Polymers from Inverted Emulsions of Vinyl Monomers by Use of Partially Neutralized Liquid Polybutadiene Treated with Acid Anhydride

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ABSTRACT

Partially neutralized liquid polybutadiene treated with succinic anhydride (SA), that is, PBSA(PNa), was prepared by partial neutralization with NaOH of adduct polymer (PBSA) from liquid polybutadiene and SA (PNa means that PBSA was partially neutralized with NaOH). PBSA(PNa) was found to act as an effective W/O-type emulsifier for vinyl monomers such as styrene, MMA, acrylonitrile, and ethylene glycol dimethacrylate. Inverted emulsions having very low viscosity were prepared from the vinyl monomers with various amounts of PBSA(PNa). By polymerization, the emulsions were transformed to a white solid which were dry to the touch. The water-containing polymers obtained are characterized by the properties of showing a very high rate of water loss. The higher the amounts of PBSA-(PNa) and of water in the polymer, the more rapid the water loss becomes. Most of physical properties increase in value by removing water. Further improvement in physical properties is observed by reinforcing with glass fiber; the flexural and impact strengths especially increase remarkably.

INTRODUCTION

Hydroxyl-terminated liquid rubbers have recently attracted considerable interest from the scientific and industrial standpoints. They are useful in such application areas as castable elastomers, sealants, caulking compounds, adhesives, coatings, potting compounds, encapsulants, and binders for rocket fuels. These liquid rubbers have reactive primary hydroxyl groups in both terminal positions; particularly, the reactivity of the hydroxyl groups toward polyisocyanates is very high. Therefore, this reaction is widely applied for chain extension and cross-linking. Meanwhile, as for ionic cross-linking, previously a paper [1] has reported ionic cross-linking of adduct polymers prepared by addition reaction of acid anhydrides to hydroxyl-terminated liquid polybutadiene (HTPB). The ionic-cured rubbers obtained showed poor physical properties and, as such, they were unsuitable for practical use.

On the other hand, it has been known that unsaturated polyester salts which are prepared by adding bases to the polyester form stable inverted emulsions, i.e., water-in-oil (W/O) type emulsions [2-4]. The basic compounds react with the free carboxyl groups of the polyester to form in situ the polyester salts which stabilize the emulsion as true emulsifying agents. By polymerization, the W/O-type emulsions are transformed to white solid copolymers which are dry to the touch. The preparation of water-containing resins by polymerization in a W/O emulsion was first reported by Bartly and von Bonin [5, 6]. They used styrene (St)-grafted poly(ethylene oxide) as an emulsifier to prepare emulsions of water in St or methyl methacrylate (MMA); by polymerization of the emulsions they obtained solid poly-St or poly-MMA containing water. The water-containing resins have many potential applications [3, 4, 7, 8]; among them, use as a low-cost molding materials is particularly attractive.

Also, the neutralized adduct polymers from HTPB and anhydride were expected to act as W/O emulsifiers for vinyl monomers. Therefore, in the present study we investigated the preparation of inverted emulsions of vinyl monomers by using the adduct polymers. It was found that the partially neutralized liquid polybutadiene treated with succinic anhydride (SA) acts as an effective W/O emulsifier. Further, properties of the polymers obtained from the inverted emulsions are also discussed.

EXPERIMENTAL

Materials

As the HTPB, Poly bd R-45 HT, a product of Idemitsu Petrochemical Co., was used; the OH value was 0.8280 eq/kg. It was demoistured

at 90-100°C under reduced pressure for at least 30 min. SA was a guaranteed reagent and used as received. Chloroform, methanol, and acrylonitrile (AN) were of extra pure grade, St was of practical grade, and MMA and ethylene glycol dimethacrylate (EDM) were of technical grade. They were all used without further purification. Dimethyl-benzylamine (DMBA) was used after distillation.

Synthesis of Partially Neutralized Liquid Poly-butadiene Treated with SA

In a 500-mL separable flask equipped with stirrer, thermometer, and condenser were placed 300 g of HTPB, 32.4 g of SA (equivalent ratio of OH:SA = 1:1.31), 0.42 g of DMBA as a catalyst, and 200 g of chloroform as a solvent. The mixture was stirred at 80-90°C for 6 h. Then, after cooling to room temperature, it was washed 3 times with water in a separating funnel to remove unreacted SA.

The chloroform solution of the adduct polymer (PBSA) thus obtained from HTPB and SA was placed in a flask equipped with stirrer, condenser, and dropping funnel. To this was added dropwise a 1% methanol solution of NaOH to the desired degree of neutralization (55%). During this time a white precipitate was produced. After the addition the supernatant liquid was removed by decantation and the precipitate was dried at 60°C under reduced pressure to remove chloroform and methanol completely. Thus the partially neutralized liquid polybutadiene treated with SA was obtained in the form of a viscous liquid. This will be hereafter denoted by PBSA(PNa) (PNa means that PBSA was partially neutralized with NaOH).

