

Preparation and Application of Low Molecular Weight Poly(vinyl chloride). III. Mechanical Properties of Blended Poly(vinyl chloride)

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SYNOPSIS

The blending effect of poly(vinyl chloride) with relatively higher molecular weight (HMW-PVC) and relatively lower molecular weight (LMW-PVC) has been investigated by measuring various mechanical properties: melt properties, tensile strength, tensile modulus, and impact strength. The blended PVC has slightly improved melt properties in comparison with the HMW-PVC used. The tensile strength of the blended PVC is related to the weight-average polymerization degree (P_w) of LMW-PVC and the LMW-PVC content. At the LMW-PVC content of 20%, the tensile strength of blended PVC is a maximum: approximately 58 MPa. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is used practically in various ways. However, PVC has a serious drawback in that it decomposes under processing and end-use conditions, with accompanying discoloration and deterioration of physical properties.

Many efforts have so far been carried out to improve the processability and mechanical properties of PVC. Lee and Chen¹ showed that the mechanical properties and processability of PVC are improved by blending PVC and methyl methacrylate (MMA)-*n*-butyl acrylate (BA) copolymers with various molecular weights and, also, that the copolymer with a high BA content acts as a lubricant, reducing the melt viscosity of PVC during processing. In addition, they elucidated that the fusion time of the blends increased with increasing the molecular weight of the copolymers.

On the other hand, Casey and Okano showed that the 50/50 blend of relatively higher molecular weight PVC (HMW-PVC) and relatively lower molecular weight PVC (LMW-PVC), of which the mathe-

matical viscosity is equal to the medium molecular weight PVC, has better melt flow than the medium molecular weight PVC for injection molding.² We have found that LMW-PVC prepared by suspension polymerization in the presence of a mercapto compound has good thermal stability and that the blends of HMW-PVC and LMW-PVC are improved regarding thermal stability and processability.³

This article presents the effects of the blending of LMW-PVC with HMW-PVC on the mechanical properties and flow behavior of blends of LMW-PVC and HMW-PVC.

EXPERIMENTAL

Materials

Vinyl chloride (VC) and *t*-butyl perpivalate were of commercial grade and used without further purification. The other chemicals were of commercial grade and distilled under reduced N₂ atmosphere. HMW-PVC samples were of commercial grade prepared by suspension polymerization (Grade: SUNAR1000D, 1300E, 1400H, Sun Arrow Chemical Co., Japan). The weight-average polymerization degrees (P_w) of HMW-PVC-1, -2, and -3 were 1020, 1320, and 1450, respectively.

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Preparation of LMW-PVC

LMW-PVC was prepared by the suspension polymerization method. A stainless-steel autoclave (10 L) was charged with 5 kg of deionized water, into which 6 g of partially saponified poly(vinyl alcohol) (PVA) (the degree of saponification was 80%), 3 g of methyl cellulose (MC), and a definite amount of dodecyl mercaptan and *t*-butyl perpivalate were added. The autoclave was evacuated, and VC was fed into it and polymerized at 60°C for 3 h with stirring. The resultant PVC was washed with methanol and then dried *in vacuo* at 40°C.

Weight-average Polymerization Degree (*Pw*)

The *Pw* was determined according to JIS K-6721 as follows: The specific viscosity was measured in nitrobenzene (0.4 g/100 mL) at 30°C by an Ubbelohde-type viscosimeter. The intrinsic viscosity [η] was calculated from eq. (1), and *Pw* was calculated by eq. (2):

$$[\eta] = \sqrt{2/CD\eta_{sp} - \ln \eta_{rel}} \quad (1)$$

where [η] is the limiting viscosity; η_{rel} , the relative viscosity; η_{sp} , the specific viscosity; and *C*, the concentration (g/mL);

$$Pw = 500 \{ \text{ant} \log [\eta]/0.168 - 1 \} \quad (2)$$

The molecular weight distribution was measured at 23°C in tetrahydrofuran solution using a gel permeation chromatograph, Waters Type-200 from Waters Associates.

Blending

HMW-PVC and LMW-PVC (100 parts by total weight) were mixed with tribasic lead sulfate (1

part) and calcium stearate (1 part) as stabilizers and stearic acid as the lubricant (0.2 parts) using a Henschel mixer. The resultant mixture was milled at 170°C for 5 min using a mill with two mixing rollers to produce 1 mm-thick sheets for measurements of mechanical properties.

