Preparation and Application of Low Molecular Weight Poly(vinyl chloride). II. Thermal Stability of Blended Poly(vinyl chloride)

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SYNOPSIS

The blending effect of poly(vinyl chloride) (PVC) with relatively higher molecular weight (HMW-PVC) and relatively lower molecular weight (LMW-PVC) has been investigated by measuring various thermal stability and fusion times. The thermal stability of the blended PVC is improved when the small amount of LMW-PVC obtained using mercapto compounds as a chain-transfer agent is blended into PVC with HMW-PVC. At the LMW-PVC content from about 5–30 wt %, the thermal stability of the blended PVC is much more improved. Furthermore, the blended PVC with LMW-PVC, obtained using mercapto compounds, exhibits significant improvement in the discoloration time. The fusion time of the blended PVC is related to the weight-average polymerization degree of LMW-PVC and the LMW-PVC content. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is used practically in various ways. PVC has a serious drawback in that it degrades under processing and end-use conditions, accompanied with discoloration and deterioration of its mechanical properties. The thermal degradation of PVC during processing is well known to be caused by the liberation of hydrogen chloride at the labile sites of the PVC molecular chain.[1-3]

To improve processability and thermal stability during molding and practical use, various stabilizers, lubricants, and impact modifiers are added to PVC. PVC with relatively lower molecular weight (LMW-PVC) has a lower melt viscosity and good miscibility for PVC with relatively higher molecular weight (HMW-PVC). However, LMW-PVC usually has the defect of poor thermal stability[4-6] and insufficient mechanical properties compared with HMW-PVC.

On the other hand, Geil[7] and other workers[8,9] defined the structure of PVC obtained by suspension polymerization as follows: A grain of PVC is the largest unit with a size of the order of 100 m, which is an agglomerate of primary particles ($\sim$ 1 μm). During processing of the grains, primary particles are broken down to produce a continuous phase. This breakdown[10,11] of the particles is an important step of the processing procedure, which is usually called fusion, and affects mechanical properties of the products and their thermal stability.[12]

Therefore, it is very important from a practical viewpoint as to how to improve thermal stability and processability without deteriorating mechanical properties. This article concerns LMW-PVC obtained using a chain-transfer agent and its blending with HMW-PVC to improve thermal stability (discoloration time, color difference) and processability (fusion time).

EXPERIMENTAL

Materials

Vinyl chloride (VC) and other chemicals were of commercial grade. HMW-PVC was of commercial grade prepared by suspension polymerization (Grade: SUNAR 700K, 1000D, and 1400H; weight-

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average polymerization degree $[P_w]$ = 720, 1020, and 1400, respectively; Sun Arrow Chemical Co., Japan). LMW-PVC samples, which were prepared by the same method as described previously,[13] were used in the present investigation.

Characterization of LMW-PVC

The weight-average polymerization degree (P_w) was determined according to JIS K-6721 as reported previously.[13]

Blending

HMW-PVC and LMW-PVC (100 parts in total) were mixed with tribasic lead sulfate (1 part) and calcium stearate (1 part) as a stabilizer and stearic acid as a lubricant (0.2 parts) using a Henschel mixer. The resultant mixture was kneaded at 170°C for 5 min using a kneader with two mixing rollers to produce sheets (1 mm thick) for the heat-aging test.

Thermal Stability

The color difference of blended PVC was measured at 23°C, as reported previously.[13] The discoloration time of blended PVC was measured at 180°C, as reported previously.[13]

Fusion Time

An oil-heated torque rheometer, Model PLV151 from Brabender Co., was used for fusion time measurement at 180°C and with a rotor speed of 60 rpm. The charged weight was 60 g. The fusion time was

