Preparation and Application of Low-Molecular-Weight Poly(vinyl chloride). V. Preparation and Characteristics of Blended Poly(vinyl chloride) by Two-Step Suspension Polymerization

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SYNOPSIS

Poly(vinyl chloride) (PVC) with relatively broader molecular weight distribution (BMD-PVC) was prepared by two-step suspension polymerization: (1) preparation of poly(vinyl chloride) with relatively higher molecular weight (HMW-PVC) and (2) successive preparation of poly(vinyl chloride) with relatively lower molecular weight (LMW-PVC) in the presence of the resultant HMW-PVC and 2-mercaptoethanol as a chain transfer agent. Some properties of BMD-PVC were investigated: fusion time, melt viscosity, discoloration time, tensile strength at yield, tensile modulus in tension, and elongation at break. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) has many and varied practical uses. However, PVC has a serious drawback: decomposition during processing and end-use conditions, with accompanying discoloration and deterioration of mechanical properties. Many investigations have been carried out to overcome this drawback.

Pezzin and Zinelli[1] have shown that PVC with various molecular weights has been prepared by suspension polymerization at 35–70°C and tensile properties (tensile modulus, tensile strength, and elongation at break) of the plasticized PVC samples are dependent on molecular weight.

Shinozaki et al.[2] have reported that tensile strength of PVC increases with increasing molecular weight. On the other hand, they have shown that the tensile modulus of PVC decreases with increasing molecular weight, because of the increase in crystallinity degree. Also, Shaw[3] has elucidated that

mechanical properties of PVC, tensile strength and impact strength, increase with increasing molecular weight, and melt flow inversely decreases.

Furthermore, Casey and Okano[4] have shown that 50/50 blended PVC with relatively higher molecular weight PVC (HMW-PVC) and relatively lower molecular weight PVC (LMW-PVC) has smaller melt flow than PVC whose molecular weight is equal to the averaged molecular weight of HMW-PVC and LMW-PVC, because of the plasticizing effect of LMW-PVC.

On the other hand, we have reported that LMW-PVC, which was prepared by suspension polymerization in the presence of mercapto compound as chain transfer agent, has good thermal stability compared with LMW-PVC obtained without mercapto compound.[5]

Also, LMW-PVC was blended with HMW-PVC, and the blended PVC was studied regarding the effect of LMW-PVC on thermal stability[6] and mechanical properties.[7] Furthermore, HMW-PVC was prepared by suspension polymerization in the presence of LMW-PVC as a process to obtain the blended PVC.[8]

Subsequently, in order to make the preparation of the blended PVC practically more preferable, we studied one-pot preparation of blended PVC, prep-

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aration of PVC with relatively broader molecular weight distribution (BMD-PVC), by the two-step suspension polymerization, in which (1) HMW-PVC was prepared and (2) then LMW-PVC was prepared in the presence of 2-mercaptoethanol and the resultant HMW-PVC.

In this study, we report on the two-step suspension polymerization and some properties of the resultant BMD-PVC.

EXPERIMENTAL

Materials

Commercial-grade vinyl chloride (VCM) used was from Sun Arrow Chemical Co., Japan. Poly(vinyl alcohol) (PVA: degree of saponification, 80%; Nippon Gosei Chemical Co., Japan) and methyl cellulose (MC: Shinetsu Chemical Co., Japan) were used as suspension agents of commercial grade. Tetrahydrofuran (THF) and 2-mercaptoethanol (MET) were supplied by Wako Pure Chemical Co., Japan. Initiator used was t-butyl peroxypivalate (PO) supplied from Nippon Oil & Fats Co., Japan.

Polymerization

BMD-PVC was prepared as follows. At the first step in the preparation of HMW-PVC, a stainless steel autoclave (2 L) was charged with 1 kg of deionized water, into which 1.6 g of partially saponified PVA, 0.7 g of MC, and 0.72 g of PO were added. The autoclave was evacuated, and VCM was fed into it and polymerized with stirring under N_2 atmosphere.

At the second step, LMW-PVC was prepared in the presence of 2-mercaptoethanol (2 g) as a chain transfer agent and the HMW-PVC grains. The details of the polymerizations are shown in Table I. The resultant BMD-PVC was washed with methanol and then dried under reduced pressure at 40°C.

Characterization of LMW-PVC

Mean polymerization degree (P_w) was determined according to JIS K-6721, as reported previously.[7]

The molecular weight distribution (M_w/M_n) was determined by gel permeation chromatography, with the aid of Type-6A with three columns (Shodex A-802, A-804, and A-806) from Shimadzu Seisakusho Co., Ltd. PVC samples were dissolved in THF (2 mg/mL). The measurement was performed at 40°C with flow rate of 1 mL/min using THF as the elution solvent.[9]

Pore Volume

Pore volume of PVC samples was measured by using a mercury porosimeter, type 200 from Carloerba Co., Ltd., according to ASTM D-2873. The sample weight was 1 g.