The *Pw* of blended PVC was calculated by the following equation:

$$Pw = Pw_1 \times W_1 + Pw_2 \times W_2 \quad (3)$$

where *Pw*₁ and *Pw*₂ are the polymerization degree of LMW-PVC and HMW-PVC, respectively; and *W*₁ and *W*₂, the weight percent of LMW-PVC and HMW-PVC, respectively.

Measurements of Mechanical Properties

Test pieces were prepared by heat-pressing the blended PVC under 50 kg/cm at 180°C for 10 min. The melt-flow was measured with a Shimadzu Koka Flow Tester, Model CFT-500, from Shimadzu Seisakusho Co. Japan. Hence, the increasing rate of the sample temperature was 3°C/min and the pressure added to the sample was from 200 to 450 kg/cm.

The tensile properties (tensile strength at yield and tensile modulus in tension) were measured at 23°C with a Toyo Baldwin Tensilon, Model UTM-5Y, from Toyo Baldwin Co., Japan. Impact strength was measured at 23°C with a Toyo Seiki universal impact tester, Model JIS K-7111, from Toyo Seiki Seisakusho Co., Japan.

RESULTS AND DISCUSSION

Preparation and Characterization of LMW-PVC

LMW-PVC was prepared in the presence of dodecyl mercaptan and the preparative conditions are shown in Table I, which also shows the weight-average po-

Table I Polymerization of VC in the Presence of Dodecyl Mercaptan^a

Sample	VC (mol/L)	Dodecyl Mercaptan (mol/L)	<i>t</i> -Butyl Peroxypivalate (mol/L)	<i>Pw</i> ^b	<i>M_w</i> / <i>M_n</i> ^c
LMW-PVC-1	7.2	0.04	0.018	530	2.6
LMW-PVC-2	7.2	0.2	0.036	320	3.2
LMW-PVC-3	7.2	1.0	0.09	200	3.3
LMW-PVC-4	7.2	5.0	0.12	130	4.2

^a Polymerized at 60°C for 3 h.

^b Determined according to JIS K-6761.

^c Obtained from GPC.

Table II Recipes for Blended PVC

Sample No.	HMW-PVC			LMW-PVC			Blended PVC <i>Pw</i> ^a	Blended PVC <i>M_w/M_n</i> ^b
		<i>Pw</i>	Wt %		<i>Pw</i>	Wt %		
1	HMW-PVC-1	1020	100	—	—	—	1020	2.1
2	HMW-PVC-1	1020	95	LMW-PVC-1	530	5	995	2.1
3	HMW-PVC-1	1020	90	LMW-PVC-1	530	10	970	2.3
4	HMW-PVC-1	1020	80	LMW-PVC-1	530	20	920	2.4
5	HMW-PVC-1	1020	70	LMW-PVC-1	530	30	870	2.5
6	—	—	—	LMW-PVC-1	530	100	530	2.6
7	HMW-PVC-1	1020	95	LMW-PVC-4	130	5	975	2.2
8	HMW-PVC-1	1020	90	LMW-PVC-4	130	10	931	3.0
9	HMW-PVC-1	1020	80	LMW-PVC-4	130	20	842	3.9
10	HMW-PVC-1	1020	70	LMW-PVC-4	130	30	752	4.5
11	—	—	—	LMW-PVC-4	130	100	130	4.2

^a Algebraical average value calculated from *Pw* and contents of HMW-PVC and LMW-PVC.^b Obtained from GPC.

lymerization degree (*Pw*) and molecular weight distribution (*M_w/M_n*) of LMW-PVC.

To keep the conversion of VC at about 60–70%, the amount of polymerization initiator was increased with increasing the amount of the chain-transfer agents. The *M_w/M_n* of LMW-PVC obtained by suspension polymerization increases with increasing content of dodecyl mercaptan. Therefore, dodecyl mercaptan would terminate the polymerization by attaching at the end of the polymer chain. As the result, the LMW-PVC obtained using dodecyl mercaptan has good thermal stability.⁴

Table II shows the composition, *Pw*, and *M_w/M_n* of blended PVC. The *M_w/M_n* of blended PVC increases with increasing LMW-PVC content and decreasing *Pw* of LMW-PVC.

