

Synthesis of Core-Shell Emulsion Copolymer of Poly(butyl acrylate)/ α -Methyl Styrene-co-Methyl Acrylate, with Application as Processing Aid of Poly(vinyl chloride)

ZHITING LI,* JUNGANG GAO, KUILIN DENG, and HONG GUO ZHU

Department of Chemistry, Hebei University, Hebei Province, Baoding, People's Republic of China

SYNOPSIS

The core-shell grafting copolymer of α -methyl styrene-methyl acrylate on poly(butyl acrylate) was synthesized. The particle morphology of latex and core-shell grafting polymerization was investigated as a function of: (a) reaction temperature; (b) initiator concentration used in the secondary polymerization; (c) monomer to polymer ratio; (d) emulsifier concentration. The compatibility of this copolymer with poly(vinyl chloride) (PVC) was determined by the method of solubility parameter and scanning electron microscopy. The rheological behavior of the blend of this copolymer with PVC was investigated. The mechanical properties of the blend were determined. The results show that this copolymer can be used as processing aid for PVC. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The modification of the properties of poly(vinyl chloride) (PVC, i.e., a "hard" polymer) by adding another polymer is a rather well-known method currently in practice. These modifiers may be divided into two basic groups. The first one involves rubber-like polymers and copolymers added to PVC to improve its mechanical properties, in particular its toughness. The structure of the materials prepared in this way, and the mechanism of the action of the modifiers, have been the object of intensive investigations by numerous authors. The other group of modifiers involves polymers used for the modification of PVC under the general denomination of processing aids. Although the mechanical properties of hard PVC are only insignificantly changed at room temperature by the addition of a modifier, the processing operations (milling, calendaring, extrusion, blow molding, and the like) in PVC melts are significantly facilitated.

Poly(methyl methacrylate) (PMMA) type modifier are usually used as processing aids of hard PVC.¹⁻³ The oligomer of poly(α -methyl styrene)

(PMS) are also used as processing aids for various resins,⁴ but copolymers of α -methyl styrene (α -MS) are not used as processing aids for PVC. Many core-shell copolymers have been synthesized and investigated,^{5,6} but the synthesis of core-shell copolymer of α -MS-methyl acrylate (MA) shell (PMSMA) on a poly(butyl acrylate) (PBA) core latex has not been suggested and has not been used as a processing aid for PVC to date.

The particle morphology in a core-shell emulsion copolymerization process is a key to control of the performance of a latex system in a given application. Many of the emulsion polymerization process parameters are known to affect the particle morphology: for example, reactivity ratios and water solubility of the monomers; mode and schedule of monomer addition; type, amount, and mode of addition of other ingredients such as emulsifier, initiator, chain transfer, or cross-linking agent; temperature; and whether the polymerization process is seeded. Much of the technological development in the emulsion polymerization field has been directed toward the manipulation of a number of these parameters in the preparation of a latex system with a suitable particle morphology for a certain application.

The object and purpose of this article is to describe the synthesis of the core-shell PBA/PMSMA

* To whom correspondence should be addressed.

copolymer latex and to investigate use as a processing aid for PVC. The miscibility of the PBA/PMSMA copolymer with PVC, its rheological behavior, and the mechanical properties of mixtures of PBA/PMSMA copolymer with PVC were investigated.

EXPERIMENTAL

Materials

The monomers, butyl acrylate (BA), MA, and divinylbenzene (DVB) were washed with aqueous sodium hydroxide to remove the inhibitor. The BA, MA, and α -MS were freshly distilled. Sodium dodecylsulfate (SDS) was used as emulsifier. Potassium persulfate ($K_2S_2O_8$) was used as initiator. All monomer, SDS, and $K_2S_2O_8$ were supplied by Beijing Chemical Reagent Company. Solvents used to determine the intrinsic viscosity of copolymers of α -MS and MA, and $Al_2(SO_4)_3 \cdot 18H_2O$, Na_3PO_4 were all analytically pure grade. Distilled deionized water (DIW) was used in all polymerizations. The chain transfer agent, tertiary dodecylmercaptan (TDM), was used as received. PVC (Yanshan, Chemical Co.), tribasic lead sulphate (TLS), dibasic lead phosphite (DLP), barium stearate (BS), and wax were all commercial grade, and were supplied by TianJin Chemical Co.