Morphology of BMD-PVC

Morphology of PVC samples were observed by using a scanning electron microscope, JSM-U3 from JEOL Ltd., attached with a PGT1000 energy-dispersive X-ray spectrometer. The fractured PVC samples were prepared by breaking down the PVC grain frozen in liquid nitrogen, with the aid of two glass plates under shear stress. The samples were coated with thin layer of gold by using a vacuum metallizer.

Compounding of BMD-PVC

BMD-PVC samples (100 parts) were mixed with tribasic lead sulfate (2 parts) and calcium stearate (2 parts) as a stabilizer and stearic acid as a lubricant (0.2 parts) by using a Henschel mixer. The resultant mixture was kneaded at 170°C for 5 min by using a kneader with two mixing rollers to produce sheets

Table I Two-Step Suspension Polymerization

| Sample No. | First Step | | | Second Step | | | | | | | VCM Conversion (%) | Yield (g) |
	VCM (g)	Temp. (°C)	Time (hr)	VCM (g)	MET (g)	PO (g)	PVA (g)	MC (g)	Temp. (°C)	Time (h)		
A	360	57	5	—	—	—	—	—	—	—	63	227
B-1	360	57	5	—	2.0	—	—	—	57	3	68	245
B-2	360	57	5	—	2.0	0.4	—	—	57	3	73	263
B-3	360	57	5	100	2.0	0.4	—	—	57	3	61	280
B-4	360	57	5	100	2.0	0.4	0.8	0.3	57	3	65	298

(1 mm thick) for heat-aging test and measurement of mechanical properties.

Melt Viscosity

The melt viscosity was measured according to JIS K-7210, with the aid of a Shimadzu Koka Flow Tester, model CFT-500, from Shimadzu Seisakusho Co., Ltd. Here, the increasing rate of sample temperature was 3°C/min and the pressure applied to the sample was 150 kg/cm^2.

Discoloration Time

Test pieces (3 × 5 × 0.1 cm) were set on aluminum foil and aged in a circulating-air oven at 180°C. Discoloration time was determined by visual observation as the time elapsed until the samples turned completely black (ASTM D-2115).

Fusion Time

An oil-heated torque rheometer, Model PLV151 from Brabender Co., was used for fusion time measurement at 180°C and with 60 rpm rotor speed. The charged weight of sample was 60 g. Test load was 10 kg/cm^2. Fusion time was determined as the period from zero time to the point of maximum torque.

Measurements of Tensile Properties

Test pieces were prepared by heat-pressing BMD-PVC under 50 kg/cm^2 at 180°C for 10 min. The tensile properties (tensile strength at yield, tensile modulus in tension, and elongation at break) were measured at 23°C according to JIS K-7113, with the aid of a Toyo Baldwin Tensilon, model UTM-5Y from Toyo Baldwin Co., Ltd. The stretching speed was 10 mm/min.

RESULTS AND DISCUSSION

Two-Step Suspension Polymerization

Table I shows the conditions for preparing BMD-PVC by the two-step suspension polymerization process. In the case of sample A, HMW-PVC is prepared. In the case of sample B-1, MET was added just after the first step polymerization was finished, in order to prepare LMW-PVC from the remaining VCM, and PO was added with MET to prepare much more LMW-PVC in the case of sample B-2. In the case of samples B-3 and B-4, VCM was added at the second step to obtain much more LMW-PVC than those in samples B-1 and B-2. As a result, the order of the PVC yield is as follows: B-4 > B-3 > B-2 > B-1 > A.

Table II shows some properties of BMD-PVC. The yield of LMW-PVC at the second step was estimated as follows: (Yield of LMW-PVC) = (yield of BMD-PVC) − (yield of sample A) assuming that yields of HMW-PVC were the same in all cases. The polymerizations at the first and second steps were successively carried out, so the above assumption is considered to be inevitable and reasonable. With increasing the LMW-PVC content, P_w of BMD-PVC decreases and M_w/M_n of BMD-PVC inversely increases. Here, the P_w of LMW-PVC was calculated by the following equation:

$$P_w = P_{w_1} \times W_1 + P_{w_2} \times W_2$$

where P_w, P_{w_1}, and P_{w_2} are the polymerization degree of BMD-PVC, LMW-PVC, and HMW-PVC, respectively; W_1 and W_2, the weight percent of LMW-PVC and HMW-PVC, respectively.[7,10]

P_w of LMW-PVC becomes larger with increasing the LMW-PVC content, because the amount of VCM polymerized at the second step increases in relation to the PO amount.

