

## Water-Containing Resin Based on Unsaturated Polyester

KAZUYUKI HORIE, ITARU MITA, and HIROTARO KAMBE,  
*Institute of Space and Aeronautical Science, University of Tokyo,  
Komaba, Tokyo, Japan*

### Synopsis

Unsaturated polyester resins containing water were prepared through two steps: formation of a stable W/O emulsion of polyester prepolymer and subsequent polymerization of the emulsion. In this paper, conditions for formation of the resins from the W/O type emulsion and the heat-protection properties of the resulting water-containing resins are reported. The stability of the emulsions was measured, and the results are discussed in relation to the gelation time, since the polymerization of the emulsions is required to proceed faster than their disintegration. It was found that with increasing viscosity of the emulsions their stability increases and the gelation time shortens. The above requirement is fulfilled at almost all regions of emulsifier concentration where stable W/O emulsions are formed. Water-containing unsaturated polyester resins exhibit a remarkable heat-protection effect at elevated temperatures (500 and 2500°C.) in comparison with polyester resins not containing water.

### INTRODUCTION

The preparation of water-containing resins through polymerization in an inverted emulsion, i.e., in a water-in-oil (W/O) emulsion, was first reported by Bartl and von Bonin.<sup>1</sup>

In our previous paper,<sup>2</sup> we showed, however, that the emulsifiers which were used by Bartl and von Bonin for vinyl monomers cannot be applied to liquids of higher polarity, such as unsaturated polyester, and that various basic compounds act as very effective W/O emulsifiers for the unsaturated polyester prepolymer. The basic compound reacts with the free carboxyl group of the polyester to form *in situ* the polyester salt which stabilizes the emulsion as a true emulsifying agent.

While the main purpose of the previous paper was to establish the mechanism of emulsification of water in the unsaturated polyester prepolymer by basic emulsifiers, the present paper deals with the polymerization mechanism of W/O emulsions of the prepolymer and water content, mechanical strength, and heat-protection effect of the resulting resins.

The mechanism of polymerization in an inverted emulsion is not very different from that of ordinary radical polymerization, but in actual preparation of the water-containing resins the polymerization reaction must be completed before the collapse of the quasi-stable emulsions. From this

point of view, the stability of the emulsions was studied semiquantitatively and is discussed in relation to the rate of polymerization.

Whether the water included in the solid unsaturated polyester resin evaporates easily or not is an important problem for their practical uses. Another interesting problem is the heat-protection effect of the resins. At elevated temperatures the transpiration cooling effect of water is very large and might be superior to the ablation effect.<sup>3</sup> If so, water-containing thermosetting resins may provide a new type of polymer with a high heat-protection capacity at elevated temperatures.

## EXPERIMENTAL

### Preparation of Water-Containing Unsaturated Polyester Resin

A commercial, general purpose, unsaturated polyester prepolymer (Estar D-32, styrene content = 30%) was used in this investigation. An aqueous solution of a basic compound such as triethanolamine (TEA) of more than some critical concentration was added to the unsaturated polyester prepolymer and a stable W/O emulsion was formed immediately by stirring. A white, dry-to-the-touch resin containing water was obtained by heating the emulsion at 60°C. with benzoyl peroxide (BPO) or other radical-type initiators.

### Measurements of Emulsion Stability

The emulsion stability was estimated from the rates of phase separation of the emulsions. Typical separation behavior of the emulsions is shown in

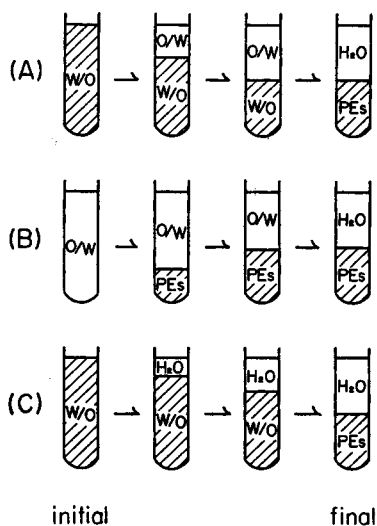


Fig. 1. Separation behavior of polyester emulsions: (A) at a low base concentration (unstable W/O); (B) at a medium base concentration (O/W); (C) above critical base concentration (stable W/O).

Figure 1. Separation curves were obtained by reading the change of the height of the interface between the separated phases in a test tube kept in a thermostat over a period of 30 hr. The measurements were carried out at 30 and 60°C.

