

Acrylic Nonaqueous Dispersion Using Butylated Melamine-Formaldehyde Resin as Dispersant

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Synopsis

A series of acrylic nonaqueous dispersions were prepared by using various kinds of butylated melamine-formaldehyde (BMF) resins as dispersant. The functional group composition of BMF to form stable dispersion was butoxy group more than 13 mol/BMF 1 mol, and methylol group ranged from 1 to 2.5 mol/BMF 1 mol. It is concluded that the anchoring of BMF to acrylic copolymer was due to the formation of covalent bond between methylol group in BMF and hydroxy group in acrylic copolymer.

INTRODUCTION

Over the past two decades significant development of nonaqueous dispersion has occurred, and wide applications other than surface coatings have been found.

Dispersion polymerization in organic media up to 1975 has been thoroughly reviewed by Barrett,¹ and many reports have been published since then, for example, the preparation of a new class of crosslinked nonaqueous dispersions² and the preparation of the monodisperse polymer particles by nonaqueous dispersion polymerization.³

As discussed by Dowbenko and Hart,⁴ the crucial component in a nonaqueous dispersion is the dispersant, and the degree to which a nonaqueous dispersion polymer can be considered a successful preparation depends predominantly on the kind of dispersant used. The most successful type of dispersant devised for use in dispersion polymerization has been based on a block or graft copolymer, which consists of two essential polymeric components; one soluble and one insoluble in the continuous phase.¹ The insoluble component, or anchor group as it is often called, associates with the disperse-phase polymer.

An ingenious approach to dispersants consists in the use of butylated melamine-formaldehyde (BMF) resins^{5,6} because the latter, in addition to being stabilizers, also function as coalescing and crosslinking agents. The exact mechanism of dispersion forming is not fully understood, and it is not clear whether BMF is linked to the main polymer by covalent bonds or by the physical adsorption onto the surface of the particle.

One of the authors investigated previously the correlation between functional group composition of BMF and its properties.⁷⁻¹⁰ In this article we

describe the adequate functional group composition of BMF functioning as a dispersant of acrylic nonaqueous dispersion (NAD) and discuss the anchoring of BMF to acrylic copolymer.

EXPERIMENTAL

Materials

All the reagents were used as received (special grade and super special grade for analysis) or purified by standard methods (commercial grade). BMF resins were prepared as previously described.⁹

Measurements

The determination of functional groups in BMF was carried out as follows. The molecular weight of the fundamental structure unit, that is melamine residue (T.), was obtained from the nitrogen content ([N]%) by micro-Kjeldahl method using the following equation as shown in the previous report.¹¹

$$T. = 14.01 \times 6 \times 100/[N]$$

The methylol group ([CH₂OH]%) and the total combined formaldehyde ([TF]%) in BMF were determined by the iodimetric method using dioxane as solvent⁷ and by the sodium sulfite method following phosphoric acid decomposition of BMF,¹² respectively. The determination of butoxy groups in BMF([OBu]%) was carried out by gas-liquid chromatography(GLC) of butanol after the phosphoric acid decomposition of BMF.¹² GLC was carried out using Yanaco G80-F equipped with a flame ionization detector and 2.25 × 3 mm (i.d.) glass column packed with 15% PEG-1000 (polyethylene glycol) on 60–80 mesh Chromosorb W.

The functional group composition of 1 mol of melamine residue was calculated by using the following equations;

$$TF(\text{mol}/T.) = (T. \times [TF]) / (100 \times 30.0)$$

$$CH_2OH(\text{mol}/T.) = (T. \times [CH_2OH]) / (100 \times 30.0)$$

$$OBu(\text{mol}/T.) = (T. \times [OBu]) / (100 \times 74.1)$$

where [TF], [CH₂OH], [OBu] are weight percent of total combined formaldehyde, methylol group, butoxy group in BMF, respectively, and T. is melamine residue.

The number-average molecular weight (\bar{M}_n) of BMF was measured by vapor pressure osmometry (VPO; Corona Model 115 osmometer) in benzene. Infrared spectra (IR) were recorded over the range 2000–750 cm⁻¹, using a JASCO A-3 infrared spectrometer. The nonvolatile content (NV) of NAD was expressed by the percentage of heating residue to original NAD (0.1–0.2 g) after drying at 120°C for 1 h. The stability of NAD was evaluated in three grades by observation of NAD in a test tube (18 × 150 mm) after standing for 7 days; good (○): the length of clear phase to that of total NAD was less than

10%, poor (Δ): the length of clear phase to that of total NAD was more than 10%, and bad (\bullet): the phase separation or aggregation occurred immediately after preparation of NAD.