The dependency of pore volume on the LMW-

Table II Properties of BMD–PVC

| Sample No. | Composition | | P_w | | | Pore Volume (cm^3/g) |
	HMW-PVC (g)	LMW-PVC (g)	BMD-PVC	LMW-PVC	M_w/M_n	
A	227	0	1013	—	2.1	0.135
B-1	227	18	942	47	2.2	0.132
B-2	227	36	884	71	2.3	0.125
B-3	227	53	861	210	2.4	0.120
B-4	227	71	850	329	2.9	0.095

PVC content is understandable. Namely, since the polymerization at the second step is carried out even in the vacancies of HMW-PVC grains, the increase of LMW-PVC content causes the decrease of the pore volume.

Morphology

It is well known that PVC grains prepared by suspension polymerization consist of three types of particles as follows[8,11]:

1. Primary particle, 1 μm
2. Agglomerated particle, 3–10 μm
3. Grain, 50–200 μm

Figures 1(a) and 1(b) show scanning electron micrographs (SEM) of the fractured section of sample A. The grain consists of agglomerated particles, of which the sizes are 1–3 μm. A fairly large

vacancy is observed in the grain, and its size is approximately 10–30 μm. Figures 2(a) and 2(b) show an SEM of a fractured section of sample B-4, which consists of HMW-PVC and LMW-PVC. The grain is also made of agglomerated particles similar to those of sample A and their sizes are approximately 1–3 μm. It is interesting that there are few vacancies observed in the grain. It shows that the polymerization of VCM is carried out inside the vacancy in the HMW-PVC grain prepared at the first step. Figures 3(a) and 3(b) show SEM and energy dispersion X-ray micrographs of the fractured section of sample B-4, respectively.

The internal structure of the grain is made of uniformly agglomerated particles as described above. White spots in Figure 3(b) show the presence of sulfur atom which is bonded to LMW-PVC. Namely, the distribution of the white spots means the fairly uniform distribution of LMW-PVC. Then this result shows that the polymerization at the second step
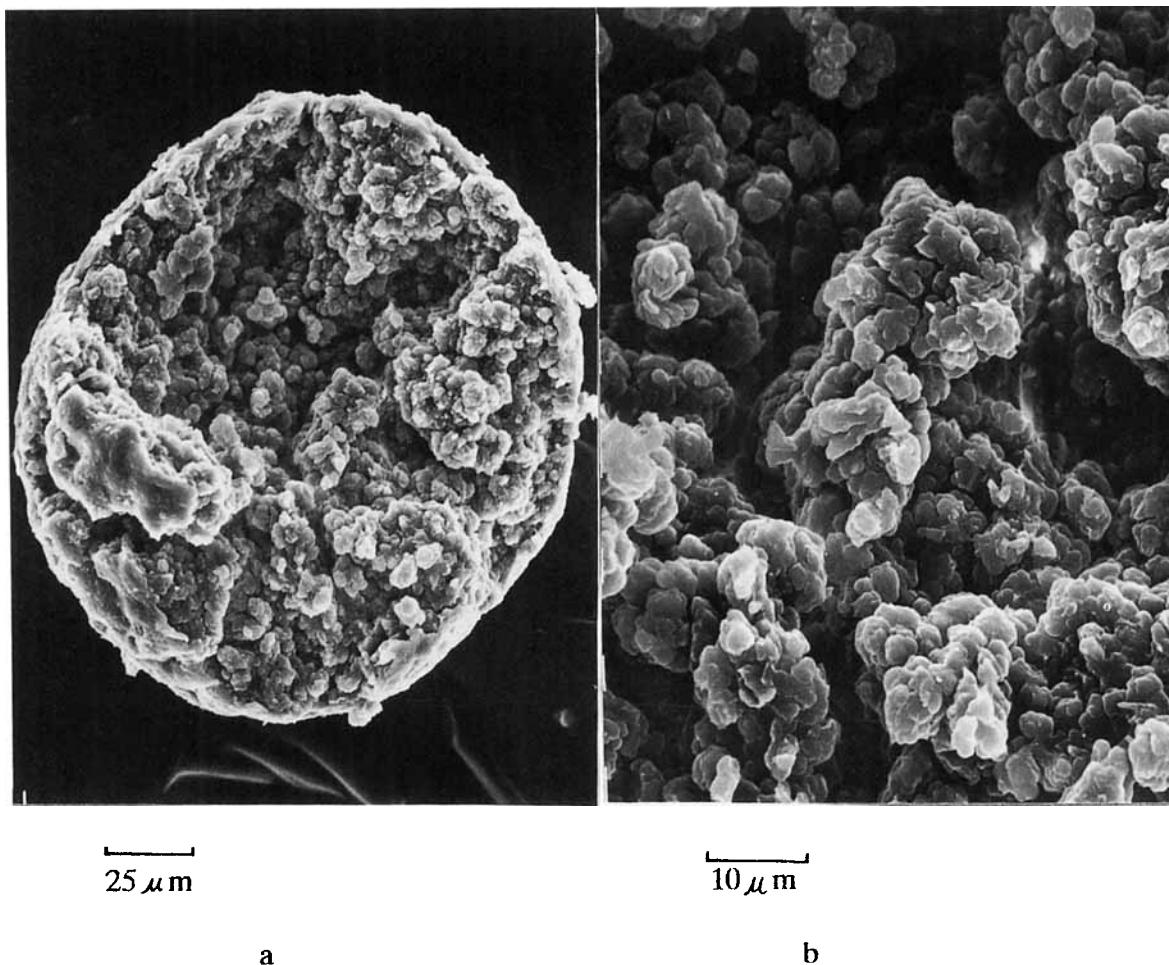