### Gelation Time

The gelation time of the water-containing resins was determined for various initiator-emulsifier systems. This is the time necessary for the emulsion to have lost its fluidity and changed to a soft jelly. The gelation time of the resins without water was also measured for reference.

### Measurements of Water Content

The water content was determined by measurements of weight loss of the water-containing resins. Coating of the surface with pure polyester film was performed by dipping the resin a few times into a liquid unsaturated polyester prepolymer.

### Tensile Measurements

The tensile strength and tensile modulus of the water-containing resins reinforced by glass mat were measured by using a TOM/2000 type universal tensile and compressive testing machine.

### Measurements of Heat-Protection Effect

A torch burner method<sup>4</sup> was used to estimate the heat-protection effect of the water-containing resins at elevated temperatures. The apparatus is illustrated in Figure 2. The test piece was lathed to a cylinder of 38 mm.

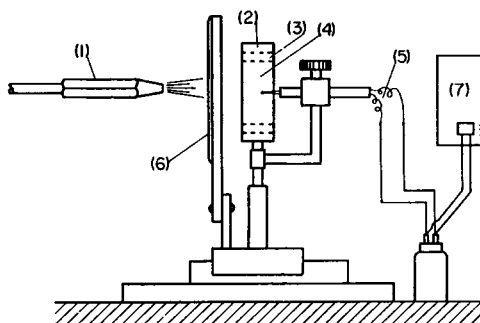


Fig. 2. Apparatus for measurement of heat-protection effect of the resins:<sup>4</sup> (1) torch burner; (2) holder of the test piece; (3) insulating material; (4) test piece; (5) chromel-alumel thermocouple; (6) shutter; (7) electromagnetic oscillograph.

diameter and 10 mm. thickness. The surface of the test piece was heated to 2500°C. by an oxygen-acetylene torch burner and the temperature 7 mm. beneath the surface was measured by a chromel-alumel thermocouple.

## RESULTS AND DISCUSSION

**Polymerization in Inverted Emulsion of Unsaturated Polyester Prepolymer**

The most important factor in producing water-containing resins is to obtain stable emulsions by employing suitable emulsifiers. As was shown by our previous work, most commercial anionic, cationic, and non-ionic emulsifiers and some graft polymers, as used by Bartl and von Bonin, were ineffective in stabilizing a W/O emulsion of unsaturated polyester prepolymer. In contrast, the salts of polyester formed by the reaction of polyester itself with various bases were very effective for the emulsification.

A stable W/O emulsion can be formed only when  $pK_a'$  values of the bases are above 6, and when the base concentrations are higher than some critical values. This critical concentration is, for all bases, 0.3–0.5 mole/g. prepolymer. Water was able to be dispersed up to 90% in the polyester prepolymer. The state of the emulsion is not affected by the order of addition of water and base. The chemical structure and the styrene content of the polyester prepolymer have no large effect on the stability of the W/O emulsion.

The state of the emulsion of unsaturated polyester prepolymer, however, varies markedly with the increase in the concentration of basic additives. Far below the critical concentration, unstable W/O emulsions are formed; at medium concentrations the phase of emulsions is inverted and O/W emulsions are formed; only above the critical concentration stable, gel-like W/O emulsions are obtained.

The words "stable" and "unstable" emulsions were used qualitatively in the discussion in the previous paper. To obtain an actual water-containing resin, however, it is only necessary for the emulsion to be kept stable before the polymerization is completed. Presently the emulsion stability at various emulsifier concentrations is studied semiquantitatively in connection with the rate of polymerization of the prepolymer.

The emulsion stability was estimated from the rates of phase separation of the emulsion. Figures 3 and 4 show phase-separation curves at 30 and 60°C. for emulsions with various concentrations of TEA as a base.

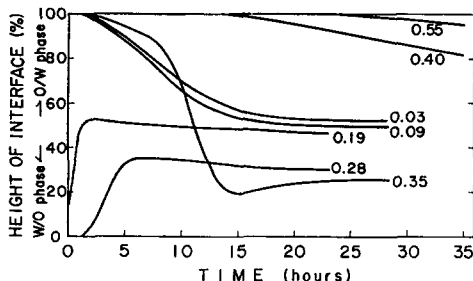


Fig. 3. Separation curves of emulsions of unsaturated polyester prepolymer at 30°C. Triethanolamine concentrations (in mmole/g.) are indicated beside the curves.