Core-Shell Emulsion Polymerization

The BA seed latex particles were made using recipes in Table I and all components were purged under N_2 for 10 min. The SDS and DIW were charged to a 4-necked glass flask (1 L), followed by a part of the BA/DVB mixture. The reaction vessel was then heated to 80°C and the mixture was stirred. The $K_2S_2O_8$ solution was added. After 15 min, the remainder of the BA/DVB mixture was added over the course of 1.5 h under nitrogen atmosphere. The reaction was then held at 85°C for an additional 2

Table I Recipe for Preparation of PBA Seed Latex

Ingredients	Recipe (g)
BA	120
DVB	5
Water	400
$K_2S_2O_8$	0.6
SDS	6
Na_3PO_4	0.8

Table II Recipe for Preparation of PBA/PMSMA Core-Shell Latex

Ingredients	Recipe (g)
Seed latex	520
α -MS	74
MA	46
$K_2S_2O_8$	0.6
Na_3PO_4	0.8
Water	100

h. The sample was precipitated by $Al_2(SO_4)_3$ solution and purified by washing with warm distilled deionized water, then dried *in vacuo*. The conversion was measured gravimetrically, usually 89–94%.

Two-stage latex polymers were prepared by charging the prepurged seed latex to a four-necked glass flask, using recipes in Table II, the mixture of α -MS, MA, and $K_2S_2O_8$ were added dropwise over 1.5 h. The reaction was held at 80°C for an additional 3 h. The Na_3PO_4 solution was used to control the pH of the reaction system at 6–7. After the polymerization reaction, an $Al_2(SO_4)_3$ solution was added to precipitate the copolymer latex. The products were purified by washing with warm distilled deionized water, and then dried *in vacuo*.

The overall percent conversion was measured gravimetrically, it was usually 93–95%. The α -MS percent conversion was determined by a bromination method.⁷

Determination of Glass-Transition Temperature (T_g)

Differential scanning calorimetry (DSC) was performed using a Shimadzu DT-40 Thermal Analyzer. The sample size was 4–6 mg of the dried latex copolymer. A heating rate of 20°C/min was used in all cases. The T_g of the copolymers were determined over a temperature range of –150–150°C.

Determination of Degree of Grafting

The degree of grafting was determined by the method of extraction,⁸ using a Soxhlet extractor with cyclohexane as the volatile extraction solvent. The ungrafted PBA was dissolved in the solvent and departed from the core-shell copolymer. The degree of grafting was calculated using a mass balance. Under the same condition, the dried seed latex was extracted. It was shown that the gel of PBA was not yielded.

Determination of Intrinsic Viscosity

The copolymer latex (PMSMA) with the same composition as the shell was synthesized by emulsion polymerization. This copolymer was dried *in vacuo* at 50°C, and then dissolved in a series of solvents. The viscosities were determined by a Ubbelohde viscometer.

Electron Microscopy

The morphology and particle size of the seed latex and core-shell latex particles was determined by transmission electron microscopy.^{5,6} The morphology of polymer mixture of PVC with PBA/PMSMA copolymer was studied by scanning electron microscopy using the method of Zelinger.² The same sample was put in acetone for 8 h, then was analyzed by the scanning electron microscopy. The miscibility of PBA/PMSMA copolymer with PVC was investigated.

Preparation of Samples

PVC was mixed with a determined quantity of processing aid (in wt %), and a lubricant (BS) and a stabilizer (TLS, DLP) was added quantitatively to this mixture. All components were first mixed in a mixer at room temperature and then milled on a laboratory two-roll mill at temperatures of 155–175°C for 10 min. Two-millimeter thick plates were pressed at temperatures of 170–190°C. After cooling in a cooling press the plates were tempered for a period of 12 h at 90°C. Dumbbell-shaped samples for tensile tests were cut from the plates. The sample for notch impact tests and hardness tests are all 120 × 15 × 5 mm.