25 μm   10 μm

a   b

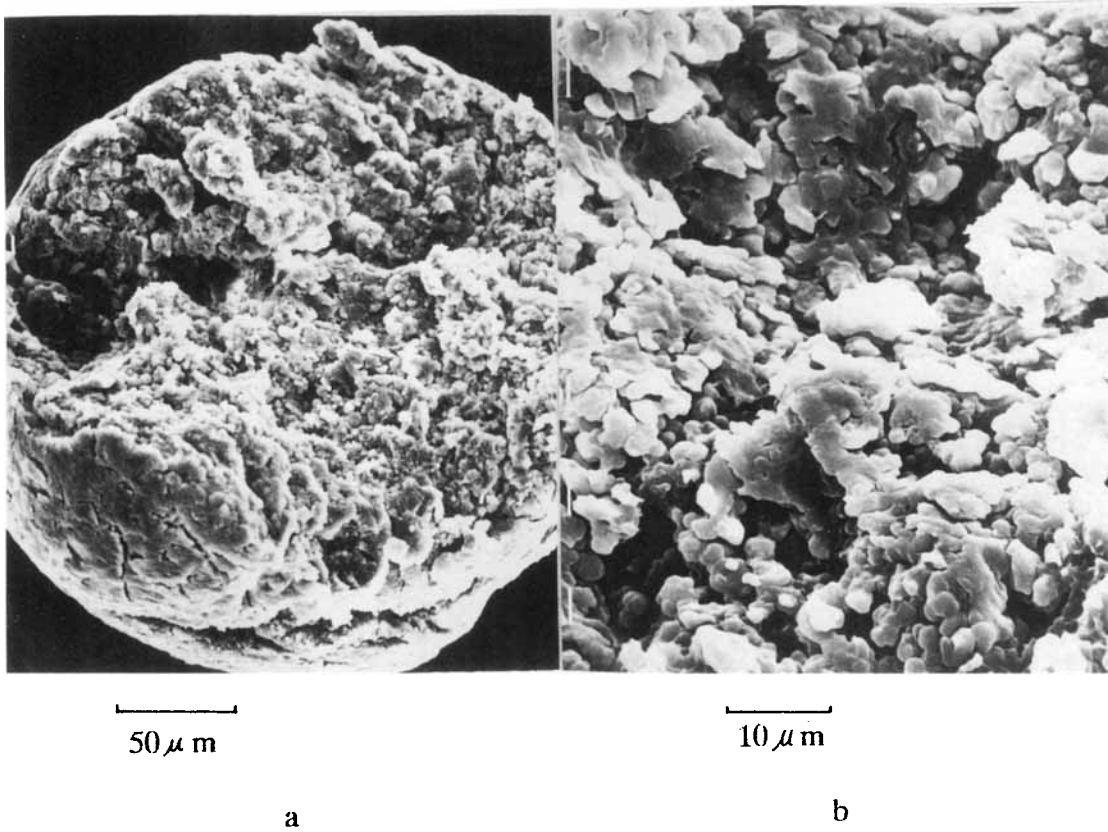**Figure 1** Scanning electron micrograph of fractured section of PVC grain (sample A).