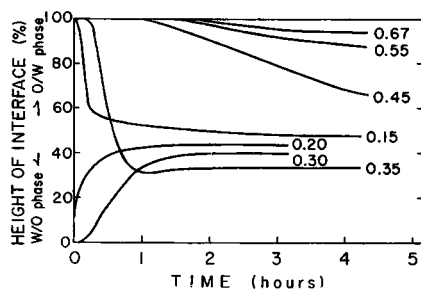


Fig. 4. Separation curves of emulsions of unsaturated polyester prepolymer at 60°C. Triethanolamine concentrations (in mmole/g.) are indicated beside the curves.

The phase separation is accelerated at higher temperatures, but the shapes of the curves and therefore the mechanism of the separation are kept unchanged. At a TEA concentration of 0.18–0.32 mmole/g., phase separation occurs at the bottom of the tube since the initial emulsion is of O/W type. The W/O emulsions with the lower TEA concentrations (less than 0.18 mmole/g.) collapse within 10 min. at 60°C. In contrast to these emulsions, W/O emulsions above the critical concentration of TEA do not collapse for more than 15 hr. at 30°C. and for 1 hr. at 60°C. This extent of stability assures the subsequent polymerization of the emulsion.

TABLE I  
(Gelation Time of Unsaturated Polyester Prepolymer (D-32)  
with Various Initiators in Inverted Emulsion or in the  
Absence of Water

Initiator*	Initiator, % based on resin	Water, % based on resin	Emulsi- fier	Emulsi- fier, mmole/g.	Tem- pera- ture, °C.	Gelation time, min.	
						W/O emul- sion	With- out water
BPO	2.0	100	TEA	0.40	60	118	
BPO	2.0	100	TEA	0.60	60	32	
BPO	2.0	100	TEA	1.00	60	14	
BPO	2.0	0	TEA	1.00	60		0.9
BPO	2.0	100	NaOH	0.60	60	19	
BPO	2.0	0	NaOH	0.60	60		68
BPO	2.0	0	None	—	60		70
AIBN	2.0	100	TEA	0.60	60	15	
AIBN	2.0	0	TEA	0.60	60		25
AIBN	2.0	0	None	—	60		25
MEKPO	2.0	100	TEA	0.60	30	52	
CoNap	2.8						
MEKPO	2.0	0	TEA	0.60	30		4.0
CoNap	2.8						

\* AIBN = azobisisobutyronitrile; MEKPO = methyl ethyl ketone peroxide; CoNap = cobalt naphthenate.

As usual the hardening of the water-containing polyester prepolymer was carried out with a radical-type initiator. The gelation times of the water-containing resins for various initiator-emulsifier systems are listed in Table I.

Some tertiary amines are known to be effective promoters of decomposition of BPO which initiates the radical polymerization. Promoters such as TEA and cobalt naphthenate are effective for hardening the unmodified unsaturated polyester prepolymer within a few minutes. It is clear, however, from Table I that they lose their efficiency in the presence of water. In the case of the BPO-sodium hydroxide or azobisisobutyronitrile-TEA system, where no such accelerative effect is known, gelation occurs faster in the presence of water than without water, or in other words, faster for the stable W/O emulsion than for the unmodified polyester prepolymer. We have already reported that the viscosity of the stable W/O emulsion is much higher than that of the unmodified polyester prepolymer and increases markedly with the increase in the concentration of the basic emulsifiers. The shorter gelation time for the stable W/O emulsions might be due to this increase in viscosity. This is supported further by the fact that the gelation time for BPO-TEA system decreases markedly with the increase in the TEA concentration, namely in the viscosity.

Though the reaction proceeds in the prepolymer phase, the viscosity of the emulsion affects the rate of polymerization. This fact offers an interesting problem from the viewpoint of the physically controlled polymerization mechanism. At any rate, the gelation times of the W/O emulsions of the unsaturated polyester prepolymer are sufficiently short to allow the prepolymer to harden before collapse of the emulsion.

### Properties of the Water-Containing Resins

The water-containing unsaturated polyester resins obtained by the polymerization of the inverted emulsions are white and dry to the touch.

They resist acids, bases, and ordinary organic solvents, just like unmodified, unsaturated polyester resins. Water-containing, fiber-reinforced plastics (FRP) are obtained by molding the modified unsaturated polyester resins with reinforcing glass fiber.