Determination of Rheological Behavior

The rheological behavior of mixtures of PBA/PMSMA latex polymer with PVC was investigated by a Shimadzu Koka Flow Tester.^{9,10} The fixed temperature method was used. The nozzle diameter was 1 mm and the nozzle length was 2.38 mm. The weight of the test specimen was 1.5 g.

Determination of Mechanical Properties

Tensile strength testing was performed using an electronic tensile tester. Dogbone-shaped samples for tensile tests were cut from the plates, the test portion of which was 25-mm long with a cross section of 2 × 7 mm. Tests were conducted at an extension rate of 12.0 mm/min at 25°C and 50% relative hu-

midity. The notch impact tests and hardness tests were carried out on an X CJ-40 impact tester and a Brinell hardness tester, respectively.

RESULTS AND DISCUSSION

Effect of Emulsion Polymerization on Grafting Reaction

The grafting reaction of the second stage onto the seed latex particle was the primary concern in this study. In the PBA/PMSMA core-shell emulsion polymerization, the grafting reaction can occur through reaction of the residual double bond in PBA or by a hydrogen abstraction mechanism in the allyl position. The effect of emulsion polymerization parameters on the grafting reaction are discussed.

Effect of Reaction Temperature

When the concentration of initiator and emulsifier and the ratio of core shell were not taken into account, using the recipe in Table II and 50/50 core-shell ratio, the emulsion polymerization as carried out at different temperatures. The proportion of α -MSMA grafted onto the PBA seed latex is shown in Figure 1. It shows the amount of grafting increases with increasing temperature, but it has a maximum in the grafting level at about 80°C. A possible explanation is the chain of PBA and initiator were acted upon when the temperature rose, but the probability for the rate of copolymer coupling termination is increased at higher temperature.

Effect of Initiator Concentration

Figure 2 shows the proportion of PMSMA grafted onto the PBA core versus the concentration of ini-

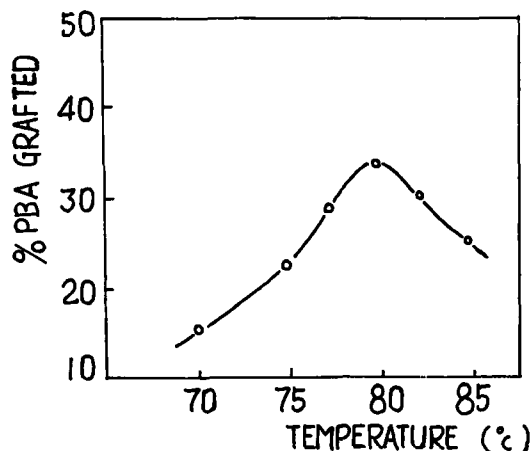


Figure 1 Temperature dependence of % PBA grafted by PMSMA for 50/50 core-shell emulsion polymerization.

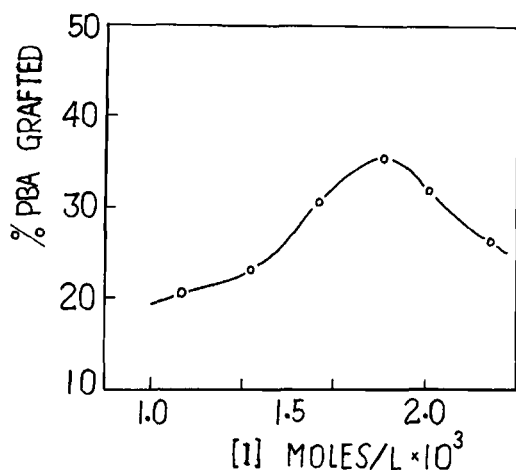


Figure 2 % PBA grafted versus concentration of initiator for a 50/50 PBA/PMSMA core-shell latex.