Preparation of Inverted Emulsions

A fixed amount of PBSA(PNa) was dissolved in St or MMA with stirring at 60°C for 30 min and a fixed amount of EDM was added to it. If necessary, AN was further added. Next, a desired amount of water was added slowly to the monomer solution with vigorous stirring at 60°C to obtain an inverted emulsion.

The emulsion stability was estimated from the rates of phase separation of the emulsions. Separation curves were obtained by reading the change of the height of the interface between the separated phases in the test tube.

Preparation of Water-Containing Polymers

To the inverted emulsion obtained above were added, with stirring at 60°C, 1.0 wt% (based on the monomer solution) of 30% dimethyl phthalate solution of methyl ethyl ketone peroxide (MEKPO) and 1.0 wt% of 10% St solution of cobalt naphthenate. It was poured into molds

and was polymerized by heating at 60°C for 4 h to give a dry-to-the-touch polymer containing water.

Infrared Spectra and Thermogravimetric Analyses (TGA)

Infrared spectra were determined with a Shimazu IR-400 instrument.

TGA were carried out in a Shimazu microthermobalance TGA-20 at a heating rate of 10°C/min in air.

Determination of Physical and Other Properties

The following physical properties were determined for the polymers containing water and also for those after removal of water: Heat distortion temperature (HDT) according to ASTM-D 648-56 (fiber stress = 4.6 kg/cm^2), flexural strength according to ASTM-D 790-66, compressive strength according to ASTM-D 695-69, impact strength according to ASTM-D 256-56 (without Izod notch), and Shore D hardness according to ASTM-D 2240.

Time dependence of water content of water-containing polymers was determined for the specimens of 12.5-13.5 × 1.27 × 1.27 cm which were cut from the resins.

RESULTS AND DISCUSSION

Synthesis of PBSA(PNa)

Adduct polymers from HTPB and anhydride are obtained by the addition reaction of the acid anhydride group with the OH group. The partially neutralized liquid polybutadiene treated with maleic anhydride showed a tendency to gelation on standing at room temperature, probably due to cross-linking caused by the double bond of the added terminal maleate group. In the treatment of HTPB with phthalic anhydride, it was not easy to add phthalic anhydride to a high extent of addition.

On the other hand, the partially neutralized liquid polybutadiene treated with SA, that is, PBSA(PNa), was stable on standing, and further, the addition reaction of HTPB and SA proceeded smoothly. Therefore, SA was used for the anhydride treatment of HTPB. Complete neutralization with NaOH of the carboxyl groups of the adduct polymer (PBSA) resulted in a decrease in solubility of the product in vinyl monomers such as St and MMA. However, partial neutralization gave a product which was soluble in the vinyl monomers. The degree of neutralization of about 55% was empirically found to be optimum. In the present study, PBSA(PNa) (degree of neutralization = 55%) was used for the investigation of the preparation of inverted emulsions.
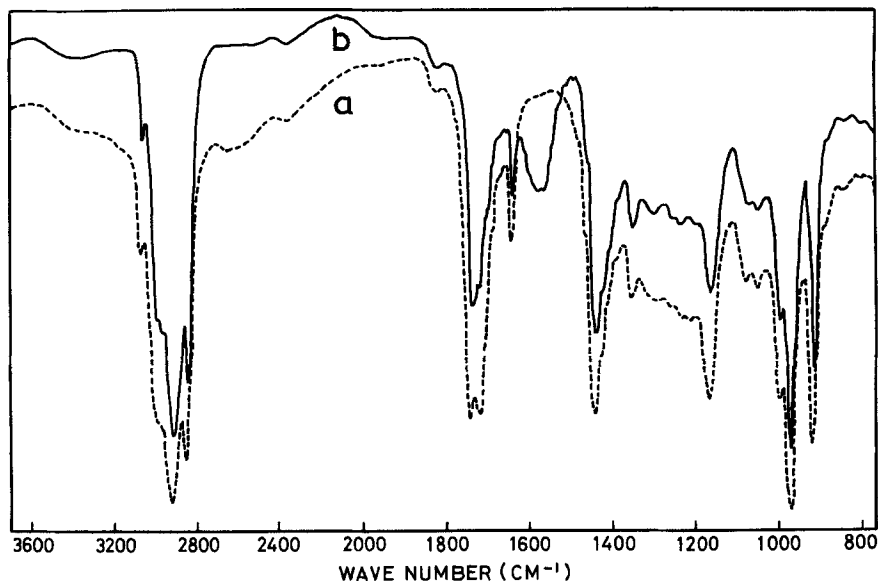
FIG. 1. Infrared spectra of (a) adduct polymer (PBSA) and (b) PBSA(PNa).

Figure 1 shows the infrared spectra of PBSA and of PBSA(PNa), obtained in the experimental section. The extent of addition of SA to HTPB was 91%. In the spectrum of PBSA, absorption bands at 1740 cm^{-1} (ester linkage), at 1720 cm^{-1} due to carboxyl group, and at 1640 cm^{-1} (C=C) are noteworthy. Meanwhile, in the spectrum of PBSA(PNa) the band at 1580 cm^{-1} due to the Na carboxylate group appeared, corresponding with a decrease in the band at 1720 cm^{-1}. This indicates that PBSA was partially neutralized.