50μm

a

10μm

b

Figure 2 Scanning electron micrograph of fractured section of BMD-PVC grain (sample B-4).
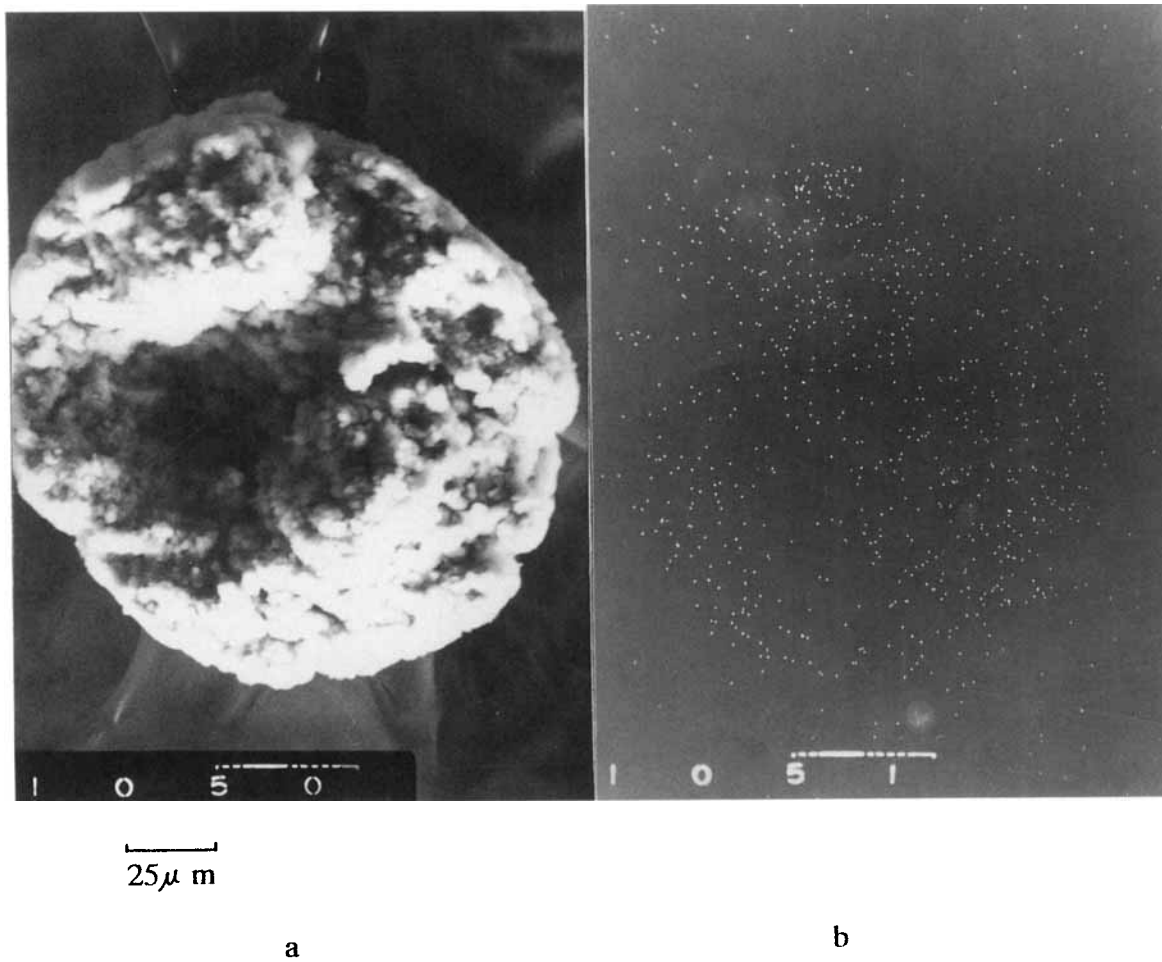

I 0 5 0

I 0 5 1

25μm

a

b

Figure 3 Scanning electron micrograph of fractured section of BMD-PVC grain (sample B-4) and mapping of S-K$_\alpha$ emissions from the same field area as in SEM.
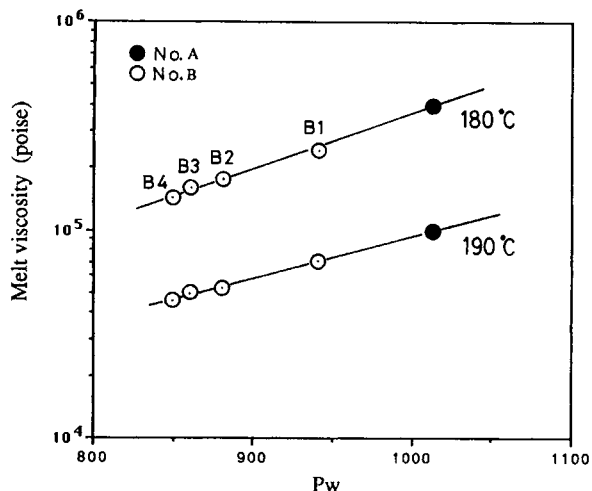
Figure 4 Dependence of melt viscosity on P_w of BMD-PVC.