tiator (mol/L) used in the seeded emulsion polymerization. The amount of grafting increased with an increasing amount of initiators, but it also exhibited a maximum. When the concentration of initiator is higher than 1.8×10^{-3} mol/L, the amount of grafting decreased with increasing concentrations of initiator. It is believed the increasing concentrations of monomer radical groups increases the rate of transition to PBA, but the probability for the rate of α -MSMA copolymer termination by combination (coupling) of radicals is greater than the rate of transfer for the copolymer radical to PBA, thus accounting for the reduced levels of grafting with increased initiator concentration. Therefore, more α -MSMA copolymer is produced than graft copolymer.

Effect of Emulsifier Concentration

When the concentration of BA and initiator were used in the recipe (Table I) and used in the 50/50

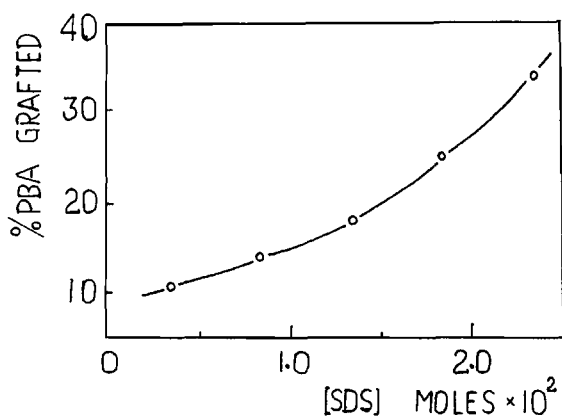


Figure 3 % PBA grafted versus surface area of the seed latex for a 50/50 PBA/PMSMA core-shell latex.

core-shell ratio, a series of experiments were run at various seed surface areas or at different emulsifier concentration for seed latex. As shown in Figure 3, the percentage of grafted PBA by α -MSMA copolymer increases linearly with increasing specific surface area of the seed latex. The result indicate that the grafting reaction is a surface-area based phenomenon, the site of initiation being in either the aqueous phase or the adsorbed emulsifier layer.⁵

Effect of Monomer to Polymer Ratio

At the same concentration of emulsifier, a series of polymerizations were carried out at different core-shell ratios. The percentage of grafted PBA by α -MSMA copolymer are listed in Table III. From the data presented in Table III, it is obvious that the amount of grafted PBA by MSMA copolymer increased as the shell-core ratio increased at the lower shell-core ratio; but the amount of grafted PBA did not increase with increasing shell-core ratio at the higher shell-core, the amount of grafted PMSMA onto PBA decreased when the shell-core increased. In order to explain the reduced levels of grafted PMSMA onto PBA as a function of increasing in shell-core ratio, recall the experiment in which grafting was investigated as a function of seed surface area. From these studies, it was concluded that grafting is a surface-controlled process. This process involves initiation either in the aqueous phase or more likely, in the adsorbed emulsifier layer, followed by capture of the growing radicals by existing monomer-swollen particles. As grafting proceeds and a certain shell thickness of the second stage polymer is reached, the grafting reaction becomes less probable due to the reduced availability of PBA. The morphology of the core-shell copolymer (PBA/PMSMA) were investigated. The particles of seed latex and core-shell copolymer latex all showed spherical geometry. The diameter of seed latex particles are usually 98–100 nm, and the diameter of core-shell copolymer latex particles are usually 126–133 nm.

The T_g of grafted copolymers for latex prepared at different core-shell ratios were determined by

Table III Percentage of Grafted PBA by PMSMA Copolymer At Different Shell-Core Ratios and the T_g of PBA/PMSMA Copolymer

Shell-core ratio	0.7	1.1	1.5	1.9	2.3
Grafting (%)	9.0	24.9	33.2	35.1	35.2
T_g (°C)		8.6	10.8	12.2	

DSC; the T_g are shown in Table III. As is seen from Table III, the T_g increased with increasing the shell-core ratio because higher T_g polymer is present in this copolymer as a shell.

