

Effects of Poly(Methyl Methacrylate-co-*n*-Butyl Acrylate) on the Properties and Processing Behavior of Poly(Vinyl Chloride)

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Synopsis

Random copolymers of methyl methacrylate/*n*-butyl acrylate with a BA content of 0–50% and $\bar{M}_v = 0.16\text{--}4.04 \times 10^6$ were synthesized and evaluated as a processing aid (PA) for poly(vinyl chloride) (PVC). Their effects on the processability and properties of PVC were investigated with respect to the composition, molecular weight, and the amount of the copolymer added. It was found that the fusion rate of PVC could be improved (i) by increasing the amount of the copolymer used, (ii) by increasing the butyl acrylate content in the copolymer, and (iii) by lowering the molecular weight of the copolymer. The effect of molecular weight, composition, and amount of copolymer on the ultimate mechanical properties of PVC was investigated. The presence of copolymer did not affect the impact strength. However, the tensile strength and elongation at break were improved, particularly at high temperature (125°C). It was also found that the "plate out" phenomenon of PVC could be significantly reduced in the presence of the processing aid.

INTRODUCTION

Poly(vinyl chloride) (PVC) is mainly amorphous with only limited crystallinity (3–10%).¹ Because of its insolubility in its own monomer, PVC resin has a unique particle structure. The grain diameter of commercial PVC is around 100 μm . The grains are composed of primary particles of the order of 1 μm . The primary particles are supposed to be built up by domains in the range of 10–100 nm.² During the fusion process, the PVC grains break up into primary particles and fuse under the action of compression force, shear force, and temperature.³ In order to improve the fusion rate of PVC, processing aid (PA) is being used occasionally. The viscosity of PA is usually lower than that of PVC and its compatibility with PVC is good so that it can wet the PVC grains effectively and increases the friction between them.^{4–7} This paper presents the results of using methyl methacrylate (MMA)/*n*-butyl acrylate (BA) copolymers as a processing aid for rigid PVC resin, and their effects on the fusion behavior, mechanical properties, and "plate out" of PVC.

EXPERIMENTAL

Synthesis and Characterization of MMA/BA Copolymer (PA)

The MMA/BA copolymers were prepared by emulsion polymerization.⁸ The intrinsic viscosities $[\eta]$ of PMMA homopolymer and MMA/BA copoly-

TABLE I

Formulation A (phr)	
S-PVC ($\overline{DP}_n = 800$)	100
Pb stearate	1.5
Ba stearate	0.5
Cd stearate	0.4
PA	x
where x varied from 0 to 10 phr.	

mers were measured by an Ubbelohde type viscometer at 25°C with CHCl_3 as the solvent. Their viscosity average molecular weights (\overline{M}_v) were calculated by the equations of Razinskaya⁹ and Wunderlich,⁸ respectively. The composition of MMA/BA copolymer was analyzed with a JEOL 100 MHz FT-NMR spectrometer. The Vicat softening temperature was determined according to the method described in ASTM D-1525, and T_g was measured by DSC.

Processing Properties of PVC/PA Blends

The Brabender Plasticorder Test. A well-mixed compound with a formulation shown below was added to the mixing chamber of a Brabender Plasticorder type PLV 151 and tested at a chamber temperature of 168°C and a rotor speed of 40 rpm. The volume of the mixing chamber was 30 mL, and the selected amounts of the compound in the mixing chamber were 25 g for PVC, 15 g for PA, and 36 g for PVC/PA blends, respectively. The reason for choosing small amount of PVC and PA in the mixing chamber is to test their fusion behavior under litter compression force (Table I).

Melting Viscosity of PVC/PA Blends. The melting viscosities of PVC/PA blends already fused in Brabender at 168°C/40 rpm were measured

TABLE II

	Formulation B (phr)	Formulation C (phr)
S-PVC ($\overline{DP}_n = 1100$)	100	100
DOP	45	45
Epoxidized soybean oil	3	3
Liquid stabilizer (Mark-2114)	—	0.85
Liquid stabilizer (Nuoskabe 3042)	0.85	—
Phosphite chelator (TP-60)	0.5	0.3
Watching red	1.0	—
PA	x	—
Cd Stearate	—	0.25
Ba Stearate	—	0.40
Zn Stearate	—	0.20
TiO ₂	—	0.50