Stability of Inverted Emulsions

St and MMA are widely used vinyl monomers. St (M_1) has good copolymerizabilities toward AN (M_2) and MMA ($M_{2'}$); for example, $r_1 = 0.41$, $r_2 = 0.04$ at 60°C [9]; $r_1 = 0.52$, $r_{2'} = 0.46$ at 60°C [10]. St-AN copolymers with an AN content of 15-30% are known to have better thermal stability and physical properties than poly-St. Similarly, poly-MMA is known to have good physical properties; its impact strength is especially excellent. Addition of a cross-linking agent to these monomers further improves the thermal and physical properties of the copolymer. EDM was used as the cross-linking agent because it has two methacrylate groups whose reactivities are almost equal
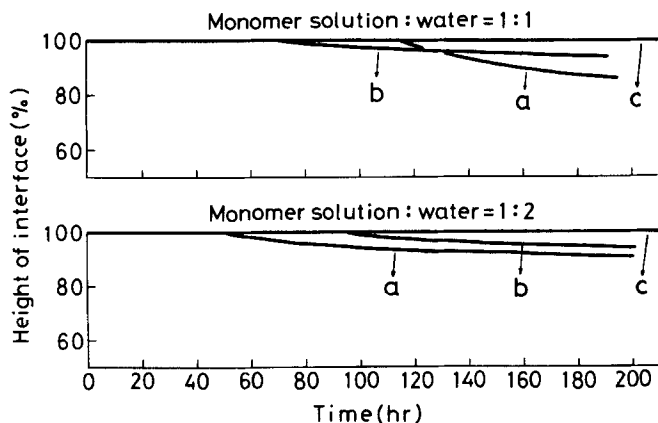
FIG. 2. Separation curves of emulsions of St-AN-EDM (3:1:1) with PBSA(PNa) at 23°C. (a) 4% of PBSA(PNa); (b) 6% of PBSA(PNa); (c) 8% of PBSA(PNa). Percentages are based on the weight of monomers.

to those of MMA. Therefore, the following two monomer systems were selected in the present study: St-AN-EDM (3:1:1) and MMA-EDM (4:1) (weight ratio).

Figures 2-5 show phase separation curves for the inverted emulsions with various amounts of PBSA(PNa) as an emulsifier. Monomer solution refers to the mixture of vinyl monomers and PBSA(PNa). At PBSA(PNa) amounts below about 4%, stable inverted emulsions could not be obtained. Inverted emulsions were obtained at PBSA(PNa) amounts of 4-8% for the St-AN-EDM system and 6-10% for the MMA-EDM system. The stability of the emulsions generally increases with an increase in the amount of PBSA(PNa). At 23°C the inverted emulsions of St-AN-EDM do not collapse for more than about 50 h (Fig. 2). Meanwhile the emulsions of MMA-EDM with 50% water are stable for more than 18 h (Fig. 3). In the emulsion with the higher water content, at 6% PBSA(PNa) phase separation occurs at both the top and the bottom of the tube. But the emulsions with the higher PBSA(PNa) content are stable for more than 22 h at 23°C. With an increase in the water content the stability of the emulsions shows a general tendency to slightly decrease. Moreover, the emulsions of St-AN-EDM are generally more stable than those of MMA-EDM on comparing the emulsions at the same water content.

The phase separation is accelerated at higher temperature (60°C). The blank emulsion (of St-AN-EDM) without PBSA(PNa) collapses within 30 min (Fig. 4). In addition, the emulsion with PBSA (not neutralized) begins to collapse immediately after preparation. From this it is apparent that PBSA(PNa) acts as a very effective W/O

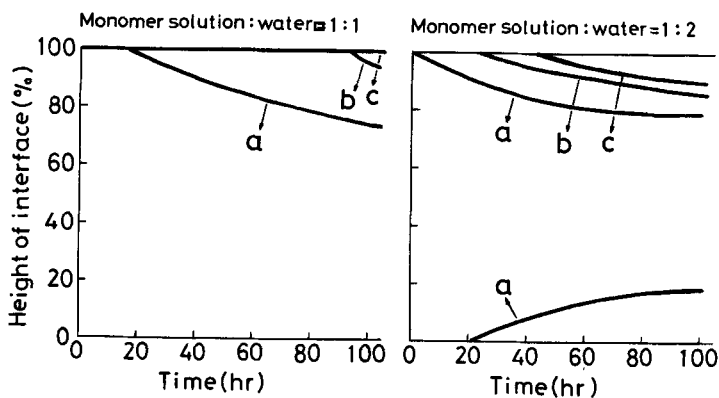Monomer solution:water=1:1   Monomer solution:water=1:2

FIG. 3. Separation curves of emulsions of MMA-EDM (4:1) with PBSA(PNa) at 23°C. (a) 6% of PBSA(PNa); (b) 8% of PBSA(PNa); (c) 10% of PBSA(PNa). Percentages are based on the weight of monomers.