Miscibility of α -MSMA Copolymer with PVC and Morphology of Mixtures

The miscibility of PBA/PMSMA copolymer with PVC can be estimated by the determination of the solubility parameter.¹¹ In order to know the miscibility of the shell (i.e. PMSMA) with PVC, the solubility parameter of PMSMA was determined by measuring the intrinsic viscosity in a series of solvents.¹² The shell polymer of PMSMA was synthesized by emulsion polymerization. Intrinsic viscosity $[\eta]$ was measured to dissolve PMSMA in a series of solvents (Table IV). As is seen from Table IV, the $[\eta]$ increases with increasing solubility of polymer in the solvent. The $[\eta]$ values are plotted against the solubility parameter δ_s of solvents used (Fig. 4), the maximum corresponds to the solubility parameter δ_p of PMSMA. From Figure 4, we obtained a δ_p of PMSMA of $19.8 \text{ J}^{1/2}/\text{cm}^{3/2}$.

The solubility parameter δ_p can be calculated from the molar attraction constant of constitutive groups¹² as

$$\delta_p = \sqrt{\sum F_{pi}^2} / \nu. \quad (1)$$

The δ_p value of PMSMA obtained from this calculation is $19.61 \text{ J}^{1/2}/\text{cm}^{3/2}$. These δ_p value are approximately the same as the solubility parameter for PVC, 19.4.¹³ Therefore, PMSMA is compatible with PVC.

The morphology of mixtures of PBA/PMSMA copolymer (core-shell ratio: 1 : 1.2) with PVC is shown in Figure 5. As is seen from Figure 5, the compatibility of PVC with PBA/PMSMA is good.

Table IV Intrinsic Viscosity $[\eta]$ of PMSMA in Various Solvents and Solubility Parameters δ_s of Solvents

Solvent	δ_s ($\text{J}^{1/2}/\text{cm}^{3/2}$)	$[\eta]$ (mL/g)
Carbon tetrachloride	17.69	46.39
Ethyl acetate	18.70	55.11
Styrene	19.06	59.20
Tetrahydrofuran	19.47	64.23
Acetone	20.03	64.96
Dioxane	20.50	64.37
Cyclohexanone	21.36	62.55
Dimethylformamide	23.98	56.86

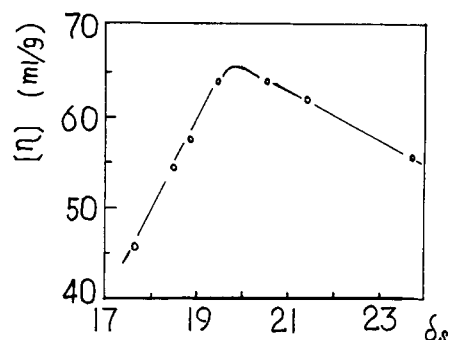


Figure 4 Relationship between intrinsic viscosity $[\eta]$ with solubility parameter δ_s of solvents.

The mixture of the PBA/PMSMA with PVC is uniform. The molecular chains expand each other on the boundary of PVC with some PBA/PMSMA particles. The holes did not appear on the sample of the mixture after it was put in acetone for 8 h (because PBA/PMSMA can be dissolved by acetone); it was only swelled by solvent.

Rheological Behavior of Mixture of PBA/PMSMA with PVC

The experimental specimens were made using the recipes shown in Table V.

The experimental temperature was fixed at 180°C , with experimental loads of 70, 80, 90, and 100 kg, respectively. The apparent shear stress τ_w , apparent shear rate r_w , and apparent viscosity η_a were calculated using the following equations. The effective shear stress at wall of nozzle is

$$\tau_w = \frac{Pr}{ZL} \quad (2)$$

where P is applied pressure (kg/cm^2); r is nozzle radius (cm); and L is nozzle length (cm).