Preparation of Acrylic Nonaqueous Dispersions

BMF (9.0 g, 70% butanol solution 12.9 g), benzoyl peroxide (BPO, 0.06 g), and isooctane (30 g) were charged to the flask (200 mL) equipped with a stirrer, thermometer, reflux condenser through which purged nitrogen, and dropping funnel (50 mL) which contained 30 g of monomer mixture [methyl methacrylate (MMA)(ethyl acrylate (EA))2-hydroxypropyl acrylate (HPA) = 5/4/1, molar ratio], lauryl alcohol (2.6 g), and BPO (0.84 g). When the temperature was raised to 80°C under nitrogen stream, the monomer mixture was slowly dripped into the flask over 5 h, and then stirring was continued for an additional 1 h. The reaction product (NAD) was allowed to cool to room temperature. Acrylic copolymer for control sample (AC) was prepared in the manner described above, provided that benzene instead of isooctane was placed in the flask in the absence of BMF and lauryl alcohol. The reaction product was then concentrated under reduced pressure and AC was dried in vacuo at 40°C.

RESULTS AND DISCUSSION

Correlation Between Dispersibility and Functional Group Contents of NAD

In regard to the functional group contents of BMF, the measured values and the calculated values from them are shown in Tables I and II, respectively. The degree of polymerization (\bar{P}_n) in Table I was determined from \bar{M}_n divided by melamine residue (T.). In Table II compositions (mol/BMF 1 mol) were obtained from mol/T. multiplied by \bar{P}_n , and T.* values were calculated

TABLE I
Characteristics of BMF

BMF no.	Composition (%)				T.	\bar{M}_n ($\times 10^{-3}$)	\bar{P}_n
	[N]	[TF]	[CH ₂ OH]	[OBu]			
BMF-1	21.5	33.9	5.63	48.3	391	1.35	3.45
BMF-2	25.1	35.0	9.13	40.3	335	1.41	4.20
BMF-3	22.0	35.9	6.05	45.8	382	1.76	4.61
BMF-4	19.3	30.5	2.41	55.2	435	1.79	4.12
BMF-5	21.5	35.4	3.76	48.9	391	1.84	4.70
BMF-6	22.6	32.4	1.68	53.4	372	1.85	4.97
BMF-7	23.0	33.1	8.63	44.9	365	1.96	5.37
BMF-8	22.1	37.6	4.66	46.4	380	2.04	5.37
BMF-9	19.9	30.4	3.36	55.0	422	2.20	5.21
BMF-10	23.2	36.2	3.15	46.5	362	2.44	6.74
BMF-11	24.9	38.1	4.90	42.2	337	2.48	7.36
BMF-12	23.0	33.6	1.64	49.3	365	2.60	7.12
BMF-13	23.0	35.3	2.38	47.5	365	2.88	7.87
BMF-14	22.2	31.8	2.32	49.8	378	2.96	7.83

TABLE II
 Functional Group Content in BMF

BMF no.	Composition (mol/T.)			Composition (mol/BMF 1 mol)			
	TF	CH ₂ OH	OBu	T.**	T.	CH ₂ OH	OBu
BMF-1	4.42	0.73	2.55	382	391	2.52	8.80
BMF-2	3.91	1.02	1.82	327	335	4.28	7.64
BMF-3	4.57	0.77	2.36	371	382	3.55	10.9
BMF-4	4.42	0.35	3.24	426	435	1.44	13.4
BMF-5	4.61	0.49	2.58	383	391	2.30	12.1
BMF-6	4.02	0.21	2.68	377	372	1.04	13.3
BMF-7	4.03	1.05	2.21	358	365	5.64	11.9
BMF-8	4.76	0.59	2.38	372	380	3.17	12.8
BMF-9	4.28	0.47	3.13	418	422	2.45	16.3
BMF-10	4.37	0.38	2.27	355	362	2.56	15.3
BMF-11	4.28	0.55	1.92	331	337	4.05	14.1
BMF-12	4.09	0.20	2.43	360	365	1.42	17.3
BMF-13	4.29	0.29	2.34	358	365	2.29	18.5
BMF-14	4.02	0.29	2.54	369	378	2.27	19.9