Figure 6 Dependence of fusion time on P_w of BMD-PVC.

proceeds inside the vacancies of the HMW-PVC grain. Therefore, most grains consist of HMW-PVC and LMW-PVC particles, but it is presumed that small amount of HMW-PVC grains and LMW-PVC grains are present.

Melt Viscosity

Figures 4 and 5 show the dependence of the melt viscosity of BMD-PVC on P_w and M_w/M_n, respectively. The melt viscosity increases with increasing P_w and with decreasing M_w/M_n, and the melt viscosity of sample A is larger than those of samples B-1 to B-4, which contain LMW-PVC. These results are explainable by the presence of LMW-PVC in BMD-PVC, because LMW-PVC behaves like an in-

ternal plasticizer and the increase of P_w means the decrease of LMW-PVC content.[7]

Fusion Time

Figures 6 and 7 show the relations of fusion time of BMD-PVC to P_w and M_w/M_n, respectively. The fusion time increases with increasing P_w and with decreasing M_w/M_n.

The fusion time of sample A is larger than those of samples B-1 to B-4. These results can be explained by considering that the increase of LMW-PVC content in BMD-PVC causes the decrease of P_w and the increase of M_w/M_n and LMW-PVC has a plasticizing effect. On the other hand, Sorvic and Hjertberg[12] have shown that the fusion time of PVC
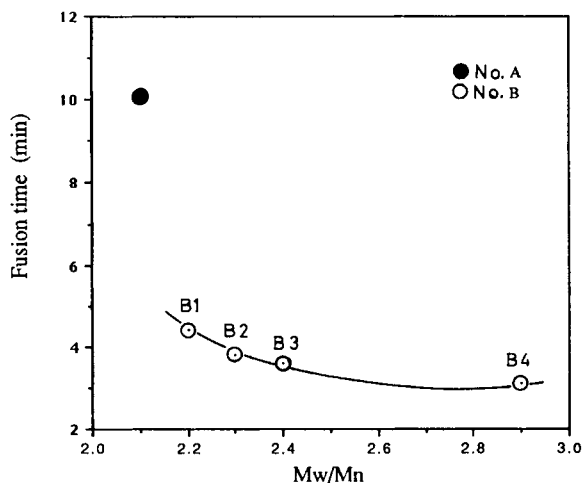

Figure 5 Dependence of melt viscosity on M_w/M_n of BMD-PVC.

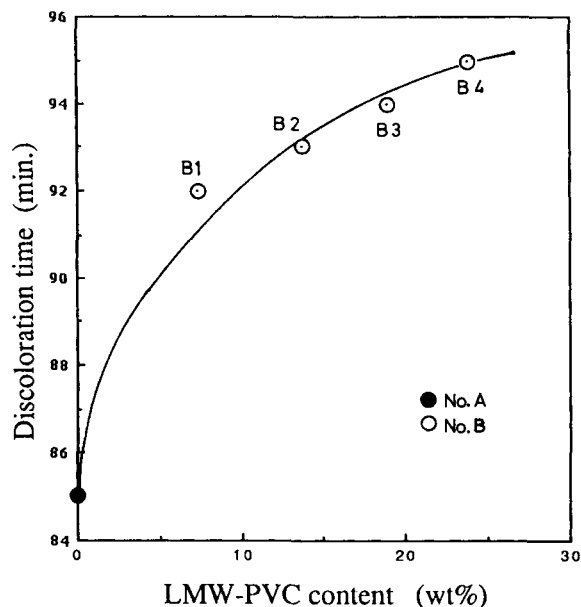**Figure 7** Dependence of fusion time on M_w/M_n of BMD-PVC.

Figure 8 Dependence of discoloration time on LMW-PVC content.

obtained by seeded suspension polymerization increased with increasing molecular weight.