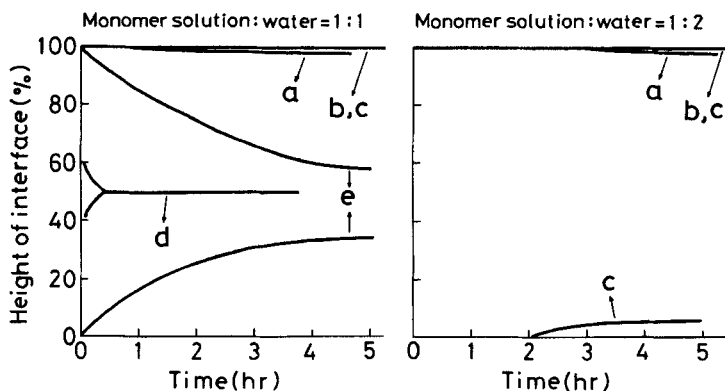Monomer solution:water=1:1   Monomer solution:water=1:2

FIG. 4. Separation curves of emulsions of St-AN-EDM (3:1:1) with PBSA(PNa) at 60°C. (a) 4% of PBSA(PNa); (b) 6% of PBSA(PNa); (c) 8% of PBSA(PNa); (d) without PBSA(PNa); (e) 4% of PBSA. Percentages are based on the weight of monomers.

emulsifier for the vinyl monomers. The inverted emulsions are generally stable for more than about 1 h at 60°C. It is noteworthy that the emulsions of St-AN-EDM with 6-8% PBSA(PNa) (water content = 50%) show no sign of phase separation even after 5 h at 60°C (Fig. 4). The extent of stability of the emulsions mentioned above assures the subsequent polymerization of the emulsion. The
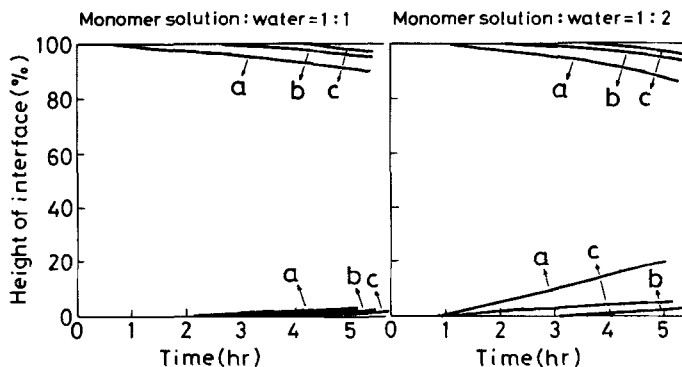
FIG. 5. Separation curves of emulsions of MMA-EDM (4:1) with PBSA(PNa) at 60°C. (a) 6% of PBSA(PNa); (b) 8% of PBSA(PNa); (c) 10% of PBSA(PNa). Percentages are based on the weight of monomers.

polymerization is considered to be completed before the collapse of the inverted emulsions. It has been reported that unsaturated poly-ester gelation occurs faster in the inverted emulsions than in the un-modified polyester [3].

As suitable W/O-type emulsifiers, compounds containing both lipophilic and hydrophilic groups in their molecular structure attract attention. The emulsifier used by von Bonin et al. [5, 6, 8] for vinyl monomers was St-grafted poly(ethylene oxide). The poly-St block in this emulsifier is lipophilic and the poly(ethylene oxide) block is hydrophilic. Suitable amounts of this emulsifier to be used for vinyl monomers were 0.5-10% based on the monomer. It has been said that in order to form an inverted emulsion, the lipophilic affinity of the emulsifier to the monomer must be stronger than its hydrophilic affinity to water; similarly, the polarity of the hydrophilic backbone of the emulsifier dissolved in the monomer must be stronger than that of the monomer. From these considerations it seems that PBSA(PNa) may be a novel effective emulsifier for inverted emulsions. This proved to be the case.

In the case of unsaturated polyester, it has been found [2] that a stable, gel-like inverted emulsion is formed only when pK_a's of the bases are above 6 and their concentrations are higher than some critical value. Minimum concentrations of bases necessary to form a stable emulsion lie in the range of 0.3-0.5 mmol/g of resin. On the other hand, PBSA(PNa) is obtained by the partial neutralization with NaOH of PBSA obtained from HTPB and SA. NaOH is a strong base. In the case of the monomers in the present study, the PBSA(PNa) amounts required to give a stable inverted emulsion are 4-10% based
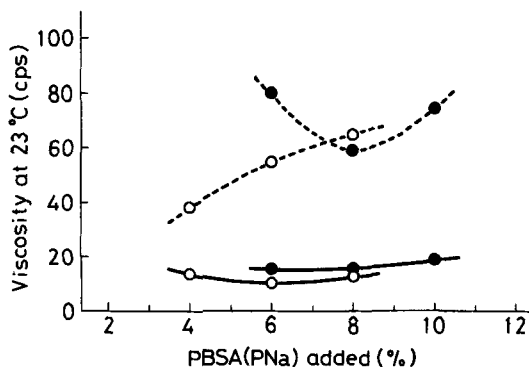
FIG. 6. Effect of amount of PBSA(PNa) added to monomers on viscosity at 23°C of inverted emulsion. (○) St-AN-EDM (3:1:1); (●) MMA-EDM (4:1). (—) Monomer solution:water = 1:1; (- -) monomer solution:water = 1:2.

