.

The activation energy for flow of samples (A, B, C, D and E) were 159.8, 170.8, 214.5, 184.9 and 172.1 kJ/mol, respectively. The change of the activation energy for flow can explain the apparent changes in

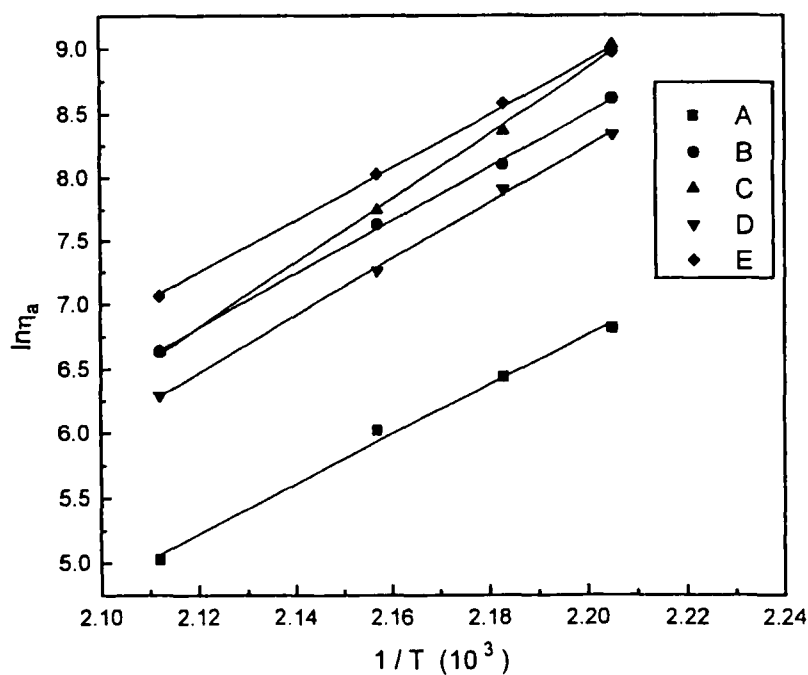


FIGURE 3 The relationship between flow activation energy of MCS with content of CPE (specimens: A, B, C, D, E).

the viscosity of the melt. The larger the activation energy became, the larger was the apparent viscosity.

Mechanical Properties and Morphology

The mechanical properties of graft-type MCS resin were estimated. The changes in impact strength and tensile strength with changes in CPE content are shown in Figure 4.

As seen from Figure 4, the tensile strength decreased, but impact strength increased with increasing content of CPE. The graft-type MCS resin formed a sea/island structure. When the content of CPE is lower, the distance between islands is larger. The crazes formed at the surface of the CPE under external actions could not reach one another, thus the brittle-tough transition could not happen. The distance between islands got shorter as the content of CPE increased.

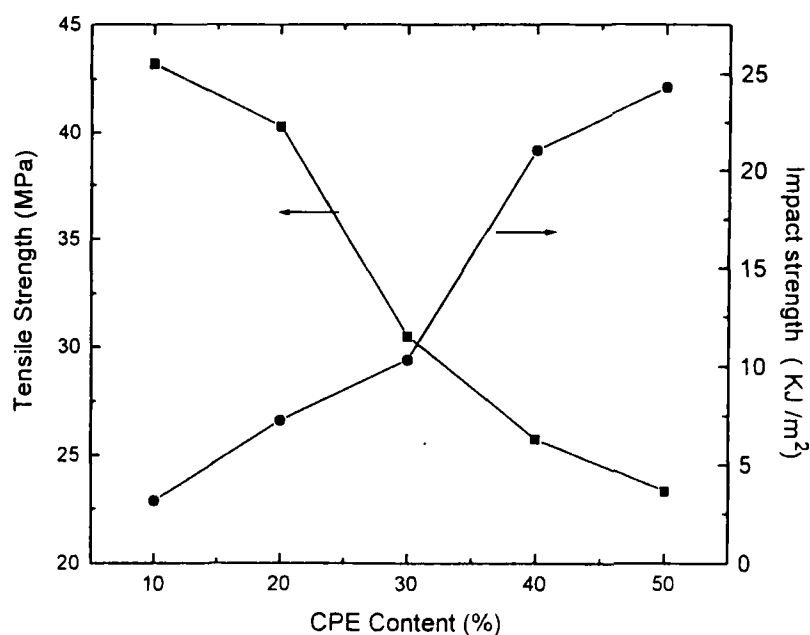


FIGURE 4 The relationship of impact strength and tensile strength with content of CPE.

The crazes absorbed lots of energy. And could not develop into cracks. This led to the impact strength increasing with increased content of CPE.