TABLE III
Characteristic Properties of MMA/BA Copolymers

Property	PMMA	BA-08	BA-15	BA-20	BA-25	BA-30	BA-40	BA-50	PVC
BA feed (% by weight)	0	8	15	20	25	30	40	50	
BA in copolymer ^a (% by weight)	0	10.2	16.5	20.7	25.6	30.9	40.2	49.8	
$[\eta]$	3.3	3.6	3.7	3.7	3.5	4.1	3.7	3.7	
$\bar{M}_v (\times 10^6)$	1.11	1.47	1.52	1.52	1.42	1.73	1.52	1.52	0.05
T_g (°C)	107	84	71	60	56	48	31	18	82
Vicat softening temp (°C)	119	98	86	75	69	64	48	35	95

^a Analyzed by FT-NMR at 40°C.

TABLE IV
Properties of BA-08 with Different Molecular Weights

Sample	M1	M2	M3	M4	M5	M6
Property						
$[\eta]$	0.95	2.0	4.0	6.1	6.8	8.1
$\bar{M}_v (\times 10^6)$	0.16	0.70	1.67	2.84	3.25	4.04
T_g (°C)				~84		
Vicat softening temp (°C)				~98		

using a Rheograph 2001 capillary rheometer. The content of PA in PVC was kept constant, 5 phr.

Plate Out Test. The plate out phenomenon was tested by a color match computer system. Two formulations shown below were blended. The color of blend B was red and that of blend C was white. Blend B was compounded in a two-roll mill set to 180°C for 10 min and discarded. Part of the added red pigment in blend B would remain on the mill, and it was carried out by blend C under the same operating conditions. The difference between the color of blend C before and after the compounding (ΔE) was then measured using a color match computer system. A larger ΔE was interpreted as a more serious plate out (Table II).

Mechanical Properties of PVC/PA Blends

The tensile strength and elongation of PVC/PA blends of formulation A were measured according to ASTM standard D-638 at 20 and 125°C, respectively. The crosshead speed was 10 mm/min at 20°C and 200 mm/min

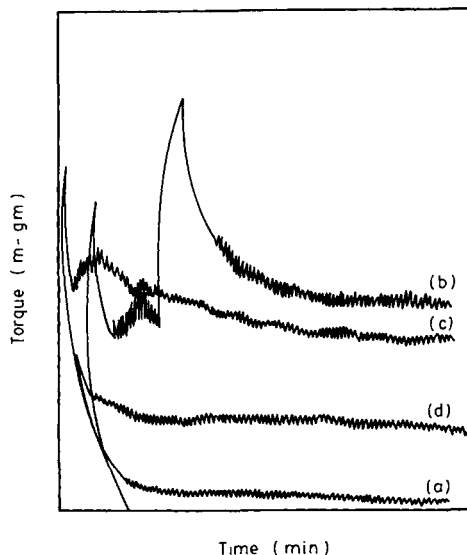


Fig. 1. Brabender torque-time curves of PVC, PMMA, and PA measured at a chamber temperature of 168°C and a rotor speed of 40 rpm: (a) PVC, 25 g; (b) PMMA, 15 g; (c) BA-20, 15 g; (d) BA-40, 15 g.

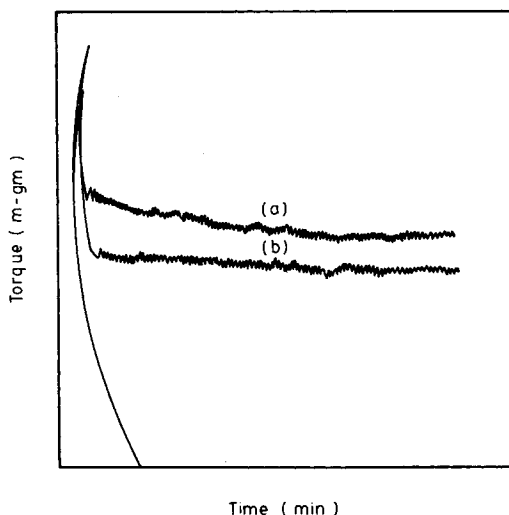


Fig. 2. The molecular weight effect on the torque-time curve of BA-08 measured at 168°C and 40 rpm: (a) $[\eta] = 8.1$, 15 g; (b) $[\eta] = 2.0$, 15 g.

at 125°C. The notched impact strength was measured according to ASTM standard D-256.