$$^a T.* = 126 + 13 \times TF + 17 \times CH_2OH + 73 \times OBu.$$

assuming methylene bond ($-\text{CH}_2-$) to be the only linkage between two triazine rings, that is

$$\begin{aligned}
 T.* &= \text{melamine}(126) + \text{methylol group}(30) + \text{butoxymethyl} \\
 &\quad \text{group}(86) + \text{methylene group}(13) \\
 &= 126 + 30 \times CH_2OH \text{ (mol/T.)} + 86 \times OBu \text{ (mol/T.)} \\
 &\quad + 13(TF - CH_2OH - OBu) \\
 &= 126 + 13 \times TF + 17 \times CH_2OH + 73 \times OBu
 \end{aligned}$$

T.* values approximately agree with experimental values (T.).

The stability of NAD, which was prepared by dispersion polymerization of acrylic monomers using BMF as dispersant, is shown in Table III.

Figure 1 illustrates the correlation between the stability of NAD and the functional group content (mol/T. or mol/BMF 1 mol) or \bar{M}_n of BMF. Among the functional groups in BMF, CH₂OH is considered an anchoring component and OBu is regarded as a soluble component. BMF having CH₂OH more than 0.7 mol/T. produced unstable NAD because of its high polarity (a), whereas a definite tendency was not recognized as to OBu (mol/T.) (b). It is considered that a certain degree of \bar{M}_n of BMF may be required to form the effective steric barrier for the stabilization of NAD, and so (c) shows the critical value of \bar{M}_n to be about 1800. OBu as soluble component is thought to play the most important role for the effective steric barrier, and BMF having OBu more than 13 mol/BMF 1 mol demonstrated its effectiveness as dispersant (e). Although the region of 1.0–2.5 mol/BMF 1 mol concerning CH₂OH was effective (d), BMF-11(CH₂OH: 4.05 mol/BMF 1 mol) also produced stable NA-11, and this was explained as being due to 14.1 mol/BMF 1 mol of OBu.

TABLE III
Stability of NAD

NAD ^a no.	BMF no.	NV (%)	Stability ^b
NA-1	BMF-1	—	●
NA-2	BMF-2	—	●
NA-3	BMF-3	—	●
NA-4	BMF-4	53	○
NA-5	BMF-5	56	△
NA-6	BMF-6	54	○
NA-7	BMF-7	—	●
NA-8	BMF-8	55	△
NA-9	BMF-9	56	○
NA-10	BMF-10	53	○
NA-11	BMF-11	58	○
NA-12	BMF-12	57	○
NB-12 ^c	BMF-12	57	△
NA-13	BMF-13	59	○
NA-14	BMF-14	56	○

^aTotal monomer; 30 g (molar ratio of MMA/EA/HPA = 5/4/1), BPO; 0.9 g, BMF; 9.0 g, isooctane; 30 g, temperature; 80°C, Time; 6 h.

^b○: good, △: poor, ●: bad.

^cMMA/EA/HPA = 5/4/0.

NA-7 was unstable in spite of \bar{M}_n (1960) of BMF-7, and this was concluded to be due to the low content of OBU (11.9 mol/BMF 1 mol) and high content of CH₂OH (5.64 mol/BMF 1 mol).

The stability of NAD was expected to be closed related to its particle size, and NADs having a particle size above 1 μm (estimated by means of electron microscope) were found to be unstable. The effect of kinds of BMF and preparation conditions on the particle size will be discussed fully in a subsequent article.

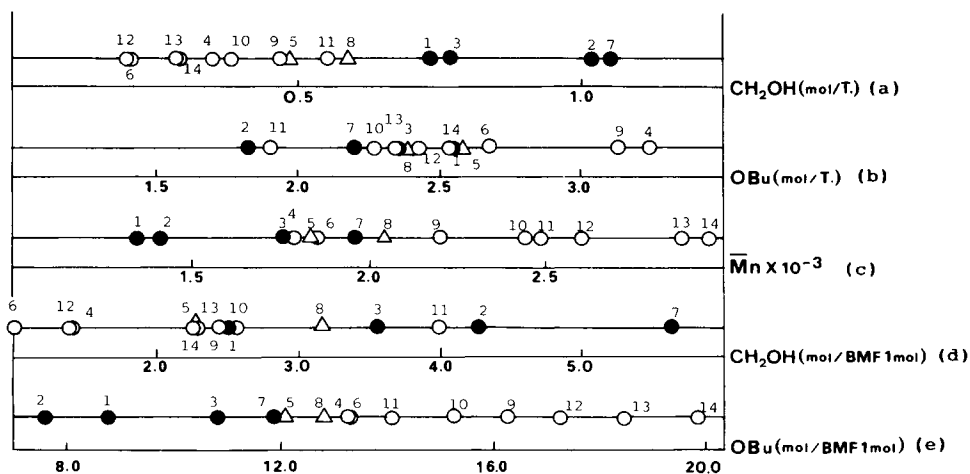


Fig. 1. Correlation between stability of NAD and functional group contents in BMF. The numbers in figure correspond to the numbers of NA in Table III.