Table I   Recipes of LMW-PVC Samples

Sample	Chain-transfer Agents (mol/mol-VC)		P_w	M_w/M_n
LMW-PVC-1	DMC	0.006	530	2.6
LMW-PVC-2	DMC	0.028	320	3.2
LMW-PVC-3	DMC	0.144	200	3.3
LMW-PVC-4	DMC	0.694	130	4.2
LMW-PVC-5	MET	0.096	260	3.1
LMW-PVC-6	TGR	0.046	220	4.2
LMW-PVC-7	TGR	0.389	120	4.8
LMW-PVC-8	TGA	0.032	210	3.6

VC: 7.5 mol/L-H_2O. Polymerization initiator: t-butylperpivalate, 0.04 mol/L-VC. Polymerization temperature/time: 60°C/ 3.0 h. DMC: dodecylmercaptan; MET: 2-mercaptoethanol; TGR: α-thioglicerol; TGA: thioglycolicacid.
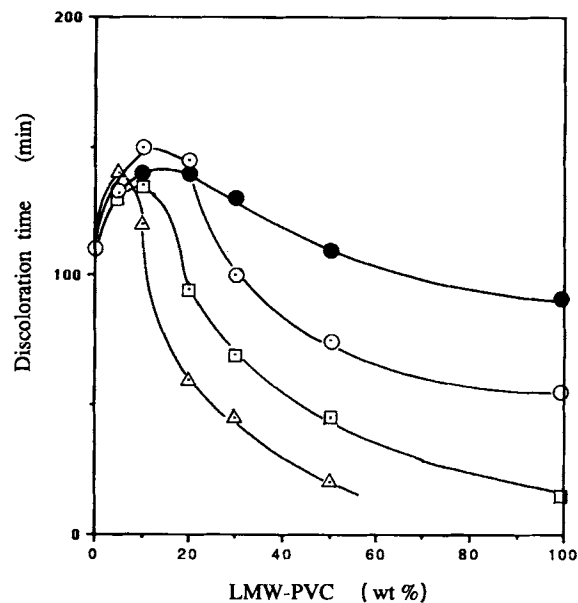

Figure 1   Dependence of discoloration time on LMW-PVC content in blended PVC with HMW-PVC-2: (●) LMW-PVC-1; (○) LMW-PVC-2; (□) LMW-PVC-3; (△) LMW-PVC-4.

determined as the period from time zero to the point of initial high torque.

RESULTS AND DISCUSSION

Table I shows the P_w and M_w/M_n of LMW-PVC obtained using different chain-transfer agents.
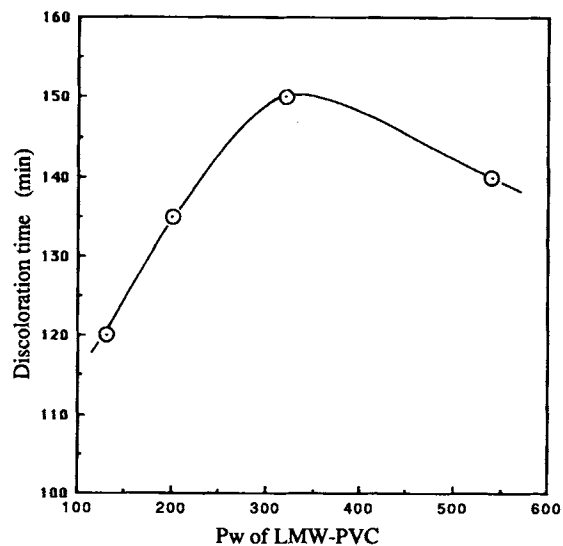