RESULTS AND DISCUSSION

Properties of MMA/BA Copolymers (PA)

The characteristic properties of MMA/BA copolymer of different composition are listed in Table III. Since the conversion of the polymerization

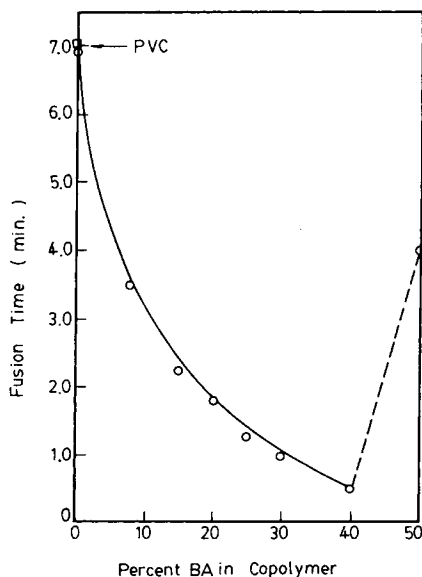


Fig. 3. Effect of PA composition on the fusion time of PVC/PA blends (PA content: 2 phr).

reached nearly 98%, the composition of the copolymers as analyzed by FT-NMR was found to be very close to that of the monomer feed. The viscosity average molecular weights (\overline{M}_v) of the copolymers always exceeded 10^6 , i.e.,

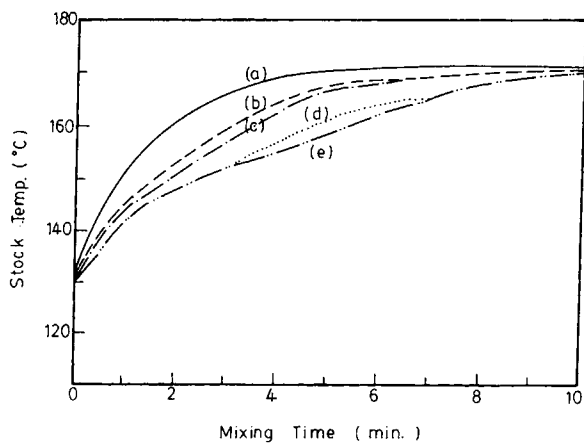


Fig. 4. Effect of PA composition on the stock temperature of PVC/PA blends (PA content: 2 phr): (a) BA-40; (b) BA-08; (c) BA-50; (d) PMMA; (e) PVC.

approximately 30 times that of PVC. The Vicat softening temperature and T_g of the copolymer decreased as the BA content increased. For sample BA-08, the Vicat softening temperature (98°C) was about the same as that of PVC (95°C). Therefore, BA-08 was chosen and a series of copolymers of different molecular weights were prepared. Their properties are listed in Table IV.

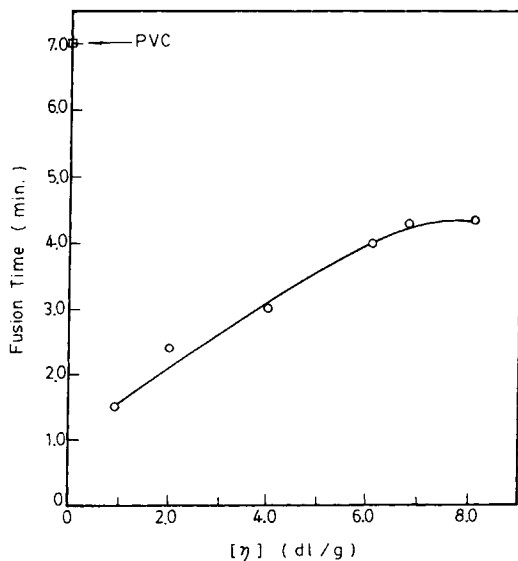


Fig. 5. Fusion time and intrinsic viscosity $[\eta]$ relationship of PVC/BA-08 blends (BA-08 content: 2 phr).

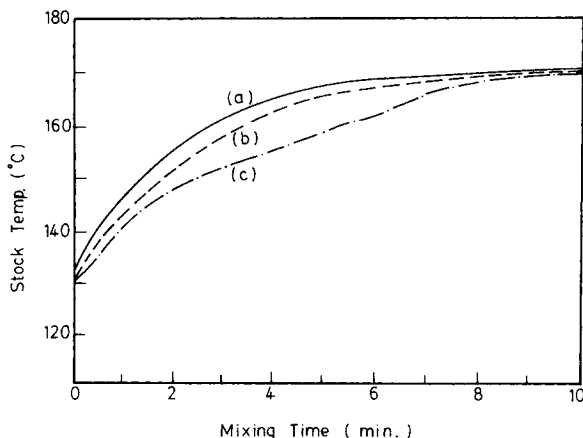


Fig. 6. Effect of BA-08 molecular weight on the stock temperature of PVC/BA-08 blends. (BA-08 content: 2 phr): (a) $[\eta] = 2.0$; (b) $[\eta] = 8.1$; (c) PVC.