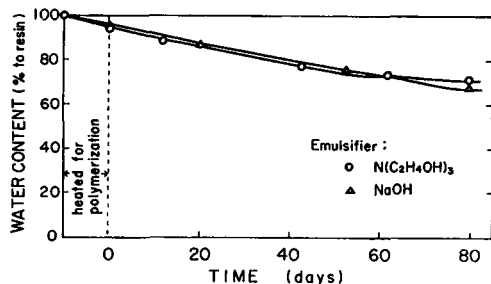


Fig. 5. Time dependence of water content of water containing resins at room temperature with various emulsifiers: (O) TEA; (Δ) NaOH.

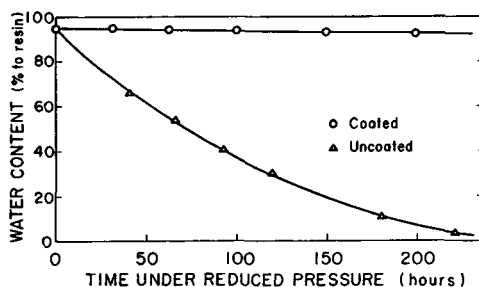


Fig. 6. Effect of coating on water content of water-containing resins under reduced pressure (about 1 mm. Hg): (O) coated; ( $\Delta$ ) uncoated. Emulsifier, triethanolamine; temperature, 25°C.

The water contents evaluated by the weight loss measurements of the resins are indicated in Figure 5. As is shown in Figure 5, at room temperature the resin retains 70% of initially added water after 60 days. Figure 6 shows that water vaporizes rapidly and escapes from the resin at a reduced pressure. The loss of water means that water droplets in the resin are connected with one another. This may be caused by the breakdown of the polymer matrix due to the contraction of the prepolymer during polymerization. Water droplets in the emulsion were ascertained to be independently dispersed in the prepolymer phase. The mean diameter of water droplets was determined with an electron microscope to be about 0.1  $\mu$ . In order to prevent the loss of water from the resin, the surface coating with pure polyester film was carried out. The effect of coating on the water loss of the water-containing resins is marked, as shown in Figure 6. The retention of water is practically complete if surface coating is used.

The hardness of the water-containing resins was 30–40, as determined by a Barcol Impressor (935). This value is reasonable in comparison with the value of 70 for the unmodified polyester resin without water.

The mechanical strengths of the water-containing resins reinforced with glass mat are shown in Table II. Water does not produce a marked decrease in the mechanical strength.

TABLE II  
Mechanical Strength of the Water-Containing Resins  
Reinforced with Glass Mat

Composition, parts			Temperature, °C.	Tensile strength, kg./mm. <sup>2</sup>	Tensile modulus, kg./mm. <sup>2</sup>
Resin	Water	Glass mat			
1	1	1	20	12.1	262
1	2	1	20	8.0–8.3	252–280

Incombustibility is the most distinctive characteristic of these resins. As the unsaturated polyester resin is thermosetting, it does not soften at higher temperatures. Water held in the resin prevents a temperature rise

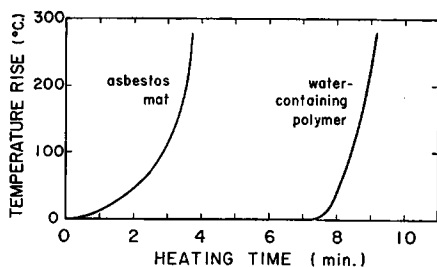


Fig. 7. Temperature rise 6.2 mm. from the surface of a water-containing resin heated at 500°C.

and when the water is consumed the surface of the resin is carbonized to some extent.

When the surface of a piece of resin 6.2 mm. thick containing 100% water was heated at 500°C., no temperature rise was observed on the other side of the piece after 7.5 min.; then the temperature began to rise and after 9 min. reached 240°C. (Fig. 7). The weight loss of the sample was 6.1% after 10 min. heating, which would be due to the vaporization of water. An unsaturated polyester resin without water began burning in a few minutes. An asbestos mat showed a temperature rise to 240°C. after 3.5 min. under the same experimental condition.