Figure 2   Dependence of discoloration time on P_w of LMW-PVC in blended PVC of 10/90 some LMW-PVC and HMW-PVC-2.
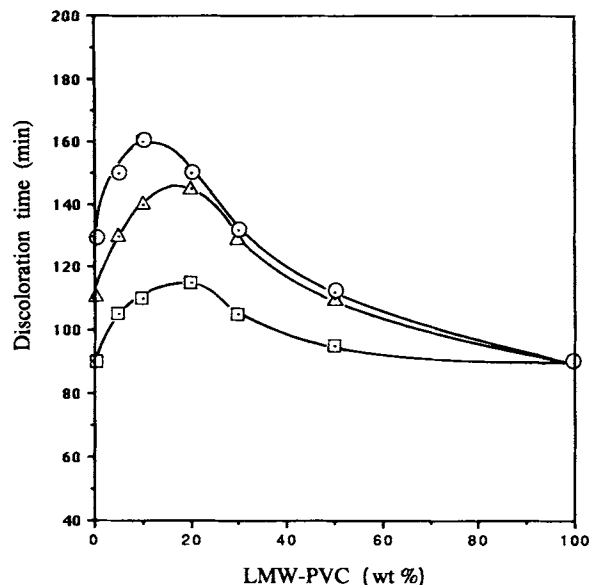
Figure 3 Dependence of discoloration time on LMW-PVC content in blended PVC with LMW-PVC-2: (□) HMW-PVC-1; (△) HMW-PVC-2; (○) HMW-PVC-3.

Figure 1 shows the relation between the discoloration time and the blend ratio of HMW-PVC with LMW-PVC having various P_w's. It is noteworthy that the remarkable improvement of the discoloration time of the blended PVC is observed in the range of an LMW-PVC content of 5–10 wt % in comparison with the HMW-PVC used, regardless of the P_w of the LMW-PVC itself. At above 10% of P_w, the discoloration time of the blended PVC gradually decreases with increasing LMW-PVC content.

The blending of HMW-PVC-2 and LMW-PVC-1 obtained using dodecylmercaptan has a good discoloration time in the range of LMW-PVC content from 0 to 50%. Although LMW-PVC-4 (P_w: 130) is deeply discolored during roll milling, the blending of LMW-PVC-4 and HMW-PVC-2 results in improvement of the discoloration time of the blended PVC containing LMW-PVC-4 of less than 10%.

Figure 2 shows the relation of discoloration time and P_w of LMW-PVC for the blended PVC with HMW-PVC-2 (90%) and LMW-PVC-1, -2, -3, and -4 (10%), respectively. The discoloration time of LMW-PVC increases with increasing P_w, as reported previously.[13] However, it is found that the discoloration time of the blended PVC obtained using LMW-PVC-2 (P_w: 340) gives a maximum value (150 min).

Figure 3 shows the discoloration time of some blended PVC of HMW-PVC (HMW-PVC-1: P_w = 720, HMW-PVC-2: P_w = 1020, HMW-PVC-3: P_w = 1400), and LMW-PVC-1 (P_w = 540). Although each discoloration time of HMW-PVC (P_w = 720) and LMW-PVC-1 (P_w = 540) is the same (90 min) as shown in Figure 3, the discoloration times of the blended PVC are improved over all compositions, and blending 20% LMW-PVC-1 to HMW-PVC-1 makes the resultant polymer stabilized by 1.3 times.

With increasing P_w of HMW-PVC, the discoloration time of blended PVC is improved in the range of lower LMW-PVC content less than 30%, which is similar to the results in Figure 1. These results show that the improvement of discoloration time of the blended PVC depends not only on the difference of P_w of HMW-PVC or LMW-PVC but also on the thermal stability of LMW-PVC.

Figure 4 shows the discoloration time of HMW-PVC-2 blended with the various amounts of LMW-PVC-5, -6, and -8 shown in Table II. The discoloration time of these blended PVC are improved, similar to the results shown in Figure 1, regardless of the molecular structure of LMW-PVC. These LMW-PVC are too poor in heat stability to be processed by roll milling at 170°C.