Fusion Behavior of PVC/BA Blends

Figures 1 and 2 show Brabender torque-time curves for PVC (25 g) and PA (15 g). Since the mixing chamber was not full, the compression was low. PVC could not be fused at all under these conditions, and the sample after processing was still powdery. On the other hand, PA was fused very easily and the torque required decreased as the BA content in PA increased. Figure 2 shows the effect of molecular weight on the fusion behavior of PA. The higher the molecular weight the larger the torque needed. Figure 3 indicates that the fusion time of a PVC/PA blend decreased with increasing BA content at constant level of PA (2 phr). The main reason for the increased

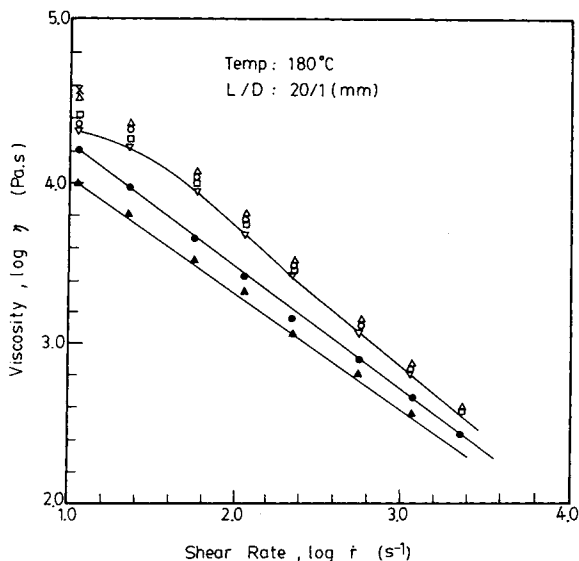


Fig. 7. Viscosity-shear rate relationship of previously fused PVC/PA blends measured at 180°C (PA content: 5 phr). (○) PVC; (X) PMMA; (△) BA-08; (□) BA-15; (▽) BA-25; (●) BA-40; (▲) BA-50.

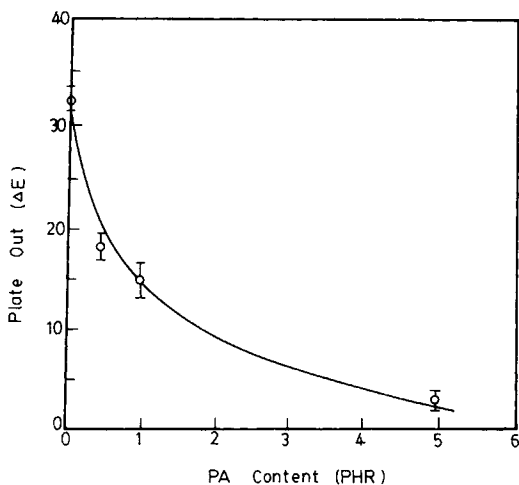


Fig. 8. Effect of PA (BA-08) content on "plate out" of PVC/PA blends.

fusion rate is suggested to be increased wetting of PVC grains by PA with high BA content. Beyond 40% by weight of BA, however, the fusion time increased again probably because the compatibility between PVC and PA becomes poor since BA is immiscible with PVC in nature. The effects of PA composition on the stock temperature are shown in Figure 4. The influence of BA content on stock temperature follows the same pattern as the influence on fusion rate. This may be explained by increased binding and compacting of the PVC grains resulting in increased grain-grain and grain-wall friction. The effects of molecular weight of PA on the fusion time and stock temperature are shown in Figures 5 and 6. It is observed that a higher molecular weight of PA prolongs the fusion time and to some extent decreases rate of stock temperature increase. The viscosity-shear rate relationships of PVC/PA blends with fixed PA composition (5 phr) are shown in Figure 7. It can be seen that the melt viscosity of previously fused PVC did not increase as the BA content in PA increased, indicating that