Processability

Previously, it was shown that LMW-PVC obtained by suspension polymerization in the presence of dodecyl mercaptan has good processability, shorter fusion time, and low viscosity.³ Figure 1 shows the (shear stress–shear rate) curves of blended PVC, determined with a flow tester at 180°C. Both the flow curves of blended PVC (sample no. 4) and nonblended PVC (HMW-PVC-1) show similar tendencies. However, the blending of LMW-PVC makes the shear stress of the blended PVC slightly lower than that of nonblended PVC. Figure 2 shows the (apparent viscosity–shear rate) curves for the same samples as shown in Figure 1. The blending of LMW-PVC makes the apparent viscosity and shear stress of blended PVC slightly lower than that of

nonblended PVC. Thus, LMW-PVC is considered to be effective as an internal lubricant, reducing the apparent viscosity.

Mechanical Properties

It is well known that the rate and extent of fusion of PVC compounds during processing affect further processing performance and development of mechanical properties in the final product.⁵ Therefore,

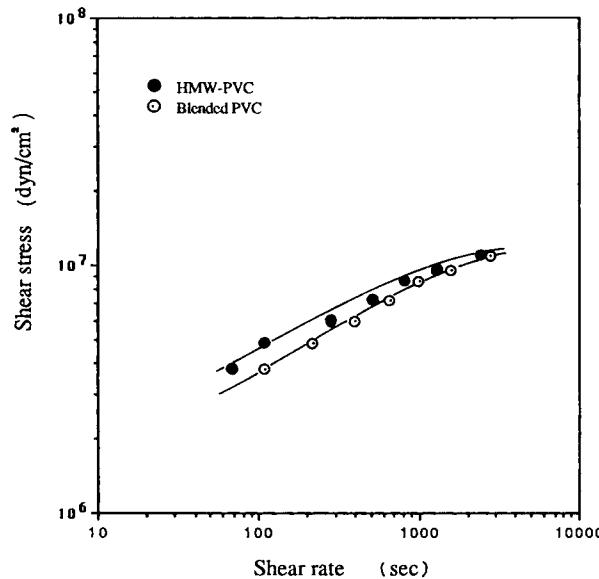


Figure 1 Effect of shear rate on shear stress: (●) HMW-PVC-1 (*Pw* 1020); (○) blended PVC of 10/90 LMW-PVC-1 (*Pw* 530) and HMW-PVC-1 (*Pw* 1020).

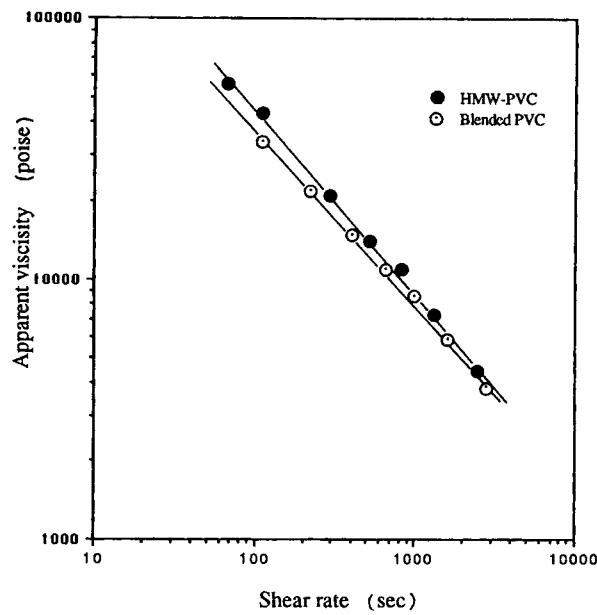


Figure 2 Effect of apparent viscosity on shear rate: (●) HMW-PVC-1 (P_w 1020); (○) blended PVC of 10/90 LMW-PVC-1 (P_w 530) and HMW-PVC-1 (P_w 1020).

it is expected that blended PVC of LMW-PVC and HMW-PVC could give good improvement of mechanical properties.

Table III shows the mechanical properties of the blended PVC. The P_w of LMW-PVC slightly affects the mechanical properties: Tensile strength and tensile modulus of the samples (nos. 12, 13, and 14) increases with increasing M_w/M_n of the blended PVC. On the other hand, in case of the samples (nos. 15, 16, and 17), the change could be scarcely recognized in tensile strength and tensile modulus. In general, LMW-PVC itself is brittle, but the blended PVC with LMW-PVC improves impact strength, as shown in Table III.