Hence, the improvement of thermal stability of blended PVC, as shown in Figure 4, is ascribed to the difference of the structure of the end group of LMW-PVC, owing to the structural difference of mercapto compounds. It is found that the excellent discoloration time of the blended PVC is observed in all cases of the LMW-PVC polymerized in the

Table II   Discoloration Time and ΔE for Blended PVC

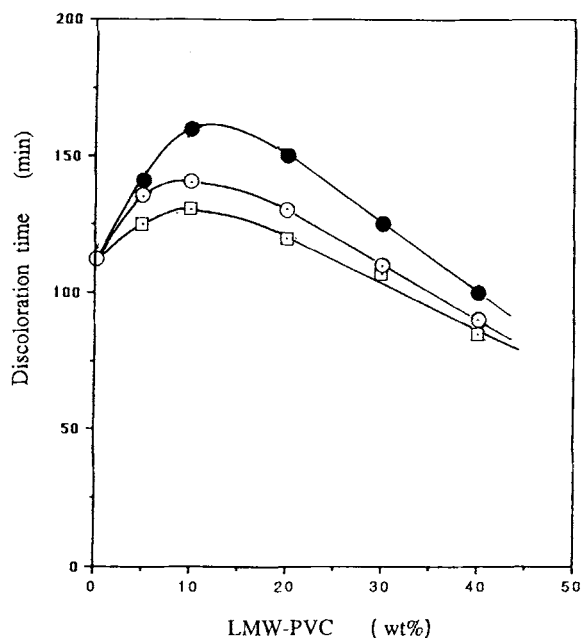| Blended PVC				Discoloration Time (min)	ΔE
HMW-PVC	%	LMW-PVC	%		
HMW-PVC-2	100	—	—	110	27.5
HMW-PVC-2	90	LMW-PVC-5	10	140	20.2
HMW-PVC-2	90	LMW-PVC-6	10	160	16.1
HMW-PVC-2	90	LMW-PVC-7	10	150	18.3
HMW-PVC-2	90	LMW-PVC-8	10	130	31.8

Figure 4 Dependence of discoloration time on LMW-PVC content in blended PVC with HMW-PVC-2: (●) LMW-PVC-5; (○) LMW-PVC-6; (□) LMW-PVC-8.

presence of mercapto compounds, in the range of 5–30 wt % of LMW-PVC content.

Fusion Behavior of Blended PVC

The processability of PVC is usually measured as the fusion time using a fusion torque-rheometer. The
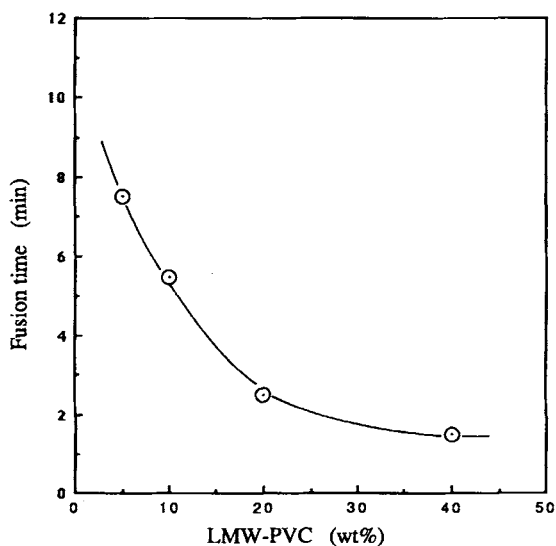
fusion time of LMW-PVC is generally shorter than that of HMW-PVC. It is well known that a grain of PVC is the largest unit with a size of the order of 100 m, which is an agglomerate of primary particles ($\sim 1\ \mu$m).[9] During processing of the PVC grains, primary particles are broken down to produce a continuous phase.[11]

Figure 5 shows the relation between the fusion time and the content of LMW-PVC-1 in the blended PVC with LMW-PVC-1 and HMW-PVC-2. The fusion time of the blended PVC decreases with increasing LMW-PVC-1 content. The fusion time, hence, is affected by the LMW-PVC content in blended PVC.

Figure 6 shows the relation between the fusion time and the P_w of LMW-PVC-1, -2, -3, and -4 obtained using dodecylmercaptan in the blended PVC with HMW-PVC-2 and LMW-PVC. The fusion time of the blended PVC increases with increasing P_w of LMW-PVC.