The efflux rate is given by:

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

where h is downward displacement of plunger (cm); s is area of plunger (cm^2); and t is effluent time of melt (s).

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

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

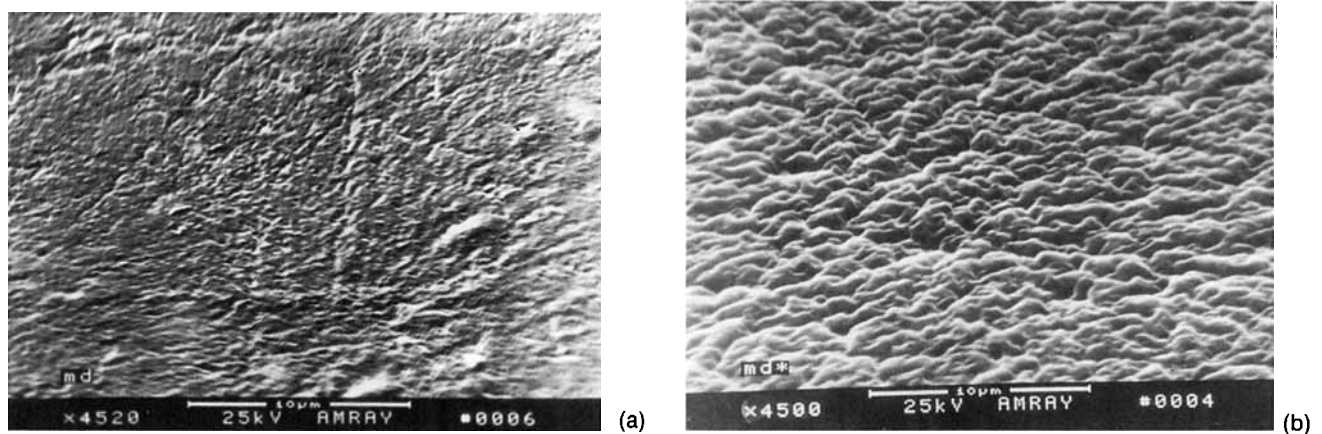


Figure 5 Scanning electron micrographs of mixture of PVC with PBA/PMSMA copolymer in a 100/10 ratio. (a) electron micrograph for mixture of PBA/PMSMA core-shell copolymer with PVC; (b) electron micrograph after the sample was put into acetone for 8 h.

The apparent viscosity is given by:

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

A plot of $\ln \eta_a$ vs. $\ln \dot{\gamma}_w$ is given in Figure 6. As is seen from Figure 6, the apparent viscosity η_a decreases with increasing shear rate. It is shown that the flow behavior of this mixture in melt is the behavior of a pseudoplastic liquid. When the PBA/PMSMA copolymer was used as a processing aid

for PVC, the melt viscosity fell and decreased with increasing the used amounts of the aid. That is, if this copolymer is used as a processing aid for PVC, it can drop the processing temperature for hard PVC.

Mechanical Properties

The notch impact strength of these specimens for mixing different amounts of PBA/PMSMA are shown in Figure 7. As is seen from Figure 7, the impact strength increases with increasing amounts

Table V Recipes of Components About Experimental Specimens

Specimen	0	1	2	3	4	5
PVC (w)	100	100	100	100	100	100
TLS	3	3	3	3	3	3
DLP	2	2	2	2	2	2
Wax	0.2	0.2	0.2	0.2	0.2	0.2
BS	2	2	2	2	2	2
PBA/PMSMA	0	4	6	8	10	12

Note: the core-shell ratio of PBA/PMSMA is 1 : 1.2.