on the monomer. The concentrations of Na$^+$ in the monomer solution, when converted into concentrations of NaOH, lie in the range of 0.015-0.036 mmol of NaOH/g of monomer solution. These values are much smaller than those of the above-mentioned minimum base concentrations necessary for the unsaturated polyester. The polarity of PBSA(PNa) is stronger than that of the above vinyl monomers. The vinyl monomers have lower polarity than the unsaturated polyester. Hence the vinyl monomers seem to require lower concentrations of hydrophilic groups in the monomer solution than the polyester to form inverted emulsions. PBSA(PNa) is considered to accumulate at the water-monomer interface, stabilizing the inverted emulsions.

Figure 6 shows the viscosities at 23°C of the inverted emulsions. The increase in water content resulted in an increase in viscosity of the emulsion. However, the viscosities were in the range of 20-80 cP. Such low viscosities are very advantageous for casting and compounding. Meanwhile, inverted emulsions prepared by von Bonin et al. [5, 6, 8] and those from the unsaturated polyester salts [2, 3] showed much higher viscosities and they were often gel-like. Thus PBSA(PNa) as a W/O emulsifier is characterized by the fact that it imparts very low viscosities to the emulsion.

Physical and Other Properties of Water-Containing Polymers

The mechanism of polymerization in an inverted emulsion is known to be not very different from that of ordinary radical
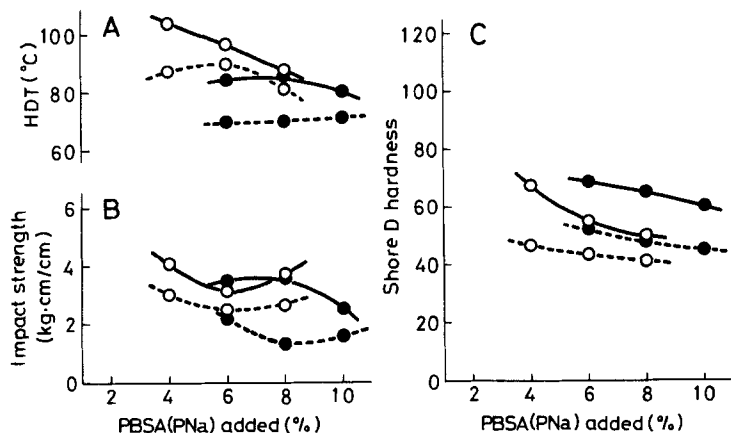
FIG. 7. Effect of amount of PBSA(PNa) added to monomers on
(A), HDT, (B) impact strength, and (C) Shore D hardness of resulting
water-containing polymers. (○) St-AN-EDM (3:1:1); (●) MMA-EDM
(4:1). (—) Resin:water = 1:1; (- -) resin:water = 1:2.

polymerization [2, 3, 5, 6]; the polymerization proceeds in the mono-
mer solution phase. The inverted emulsions described above could
be polymerized with radical-type initiators such as MEKPO to give
dry-to-the-touch polymer containing water.

Figures 7 and 8 show physical properties of the water-containing
polymers obtained. Generally the physical properties show a tendency
to decrease in value with an increase in the amount of PBSA(PNa),
especially for flexural and compressive strengths. This might be
due mainly to an increase in the plasticizing effect by PBSA(PNa).
Moreover, the polymers with 50% water showed better physical
properties than those with a higher water content; such a trend is
generally observed for water-containing polymers [8] and cured
unsaturated polyester resins [7]. The St-AN-EDM polymer which
contains 50% water and 4% PBSA(PNa) showed the best physical
properties. In addition, it is noteworthy that MMA-EDM polymers
with 50% water show high Shore D hardness, flexural, and compres-
sive strengths over the wide range of PBSA(PNa) amounts studied.