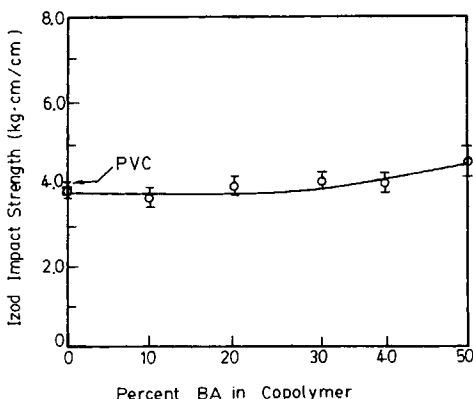


Fig. 9. Effect of PA composition on the Izod impact strength of PVC/PA blends (PA content: 5 phr).

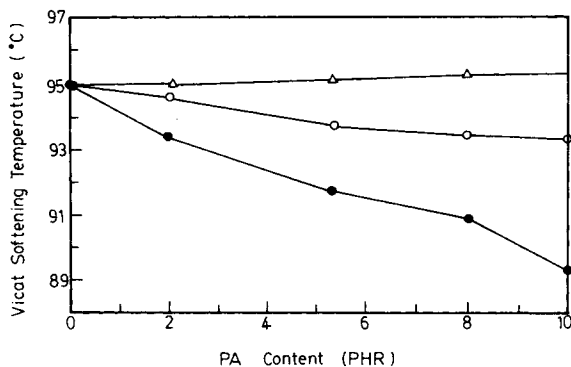


Fig. 10. Effect of PA content on the Vicat softening temperature of PVC/PA blends: (Δ) BA-08; (\circ) BA-20; (\bullet) BA-50.

the equilibrium torque after fusion was not affected. Thus, although the addition of PA increases the torque during the fusion of PVC, it does not increase the viscosity of the PVC melt when the fusion is completed. Moreover, PA with a high BA content is suggested to act as a lubricant, reducing the viscosity and improving the mobility of the PVC melt during processing.

"Plate Out" Phenomenon of PVC/PA Blends

Some additives, such as pigments, lubricants, or stabilizers, may migrate and stick to the calender surface or the die edge during processing due to poor compatibility with PVC. This phenomenon is called "plate out" and may affect the homogeneity and in the end the cost of the product. The results given in Figure 8 show that the use of PA can reduce "plate out"

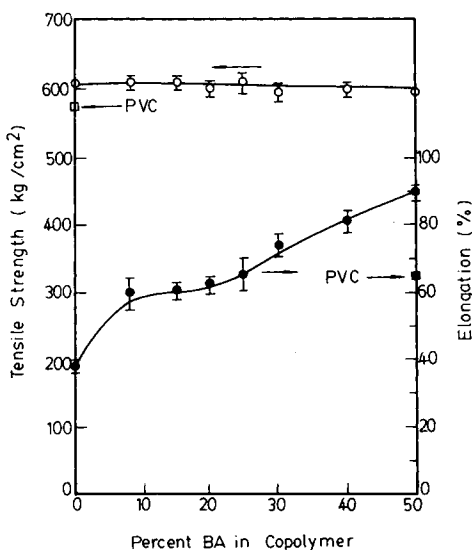


Fig. 11. The tensile strength and elongation of PVC/PA blends measured at 20°C (PA content: 5 phr).

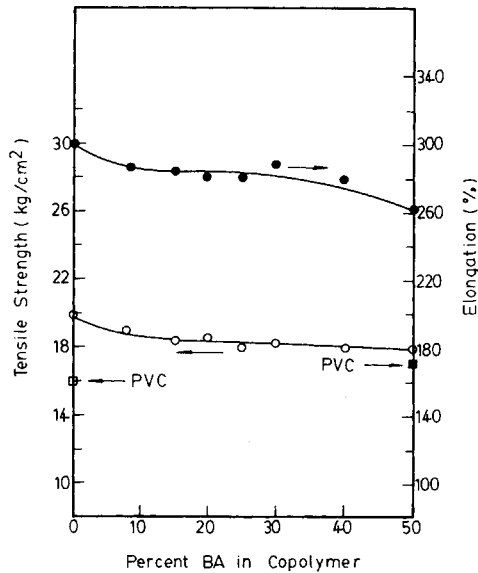


Fig. 12. The tensile strength and elongation of PVC/PA blends measured at 125°C (PA content: 5 phr).

in proportion to the amount added. This is due to the binding ability of PA, preventing migration of additives in PVC at high temperatures.