The fusion time of the other blended PVC with HMW-PVC and LMW-PVC are shown in Table III. The fusion time of nonblended PVC increases with increasing P_w. The fusion time of HMW-PVC-3 (P_w: 1400) is not observed.

However, blending of LMW-PVC with HMW-PVC engenders a drastic decrease in the fusion time. The fusion time of blended PVC with HMW-PVC-3 and LMW-PVC-2 is 7.5 min. Hence, it is found that this fusion time is similar to that of HMW-PVC-2 (P_w: 1020). The effect of decreasing the fu-
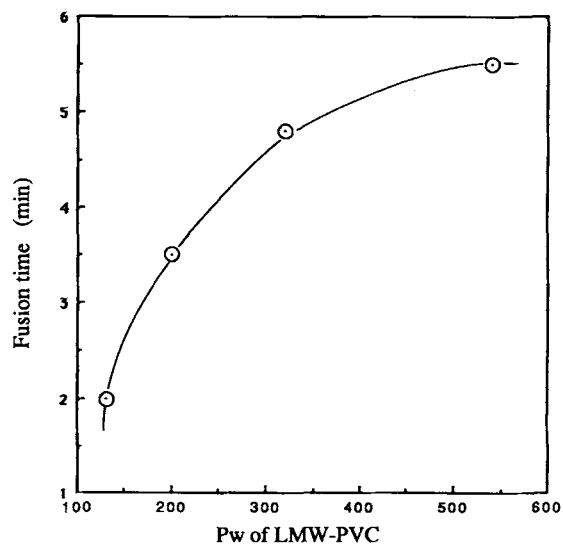

Figure 5 Dependence of fusion time on LMW-PVC-1 content in blended PVC with HMW-PVC-2.

Figure 6 Dependence of fusion time on P_w of LMW-PVC in blended PVC of 10/90 some LMW-PVC and HMW-PVC-2.

Table III   Fusion Time of Blended PVC

Blended PVC						Fusion[a] Time (min)
HMW-PVC	P_w	%	LMW-PVC	P_w	%	
HMW-PVC-1	720	100				4.5
HMW-PVC-2	1020	100				11.0
HMW-PVC-3	1400	100				No fusion
HMW-PVC-2	1020	80	LMW-PVC-2	320	20	3.2
HMW-PVC-2	1020	80	LMW-PVC-3	200	20	3.0
HMW-PVC-3	1400	90	LMW-PVC-1	530	10	12.0
HMW-PVC-3	1400	90	LMW-PVC-2	320	10	9.0

[a] Estimated by using a Brabender plasticorder at 180°C.

sion time is independent of the kind of chain-transfer agent used.

LMW-PVC is also compatible with HMW-PVC. Thus, although it was heat-sensitive, LMW-PVC promotes the fusion of the HMW-PVC and reduces the internal friction of the polymer molecules in the first stage of the fusion process, resulting in the increase of the thermal stability of blended PVC in the special region of the LMW-PVC content (5–30%).

CONCLUSION

Thermal stability of blended PVC with HMW-PVC and LMW-PVC, which were prepared by suspension polymerization in the presence of some mercapto compounds, was studied. Discoloration time of the blended PVC is dependent on the amounts of LMW-PVC and its polymerization degree. In particular, the discoloration time of the blended PVC with LMW-PVC (P_w = 530) remarkably increases compared with those of LMW-PVC (P_w = 320, 200, 130). Furthermore, blending of some amount of LMW-PVC (about 5–30%) increases the discoloration time of the blended PVC compared with those of HMW-PVC itself.

The fusion time of the blended PVC decreases with decreasing of the polymerization degree and amounts of LMW-PVC. Therefore, LMW-PVC promotes the fusion of HMW-PVC and reduces the internal friction of the PVC molecules.

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