The dependence of impact strength and tensile strength on the content ratio of MMA/St, at 20% CPE is shown in Figure 5.

As seen from Figure 5, the tensile strength and impact strength both increased with the ratio of MMA/St (in Wt.). Because MMA is compatible with CPE, the compatibility improved with increasing MMA content.

Figure 6 shows the morphology of tensile fractured surface.

As seen in Figure 6(a), some parts of the flat surface exhibit a brittle break, which is the fractured surface of PMS copolymer. Other parts of the fracture surface have some holes and exhibit toughening break. The fracture surface of (b) exhibits a toughened break. That is, when other conditions were not changed, MCS resin become toughened (b) from brittle (a) with increases in the content of CPE.

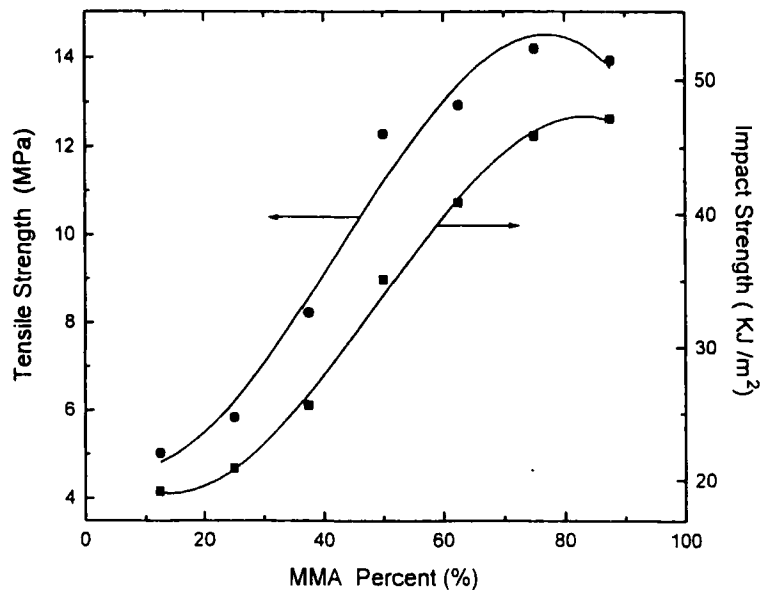
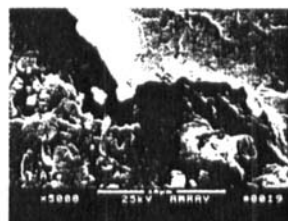
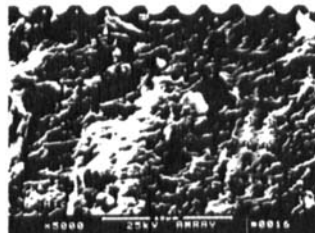


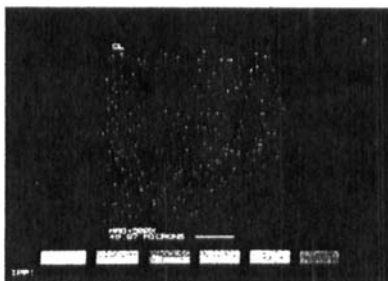
FIGURE 5 The relationship of impact strength and tensile strength with the weight ratio of MMA/St, at 20% CPE.



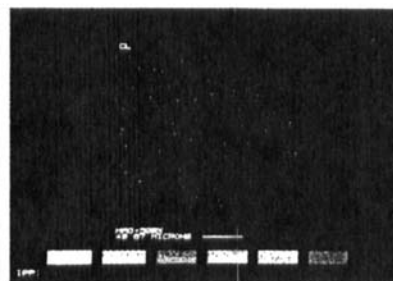
a content of CPE (10%)



b content of CPE (20%)



c content of CPE (10%)



d content of CPE (20%)

FIGURE 6 Scanning electron micrographs of tensile fractured surface of the blends (a, b), and graph (c, d) of CPE distribution in the MCS resin.

Figures 6(c) and (d) show the CPE distribution in the MCS resin. The CPE distribution was more uniform in Figure 6(d) than in Figure 6(c).

CONCLUSIONS

- (1) Graft efficiency of graft-type MCS resin shows dependence on the concentration of benzoyl peroxide and CPE content. Graft efficiency increased with increasing concentration of benzoyl peroxide, and with the increasing content of CPE.
- (2) When the weight ratio of MMA/St is fixed, the impact strength increased with the increasing content of CPE, and the apparent viscosity reached the highest point when the content of CPE was 20%.
- (3) When the content of CPE (20%) was fixed, the impact strength of the resin increased with increasing MMA content in the range of MMA/St weight percent of 10~80.

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