Figures 9-12 show the time dependence of water content of the
water-containing polymers. At room temperature (23°C) water
escapes from the polymers, and the loss of water becomes more
rapid with an increase in the amount of PBSA(PNa) and with an in-
crease in the water content (Figs. 9 and 10). The water loss indicates
that water droplets in the polymer are connected. It follows from
this that the water droplets become more connected with an increase
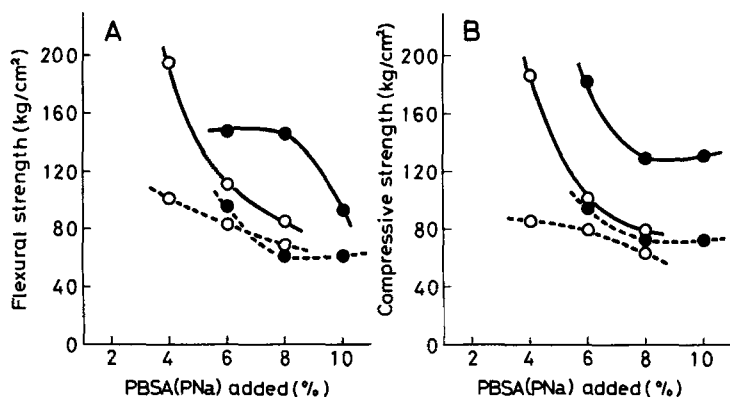in the amount of PBSA(PNa). This also might be a cause for the

FIG. 8. Effect of amount of PBSA(PNa) added to monomers on (A) flexural and (B) compressive strengths of resulting water-containing polymers. (○) St-AN-EDM (3:1:1); (●) MMA-EDM (4:1). (—) Resin:water = 1:1; (- -) resin:water = 1:2.
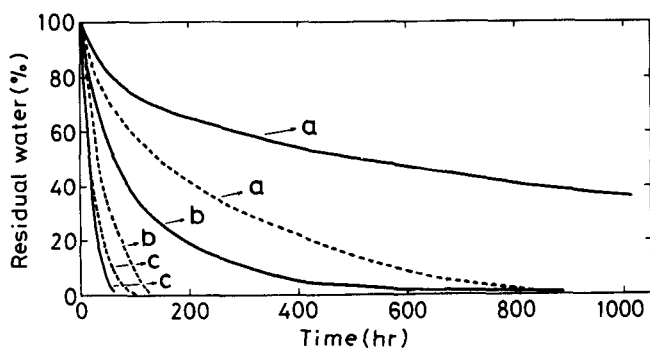

FIG. 9. Time dependence of water content of water-containing polymers of St-AN-EDM (3:1:1) with PBSA(PNa) at 23°C. (a) 4% of PBSA(PNa); (b) 6% of PBSA(PNa); (c) 8% of PBSA(PNa). (—) Resin: water = 1:1; (- -) resin:water = 1:2.

above-mentioned trend for the physical properties to decrease in value with an increase in the PBSA(PNa) content.

The water-containing unsaturated polyester resin obtained by the polymerization of the inverted emulsion from the polyester salt (water content = 50%) retained 70% of the initially added water after 60 d at room temperature [3]. Similarly, in the water-containing poly-St
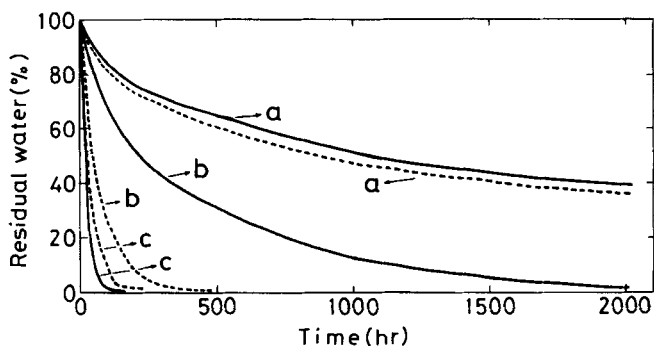
FIG. 10. Time dependence of water content of water-containing polymers of MMA-EDM (4:1) with PBSA(PNa) at 23°C. (a) 6% of PBSA(PNa); (b) 8% of PBSA(PNa); (c) 10% of PBSA(PNa). (—) Resin: water = 1:1; (- -) resin:water = 1:2.
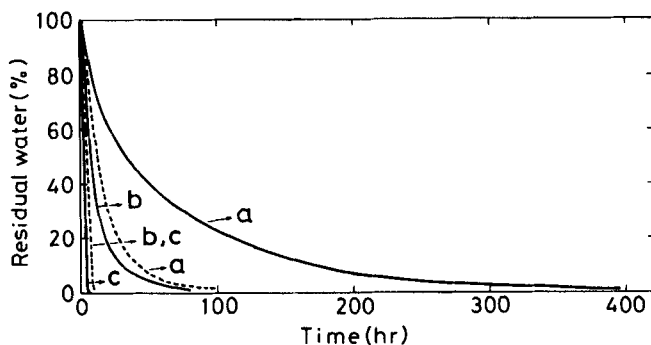
FIG. 11. Time dependence of water content of water-containing polymers of St-AN-EDM (3:1:1) with PBSA(PNa) at 60°C. (a) 4% of PBSA(PNa); (b) 6% of PBSA(PNa); (c) 8% of PBSA(PNa). (—) Resin: water = 1:1; (- -) resin: water = 1:2.