The heat-protection effect at much higher temperatures was measured by a torch burner method. Figure 8 indicates that the resin containing 200% water, when heated at 2500°C., exhibited no temperature rise after 31.5 sec., whereas the temperature of the resin without water gradually rises after heating. The difference shows clearly the high heat-absorption capacity of the water-containing resins at elevated temperatures. During heating the surface of the test piece is eroded gradually but all the pores of the unaffected part of the resin are still filled with water. In the case of the water-containing resin, the removal of the material by heat is not only caused by a simple ablation process but also by the erosion and the sloughing of the materials on the explosion of the water droplets. This undesirable loss of

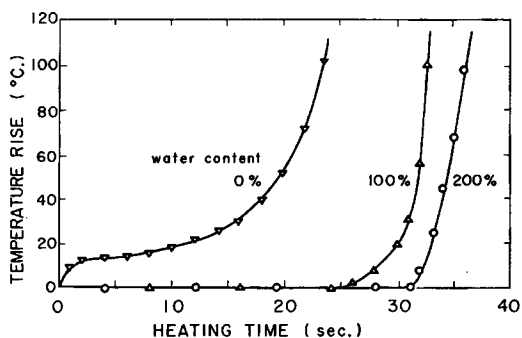


Fig. 8. Temperature rise 7.0 mm. from the surface of a water-containing resin heated at 2500°C.



the materials may lower the efficiency of the heat-protection by the resin. The settlement of this problem is left to further investigation.

The authors express their gratitude to Prof. K. Ikeda of our Institute for his kind permission to use his torch burner system. Special thanks are due to Toyo Koatsu Kogyo Co., Ltd., for supplying the unsaturated polyester prepolymer.

### References

1. H. Bartl and W. von Bonin, *Makromol. Chem.*, **57**, 74 (1962).
2. K. Horie, I. Mita, and H. Kambe, *J. Appl. Polymer Sci.*, **11**, 57 (1967).
3. W. D. Allingham, *ARS Journal*, **32**, 945 (1962).
4. K. Ikeda, T. Furuta, and M. Sakamaki, *Aero. Res. Inst., Univ. Tokyo, Syuho*, **2**, 428 (1961).

### Résumé

Des résines de polyester insaturé contenant de l'eau ont été préparées en deux étapes; à savoir la formation d'une émulsion stable du type W/O de prépolymère de polyester et la polymérisation de l'émulsion. Dans ce manuscrit, on décrit les conditions nécessaires pour former les résines au départ d'une émulsion du type W/O et la propriété de protection thermique de cette résine contenant de l'eau. La stabilité des émulsions a été mesurée et discutée en rapport avec leur temps de gélification puisque la polymérisation des émulsions doit se passer plus rapidement que leur désintégration. On a trouvé qu'avec une viscosité croissante des émulsions leur stabilité croît et la durée de gélification diminue et que le traitement ci-dessus est rempli pratiquement pour toutes les concentrations en émulsifiant lorsque des émulsions du type W/O stables sont formées. Les résines polyesters insaturées contenant de l'eau manifestent un effet de protection thermique remarquable à des températures élevées (500 et 2.500°C) en comparaison avec des résines polyesters ne contenant point d'eau.

### Zusammenfassung

Ungesättigte, wasserhaltige Polyester-Harze wurden in zwei Stufen hergestellt, und zwar durch Erzeugung der stabilen W/O-Emulsion der polymeren Polyester-Vorstufe und durch Polymerisation der Emulsion. In dieser Abhandlung werden die notwendigen Bedingungen für die Bildung der Harze in der W/O-Emulsion und die Wärmeschutzeigenschaften der entstandenen wasserhaltigen Harze beschrieben. Die Stabilität der Emulsion wurde gemessen und in Zusammenhang mit deren Gelierzeit diskutiert, da die Polymerisation der Emulsionen rascher verlaufen muss als deren Zerfall. Es wurde gefunden, dass die Stabilität der Emulsionen mit steigender Viskosität unter Verkürzung der Emulsionen mit steigender Viskosität unter Verkürzung der Gelierzeit zunimmt, und dass die obige Voraussetzung in nahezu allen Bereichen der Emulgatorkonzentration, in denen stabile W/O-Emulsionen gebildet werden, erfüllt ist. Wasserhaltige ungesättigte Polyester-Harze zeigen, verglichen mit Polyester-Harzen ohne Wasser, bei hohen Temperaturen (500 und 2.500°C) einen bemerkenswerten Wärmeschutzeffekt.

Received May 10, 1967  
Prod. No. 1662