TABLE IV
Stability of NA-12 and NB-12

NAD no.	Ratio of dispersion phase to total phase (%)		
	60 days	80 days	100 days
NA-12	99	98	98
NB-12	60	50	50

Anchoring of BMF to Acrylic Copolymer

NA-12 and NB-12 were prepared under the same reaction conditions except for the absence of HPA (Table III). Their dispersibilities were evaluated by the ratio of the length of dispersed phase to that of total NAD after standing for a prescribed number of days, and the result is shown in Table IV. As is evident from Table III, NA-12 was much more stable than NB-12, and this difference was concerned exclusively in the existence of HPA. In the case of NB-12, the interaction between BMF and acrylic copolymer was only a physical entanglement, whereas in NA-12 the covalent bond—or at least hydrogen bond—between methylol group of BMF and hydroxy group of acrylic copolymer was conceivable.

Since BMF was also subjected to self-condensation during the reaction, BMF-12 was heated without compounding acrylic monomers according to the procedure previously described for the preparation of NAD, and the product (BMF-120) was used for a control sample of NAD. The latter was prepared by the following procedure. After control, acrylic copolymer (AC) and BMF-120 were blended with the same ratio of acrylic monomers to BMF-12 and dissolved uniformly in acetone, the mixture was concentrated to 60% non-volatile content under reduced pressure (CNA), because complete dryness brought no transfer of BMF-120 to the cyclohexane phase in extraction as described later.

To examine the interaction between BMF and acrylic copolymers, the extraction of NAD with cyclohexane, which completely dissolved BMF-12 and BMF-120 but not AC, was carried out. The procedure of extraction was as follows. NAD(NA-12, NB-12) or CNA 10 g and cyclohexane 10 g were charged to a centrifuge tube and the latter was shaken well for 1 h, and then the mixture was separated by centrifugation. The supernatant was used for the measurement of infrared (IR) spectra, and was then evaporated to dryness. Cyclohexane was added again to the residue of centrifugation and the same operation was repeated five times.

IR spectra of AC and BMF-120 were measured to use the absorbance ratio of each characteristic absorption band as a measure of the weight ratio of acrylic copolymer to BMF in extract of NAD. It was observed that the carbonyl(ester) stretching band at 1730 cm^{-1} of AC was not noticed in BMF-120, while the triazine skeletal vibration band at 815 cm^{-1} of BMF-120 was not detected in AC. E_{1730} and E_{815} represent the absorbance of each characteristic absorption band, respectively. The calibration was obtained from the absorbance ratio (E_{1730}/E_{815}) with different weight ratio of AC to BMF-120. The calibration curve is repressed in Figure 2, which shows a good linear correlation.

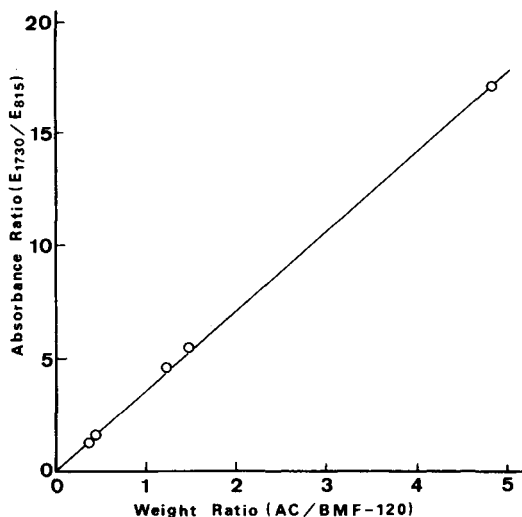


Fig. 2. IR calibration curve for determining weight ratio of AC/BMF-120 using absorbance ratio.