from the inverted emulsions prepared by von Bonin et al. [8], the samples with 60 and 70% water showed 10% weight loss after 80 and 30 d, respectively. Meanwhile, in the present study the MMA-EDM polymer with 50% water and 6% PBSA(PNa) showed the slowest water loss, but the water loss was 56% after 63 d (Fig. 10). Thus the water-containing polymers in the present study are characterized by the properties of showing a much higher rate of water loss. Moreover, the St-AN-EDM polymers lose water more rapidly than the MMA-EDM
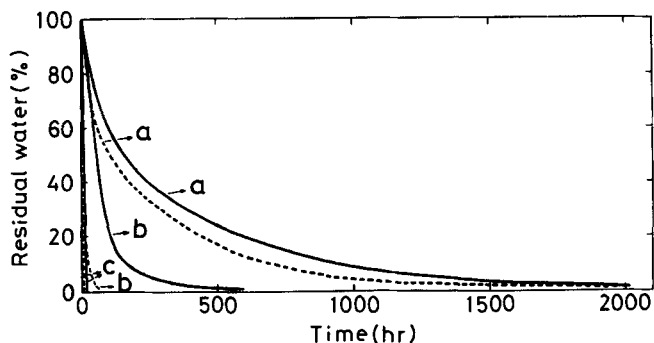
FIG. 12. Time dependence of water content of water-containing polymers of MMA-EDM (4:1) with PBSA(PNa) at 60°C. (a) 6% of PBSA(PNa); (b) 8% of PBSA(PNa); (c) 10% of PBSA(PNa). (—) Resin: water = 1:1; (- -) resin:water = 1:2.

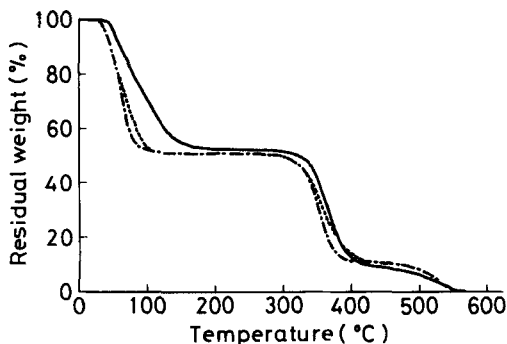FIG. 13. TGA curves of water-containing polymers of St-AN-EDM (3:1:1) with PBSA(PNa). (—) 4% of PBSA(PNa); (- -) 6% of PBSA(PNa); (- -) 8% of PBSA(PNa). Resin:water = 1:1.

ones, indicating that in the former polymers water droplets are more connected.

The loss of water is accelerated markedly at higher temperature (60°C), but the order of the rate of water loss is almost unchanged (Figs. 11 and 12). It is noteworthy that the polymers with a high PBSA(PNa) content show extremely rapid water loss, and they lose almost all of their water within 10-20 h at 60°C.

The very high rates of water loss shown by the water-containing polymers in the present study are advantageous for obtaining foamed materials.
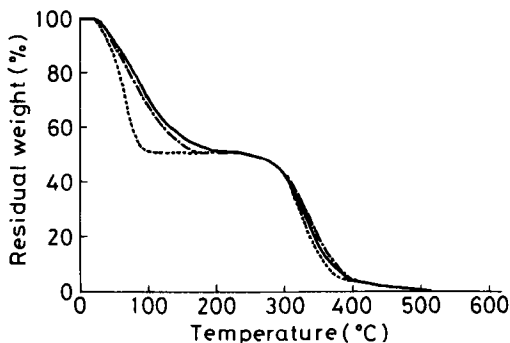
FIG. 14. TGA curves of water-containing polymers of MMA-EDM
(4:1) with PBSA(PNa). (—) 6% of PBSA(PNa); (- -) 8% of PBSA(PNa);
(- -) 10% of PBSA(PNa). Resin:water = 1:1.

Thermal Behavior of Water-Containing Polymers

Figures 13 and 14 show TGA curves of the water-containing poly-
mers from inverted emulsions with 50% water. Weight loss begins
below about 40°C, above which the weight loss proceeds rapidly up to
the residual weight of about 50%. It is of interest to note that the
higher the amount of PBSA(PNa) in the polymer, the more rapid the
weight loss becomes. This trend correlates well with that observed
for the above-mentioned isothermal time dependence of the water
content of the polymers. Therefore the initial weight loss is due to
the removal of water in the polymers. This also means that the re-
moval of water in the polymer is very easy. The plateaus observed
at about 50% residual weight correspond to the formation of polymer
without water. Decomposition of polymer proceeds above about 300°C
for the St-AN-EDM polymers and 260°C for the MMA-EDM ones.
Thus the former are thermally more stable than the latter.