Table VI Tensile Strength and Hardness of Improved PVC

Property	Species					
	0	1	2	3	4	5
Tensile strength (N/cm ²)	4310	4268	4034	3912	3668	3588
Hardness (kg/mm ²)	25.5	23.4	23.7	23.2	22.2	21.3

of PBA/PMSMA. Therefore, PBA/PMSMA not only drops the processing temperature of hard PVC and η_a , but it can also increase the impact strength of hard PVC. This property is not the same as general commercial resistant impact aid, which is to increase the impact strength of hard PVC, but the processing viscosity η_a is also increased.⁹ It is also not the same for the usual processing aid for hard PVC, which cannot increase the impact strength of hard PVC.²

The PBA/PMSMA has a lower T_g and is a pliable component in this system. The shell of PMSMA has good compatibility with PVC. When this material is subjected to impact, the PBA/PMSMA particles become centers of stress, crazes or shear bands occur and absorb significant amounts of energy in this region. On the other hand, these pliant particles can confine the development of crazes and prevent break of materials.¹³

The tensile strength and hardness for improved PVC by PBA/PMSMA are shown in Table VI. The tensile strength and hardness decrease with increasing the amount of PBA/PMSMA. This result is similar with the general commercial processing aid and resistant impact aid.^{2,9}

CONCLUSIONS

1. In the core-shell emulsion polymerization of α -MS and MA on PBA, the amount of graft-

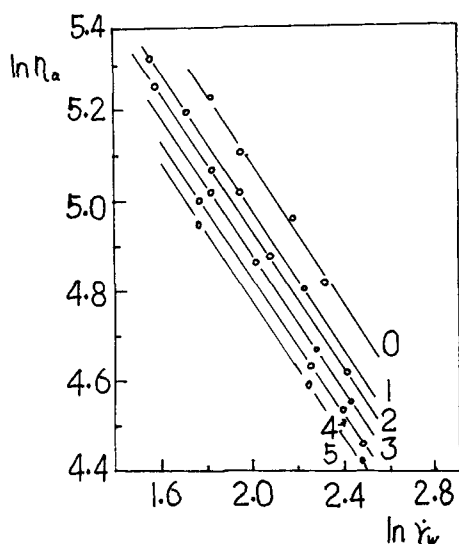


Figure 6 Apparent viscosity η_a of mixture melt versus shear rate $\dot{\gamma}_w$ for the mixture of PBA/PMSMA copolymer composition with PVC at 180°C (specimens 0, 1, 2, 3, 4, and 5).

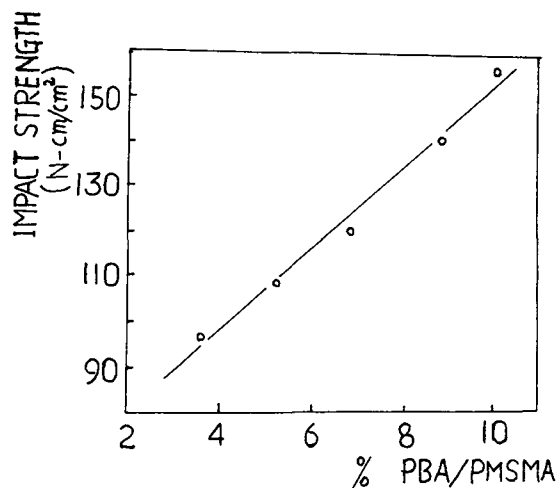


Figure 7 Relationship of impact strength with the ratio of PBA/PMSMA core-shell copolymer to PVC.

ing is controlled by reaction temperature, initiator concentration, emulsifier concentration, and core-shell ratio. The possibility of grafting is increased with raising the temperature to 80°C. The percentage of grafting increased with increasing emulsion polymer surface area. It is controlled by the specific area of the particle.

2. The α -MSMA copolymer and core-shell PBA/PMSMS latex has a good compatibility with PVC. Their solubility parameters are close to the solubility parameter of PVC.
3. The PBA/PMSMA copolymer can be used as a processing aid for hard PVC, which can decrease the processing temperature and melt flow viscosity of hard PVC, but also can increase its impact strength.
4. When PBA/PMSMA was mixed with PVC, the tensile strength and hardness decreased. The added amount of PBA/PMSMA copolymer was 7–10%.

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