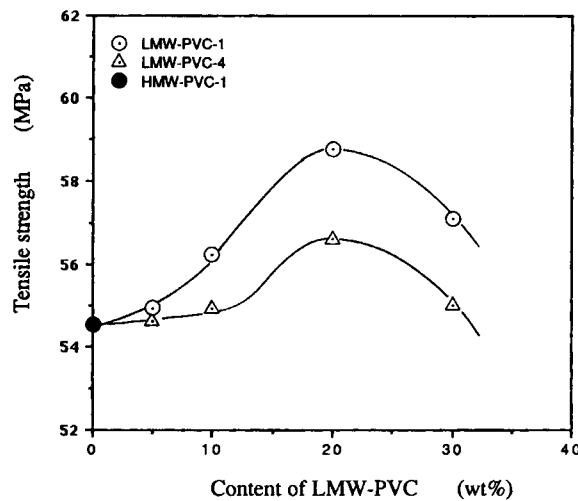


Figure 3 Dependence of tensile strength on LMW-PVC content in blended PVC: (○) LMW-PVC-1 (P_w 530); (△) LMW-PVC-4 (P_w 130); (●) HMW-PVC-1 (P_w 1020).

Tensile Properties

Figure 3 shows the relation between tensile strength of the blended PVC and LMW-PVC content. Tensile strength of the blended PVC is higher than that of nonblended PVC (HMW-PVC-2). Blending of LMW-PVC-4 (P_w = 130) gives higher tensile strength in comparison with that of LMW-PVC-1 (P_w = 530). In addition, both blended PVCs give a maximum value of tensile strength at 20% by weight of LMW-PVC.

Figure 4 shows the relation between tensile strength and the P_w of blended PVC with 10% LMW-PVC content and nonblended PVC (HMW-PVC-1). The tensile strength of blended PVC is higher than that of nonblended PVC and increases with decreasing P_w of the blended PVC, namely, the P_w of LMW-PVC.

Table III Mechanical Properties of Blended PVC

Sample No.	HMW-PVC		LMW-PVC		Blended PVC (M_w/M_n)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Impact Strength (J/m)
	P_w	%	P_w	%				
12	1320	100	—	—	2.1	53.3	1370	45.1
13	1320	90	530	10	2.4	54.4	1400	51.9
14	1320	90	320	10	2.7	54.9	1490	50.9
15	1450	100	—	—	2.2	54.7	1430	50.0
16	1450	90	530	10	2.4	54.2	1390	50.9
17	1450	90	320	10	2.8	55.3	1400	49.0
18	—	—	530	100	2.6	—	—	11.7

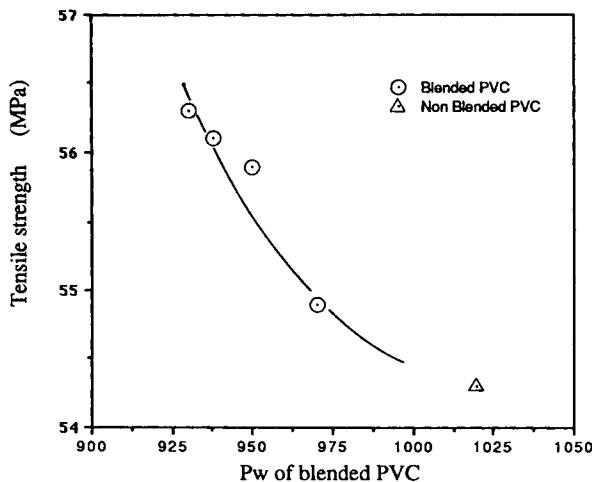


Figure 4 Dependence of tensile strength on P_w of blended PVC of approximately 10/90 LMW-PVC and HMW-PVC-1 (P_w 1020): (○) blended PVC; (Δ) non-blended PVC.

Figure 5 shows the relation between tensile strength and M_w/M_n of blended PVC. The tensile strength of blended PVC increases with increasing M_w/M_n of blended PVC.