These results are supported by the fact that fusion time becomes shorter with increasing LMW-PVC content in blended PVC of HMW-PVC and LMW-PVC.[6] Furthermore, the fusion time should relate to morphology of PVC grain, grain structure in other words. In the case of samples B-1 to B-4, LMW-PVC is pretty uniformly dispersed in the BMD-PVC grain, and vacancy is scarcely found in the grain, as shown before. These are the reason why BMD-PVC has shorter fusion time than HMW-PVC (sample A).
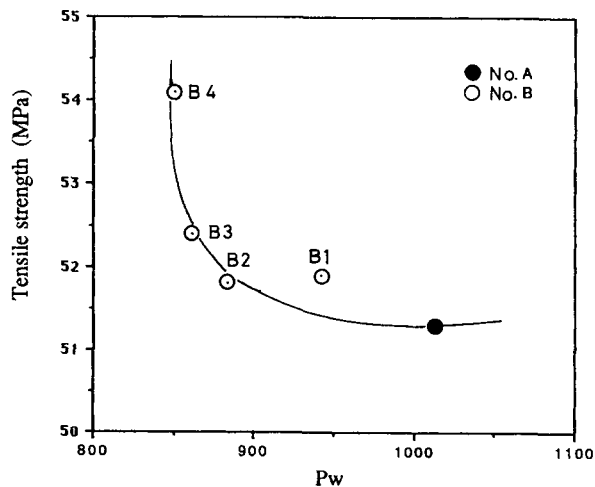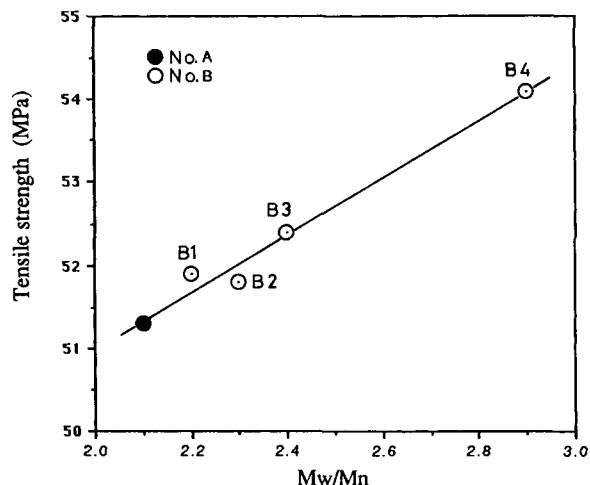

Figure 10 Dependence of tensile strength on M_w/M_n of BMD-PVC.

Discoloration Time

In general, thermal stability of LMW-PVC is poor.[13,14] However, we have reported that LMW-PVC prepared in the presence of mercapto compounds has better thermal stability (longer discoloration time) than PVC with the same P_w, prepared at relatively higher temperature by using no mercapto compounds.[5] Furthermore, the LMW-PVC was effective in improving discoloration time of blended PVC of LMW-PVC and HMW-PVC, which were separately prepared.[6]

Figure 8 shows the dependency of discoloration time of BMD-PVC on the LMW-PVC content. The discoloration times of samples B-1 to B-4 are longer
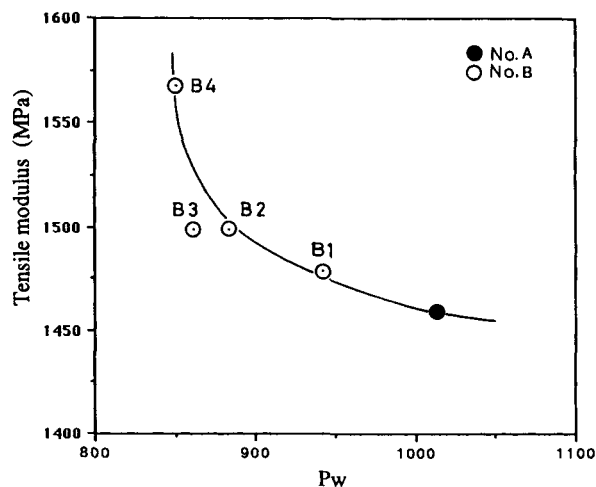

Figure 9 Dependence of tensile strength on P_w of BMD-PVC.

Figure 11 Dependence of tensile modulus on P_w of BMD-PVC.

than that of sample A, and the discoloration time increases with increasing the LMW-PVC content. These results are reasonable as described above.

Tensile Properties

Figures 9 and 10 show the dependencies of tensile strength of BMD-PVC on P_w and M_w/M_n, respectively. The tensile strength increases with decreasing P_w and with increasing M_w/M_n, and the tensile strengths of samples B-1 to B-4 are larger than that of sample A. These results are very interesting, considering that tensile strength generally increases with increasing P_w.[1-3]

The difference in the tendencies between tensile strength and P_w is explained as follows. Both the melt viscosity and the fusion time of BMD-PVC decreases with decreasing P_w, owing to plasticizing effect of LMW-PVC, so the internal structure of the molded test pieces becomes tighter than that of sample A and with increasing the LMW-PVC content. On the other hand, the dependency on M_w/M_n is similarly understandable, because the increase of M_w/M_n is caused by the increase of the LMW-PVC content. Also, the dependencies shown in Figures 9 and 10 are similar to those regarding blended PVC of LMW-PVC and HMW-PVC, which were separately prepared.[7] Figures 11 and 12 show the effects of P_w and M_w/M_n to the tensile modulus of BMD-PVC, respectively. The increase of P_w causes the decrease of tensile modulus, and this tendency is similar to that reported about nonblended PVC by Shinozaki et al.[2] On the other hand, the tensile modulus linearly increases with increasing M_w/M_n.