Physical Properties of Polymers after Removal of Water

As described above, it is very easy for water to escape from the
water-containing polymers used in the present study. Therefore the
water-containing polymers were dried at 60°C into the polymers
without water (foamed materials).
Figures 15 and 16 show the physical properties of the polymers
after the removal of water. It is apparent that most of the physical
properties increase in value by removing water. This is due to a
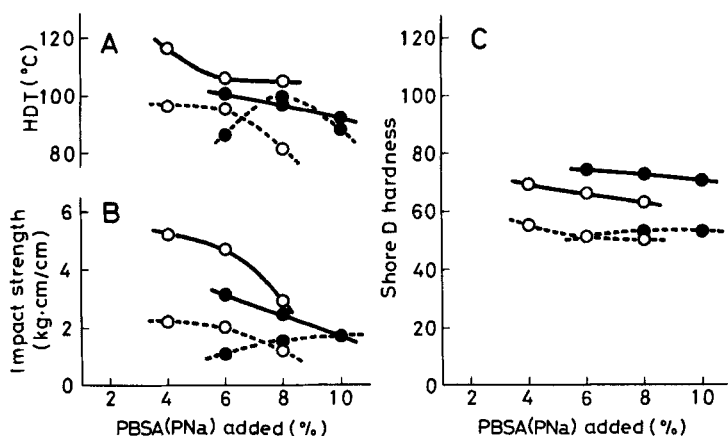decrease in the plasticizing effect caused by water. For example, in

FIG. 15. Effect of amount of PBSA(PNa) added to monomers on (A) HDT, (B) impact strength, and (C) Shore D hardness of resulting polymers after removal of water. (○) St-AN-EDM (3:1:1); (●) MMA-EDM (4:1). (—) Resin:water = 1:1; (- -) resin:water = 1:2.
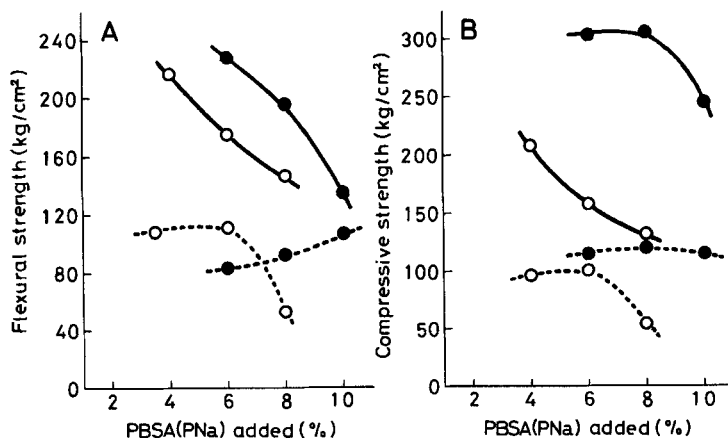
FIG. 16. Effect of amount of PBSA(PNa) added to monomers on (A) flexural and (B) compressive strengths of resulting polymers after removal of water. (○) St-AN-EDM (3:1:1); (●) MMA-EDM (4:1). (—) Resin:water = 1:1; (- -) resin:water = 1:2.

TABLE 1. Effect of Glass Fiber on Physical Properties of Polymers after Removal of Water

Properties	Monomer solution[a] :water = 1:1		Monomer solution[b] :water = 1:2	
	Without glass fiber	10 parts[c] of glass fiber	Without glass fiber	8.3 parts[c] of glass fiber
Heat distortion temperature (°C)	106	130	96	120
Flexural strength (kg/cm^2)	175	212	107	213
Compressive strength (kg/cm^2)	158	188	97	121
Impact strength (kg.cm/cm)	4.7	8.4	2.2	Did not break
Shore D hardness	67	64	55	54
Specific gravity	0.52	0.54	0.35	0.39

[a]Amount of PBSA(PNa) = 6% based on St-AN-EDM.
[b]Amount of PBSA(PNa) = 4% based on St-AN-EDM.
[c]Parts based on the inverted emulsion.

the St-AN-EDM polymer from the inverted emulsion with 50% water and 6% PBSA(PNa), the following increases in value are observed: for HDT, from 97 to 106°C; for Shore D hardness, from 54 to 67; for flexural strength, from 110 to 175 kg/cm^2; and for compressive strength, from 100 to 158 kg/cm^2. In addition, in the MMA-EDM polymer from the emulsion with 50% water and 8% PBSA(PNa), the increases are as follows: for HDT, from 86 to 98°C; for Shore D hardness, from 66 to 73; for flexural strength, from 147 to 195 kg/cm^2; and for compressive strength, from 129 to 305 kg/cm^2. It is noteworthy that the compressive strength of the latter polymer is close to that [7] of concrete (316 kg/cm^2).

Next, the effect of glass fiber on the physical properties of polymers after the removal of water was investigated for the St-AN-EDM system. The results are shown in Table 1. Clearly, most of the physical properties are improved by reinforcing with the glass fiber. However, the increase of specific gravity is very small. It is noteworthy that, in the polymer based on the emulsion at a monomer solution:water ratio of 1:2, the flexural strength markedly increases from 107 to 213 kg/cm^2 by using the glass fiber. In addition, remarkable improvement also appears in the impact strength; the samples did not break during the determination.

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