Figure 6 shows the relation between the tensile modulus of blended PVC and LMW-PVC (LMW-PVC-1, P_w = 530) content. Here, it is shown that the blending of LMW-PVC increases the tensile modulus more than that of HMW-PVC-1, as shown in Figure 3. Therefore, PVC with higher tensile

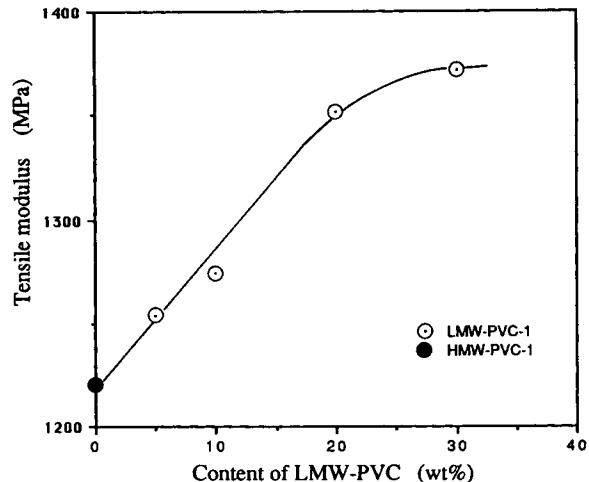


Figure 6 Dependence of tensile modulus on LMW-PVC content in blended PVC of HMW-PVC-1 (P_w 1020) and LMW-PVC-1 (P_w 530): (○) LMW-PVC-1 blended PVC; (●) HMW-PVC-1.

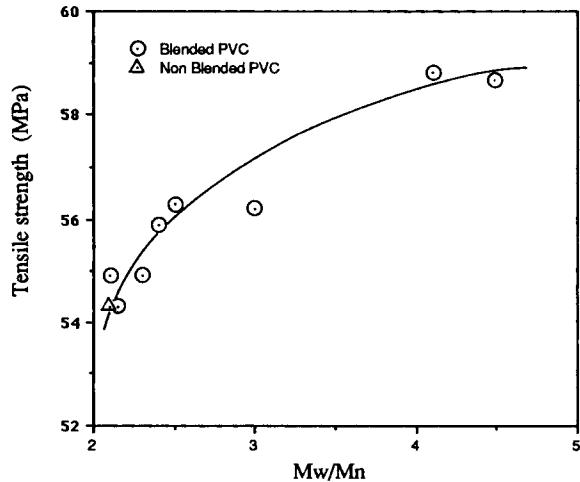


Figure 5 Dependence of tensile strength on M_w/M_n of blended PVC of approximately 10/90 LMW-PVC and HMW-PVC-1 (P_w 1020): (○) blended PVC; (Δ) non-blended PVC.

strength and tensile modulus can be produced by blending LMW-PVC and HMW-PVC.

Impact Strength

Figure 7 shows the relation between impact strength and LMW-PVC content of blended PVC. The impact strength of blended PVC decreases with increasing LMW-PVC content. In addition, the impact strength of blended PVC increases with in-

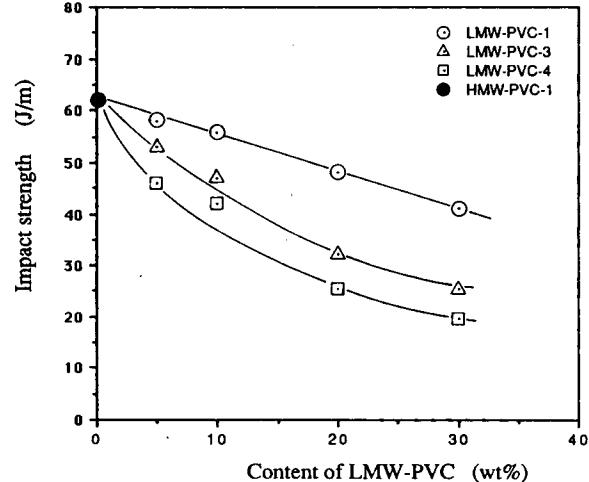


Figure 7 Dependence of impact strength on LMW-PVC content in blended PVC: (○) LMW-PVC-1 (P_w 540); (Δ) LMW-PVC-3 (P_w 200); (□) LMW-PVC-4 (P_w 130); (●) HMW-PVC-1 (P_w 1020).

creasing P_w of LMW-PVC (LMW-PVC-1 > LMW-PVC-3 > LMW-PVC-4), but those values are lower than that of nonblended PVC (HMW-PVC-1). The impact strength of blended PVC is affected mainly by the brittleness of the LMW-PVC molecular chain, as shown in Table III.