The experimental results that were obtained from the extraction of NAD with cyclohexane are shown in Table V. The acrylic copolymer content of sample (NA-12 and NB-12) was calculated from the feed ratio of acrylic monomers to BMF-12 and was adjusted to 76.9%. The recoveries of the extract ranged from 95 to 97%, and the residue content of NA-12 (57.2%) was markedly small compared with the other two (NB-12: 71.5%, CNA: 72.5%) which were close to the acrylic copolymer content before extraction (76.9%).

TABLE V
Extraction of NAD with Cyclohexane

Sample ^a		Extract					
No.	Nonvolatile matter (g)	Nonvolatile matter		Acrylic copolymer		Transfer amount (%) ^c	[η] (%)
		(g)	(%)	Content in (g) ^b	supernatant (%)		
NA-12	5.162	2.103 ^d	42.8	0.816	38.8	21.6	— 0.8
	residue	2.806	57.2				
	(total)	(4.909)	(100.0)				
NB-12	6.189	1.697 ^d	28.5	0.521	30.7	11.4	— 0.2
	residue	4.257	71.5				
	(total)	(5.954)	(100.0)				
CNA	4.962	1.328 ^d	27.5	0.192	14.4	5.2	— 0
	residue	3.500	72.5				
	(total)	(4.828)	(100.0)				

^aAcrylic copolymer content was 76.9% (calculated from the feed ratio of acrylic monomers/BMF-12 or AC/BMF-120).

^bCalculated from calibration curve (Fig. 2).

^cCalculated from following equation; (content in supernatant (b) \times 100)/(total nonvolatile matter \times 0.769).

^dThe extract was repeated five times (in CNA four times).

This lowering indicates the transfer of acrylic copolymer to cyclohexane phase in spite of its insolubility in cyclohexane, and this transfer is supported by IR absorbance ratio of supernatant. The supernatant of NA-12 had larger absorbance ratio compared to that of NB-12, whereas in the residue the case was reversed. This shows that the ratio of acrylic copolymer in component migrated to supernatant was higher in NA-12 than in NB-12. On the other hand, the residue of NA-12 had more BMF than that of NB-12, and this was also supported by the difference of nitrogen content ($[N]$) of both residues. In the case of CNA, the sample of extraction was used in the form of 60% acetone solution, hence the transfer of AC to supernatant might be inevitable. The absorbance ratios of supernatant were nevertheless markedly low, and the peak at 815 cm^{-1} in the residue was not detected. Therefore, it seems to be satisfactory to consider that AC in CNA does not migrate essentially from residue to supernatant.

The results obtained in extraction can be summarized as follows. The extraction by shaking of NA-12 with cyclohexane brought about the transfer of acrylic copolymer component to the supernatant and the remaining of BMF-12 in the residue, whereas in CNA AC scarcely migrated to the supernatant and BMF-120 was not detected in the residue. In NB-12 acrylic copolymer component and BMF-12 were observed in the supernatant and the residue, respectively, but the amount was less than in NA-12. In the case of CNA, the interaction between BMF-120 and AC was only a physical entanglement; therefore, both were separated by the extraction with cyclohexane in the supernatant and the residue, respectively, except for small amount of AC in the supernatant accompanying acetone. It was the same with NB-12; however, in this case, unlike CNA, BMF-12 was present throughout the preparation of NB-12, and hence the degree of entanglement might be so tight that the acrylic copolymer component together with BMF-12 migrated to the supernatant and some BMF-12 remained in the residue. In the case of NA-12 the transfer amount of acrylic copolymer component to the supernatant was approximately doubled for that of NB-12, and $[N]$ in the residue was about four times. This can be explained by the formation of the covalent bond between the methylol group of BMF-12 and the hydroxy group of HPA in acrylic copolymer; that is, acrylic copolymer-grafted BMF-12 was distributed in the supernatant and residue corresponding to the degree of grafting.

After three samples (NA-12, NB-12, and CNA) were evaporated to dryness under reduced pressure, equivalent weight of isooctane was added and redispersed again by shaking for 1 h. In the case of CNA, no redispersion was observed, and in NB-12, the dispersion during shaking was separated into two phases immediately after shaking was stopped, whereas in NA-12, stable dispersion was obtained. This suggests the formation of graft copolymer between BMF-12 and acrylic copolymer.

In the present investigation the covalent bond between BMF and acrylic copolymer was not proved directly, but the tests of stability, extraction, and redispersion of samples all indicate that the anchoring of BMF to acrylic copolymer, including HPA was due, at least in part, to the formation of covalent bond.

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