The Effects of PA on the Physical Properties of PVC

While the impact strength of PVC is hardly affected by the addition of PA as shown in Figure 9, the Vicat softening temperature is lowered (Fig. 10). The higher the BA content in PA and the more PA added to PVC, the

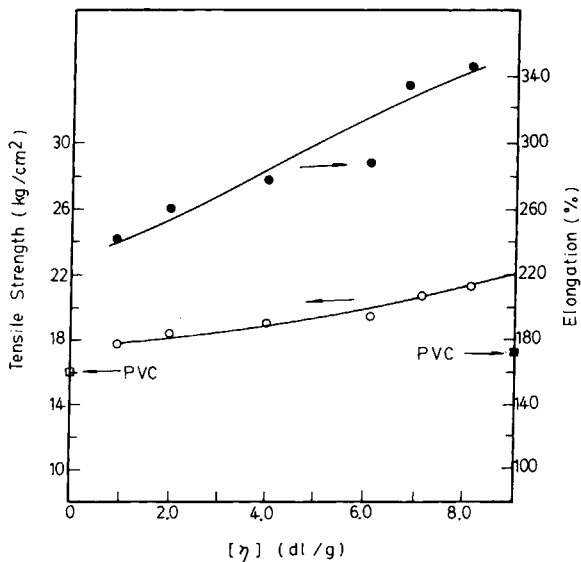


Fig. 13. Effect of BA-08 molecular weight on the tensile strength and elongation of PVC/BA-08 blends measured at 125°C (BA-08 content: 5 phr).

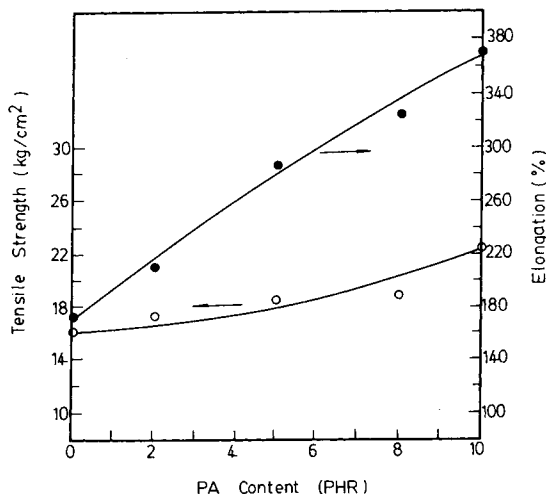


Fig. 14. Effect of PA (BA-08) content on the tensile strength and elongation of PVC/PA (BA-08) blends measured at 125°C.

lower the Vicat softening temperature. The same trend of T_g for PVC/PA blends is observed and shown in Table III. However, sample BA-08 has about the same Vicat softening temperature as PVC and its addition does not change the thermal properties of PVC. Figure 11 shows the tensile strength and elongation of PVC/PA blends measured at 20°C. The addition of 5 phr PA to PVC results in a very small increase (approximately 9%) in tensile strength, probably caused by the high molecular weight of PA, and obviously not affected by its composition. The ultimate elongation of the PVC/PA blend varies with the BA content in PA. When the BA content in PA is less than 25%, a slight decrease in elongation is observed. As the BA content in PA exceeded 30%, the molecular chains are likely to become more flexible and increase the elongation of the PVC/PA blends accordingly. However, at an elevated temperature (125°C), both the tensile strength and elongation of the blends are much higher in relation to PVC and independent of the PA composition (Fig. 12). This is due to the increased influence, in the rubbery zone of PVC, of addition of long PA chains (high \overline{M}_w) increasing the number of entanglements. Figures 13 and 14 show that either by increasing the molecular weight or by increasing the amount of PA a higher tensile strength and particularly a higher elongation of the PVC/PA blends is obtained. This is beneficial for secondary processing, such as vacuum forming or blow molding.

CONCLUSIONS

A family of MMA/BA copolymers were synthesized and characterized. When the BA content was less than 40% by weight, the copolymers could be used as a processing aid (PA) for PVC due to good compatibility between the components. The fusion rate of PVC could be improved (i) by increasing the amount of the copolymer, (ii) by increasing the BA content in copolymer, and (iii) by lowering the molecular weight of the copolymer. The addition of the copolymer improved the tensile strength and elongation of PVC.

especially at an elevated temperature. This beneficial effect would be of interest to secondary processing. The additive also significantly reduced the "plate out" of PVC.

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