Shaw elucidated that the mechanical properties of PVC (tensile strength and impact strength) increases with increasing the molecular weight but that melt-flow contrarily decreases.⁶ Therefore, the results described above are reasonably explicable.

Figure 8 shows the relation between the impact strength and P_w of blended PVC. Impact strength increases with increasing P_w of blended PVC and increasing P_w of the LMW-PVC used. Figure 9 shows the relation between the impact strength and M_w/M_n of blended PVC. The impact strength of blended PVC decreases with increasing M_w/M_n on blended PVC. Therefore, the melt structure of LMW-PVC strongly affects the mechanical properties of blended PVC. Moreover, LMW-PVC with relatively higher molecular weight used in blended PVC causes less reduction in impact strength. Blending LMW-PVC with HMW-PVC would result in a tighter melt structure, owing to LMW-PVC having a lower melt temperature, lower melt viscosity, and shorter fusion time in comparison with those of HMW-PVC.

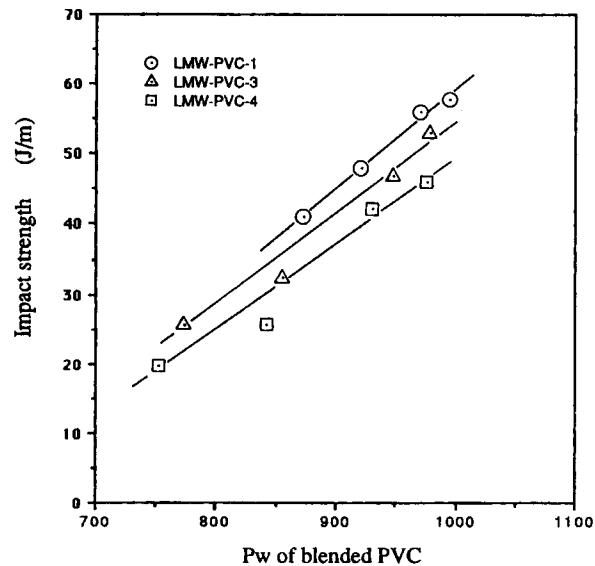


Figure 8 Dependence of impact strength on P_w of blended PVC: (○) LMW-PVC-1 (P_w 530); (△) LMW-PVC-3 (P_w 200); (□) LMW-PVC-4 (P_w 130).

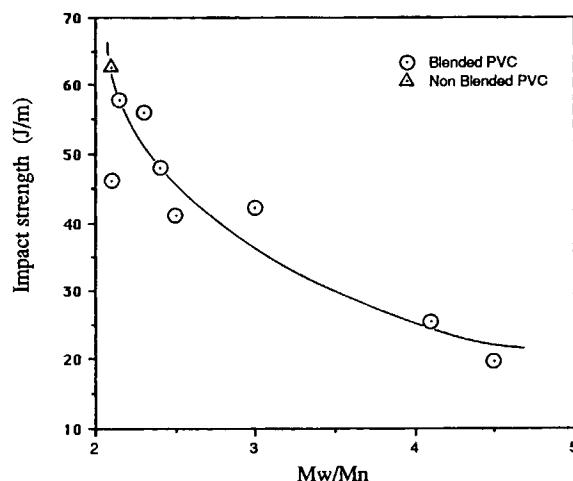


Figure 9 Dependence of impact strength on M_w/M_n of blended PVC of approximately 10/90 LMW-PVC and HMW-PVC-1 (P_w 1020): (○) blended PVC; (△) non-blended PVC.

CONCLUSION

Blending effects of LMW-PVC with HMW-PVC were investigated in relation to tensile strength, tensile modulus, impact strength, and flow rate. The flow properties of blended PVC are slightly improved by blending LMW-PVC. Tensile strength and tensile modulus of blended PVC increases with increasing LMW-PVC content and decreasing P_w of LMW-PVC. Tensile properties, hence, are affected by the M_w/M_n of blended PVC. On the other hand, the impact strength decreases with increasing LMW-PVC content and, especially, with decreasing P_w of LMW-PVC.

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