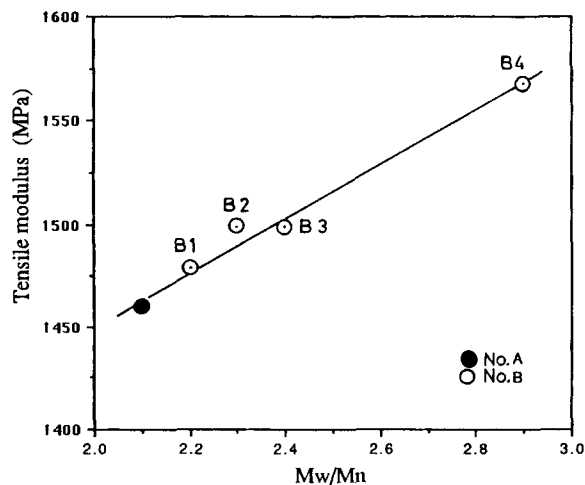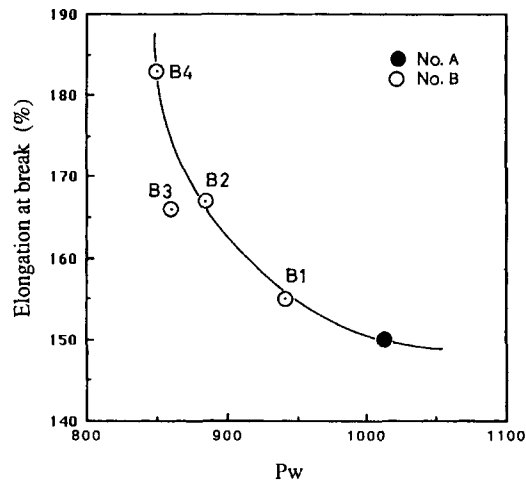Figures 13 and 14 show the effects of P_w and $M_w/$

Figure 13 Dependence of elongation on P_w of BMD-PVC.

M_n to the elongation of BMD-PVC, respectively. The obtained tendencies are similar to those of tensile strength and are similarly explainable by the plasticizing effect of LMW-PVC. Here, it is noteworthy that the relation between P_w and elongation is reverse to that of plasticized PVC, reported by Pezzin and Zinelli,[1] but the detail should be studied further.

As described above, BMD-PVC prepared by the two-step polymerization contains LMW-PVC that behaves like a plasticizer. Therefore, BMD-PVC has well-balanced properties, thermal stability, good processability, and mechanical properties, in comparison with HMW-PVC. However, more detailed study should be carried out in order to apply the
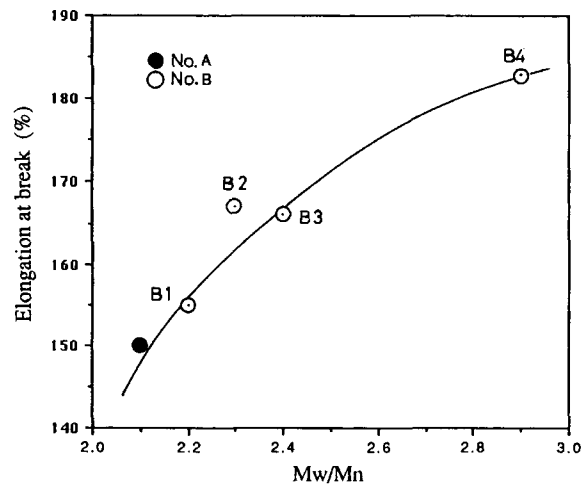

Figure 12 Dependence of tensile modulus on M_w/M_n of BMD-PVC.

Figure 14 Dependence of elongation on M_w/M_n of BMD-PVC.

two-step suspension polymerization for practical uses.

CONCLUSION

PVC with relatively broader molecular weight distribution (BMD-PVC) was prepared by the two-step suspension polymerization: (1) ordinary suspension polymerization to prepare PVC with relatively higher molecular weight (HMW-PVC) and (2) subsequent suspension polymerization in the presence of 2-mercaptoethanol as a chain transfer agent and the resultant HMW-PVC in order to prepare blended PVC of HMW-PVC and relatively lower molecular weight (LMW-PVC). BMD-PVC has more well-balanced properties of thermal stability, processability, and mechanical properties, in comparison with HMW-PVC in relation to polymerization degree and molecular weight distribution. It can be attributed to the behavior of LMW-PVC as a thermal stabilizer and a plasticizer.

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