

## **ISOTHERMAL DEGRADATION OF PVC/MBS BLENDS**

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### **Abstract**

The process of thermal degradation of poly(vinyl chloride)/poly(methyl methacrylate-butadiene-styrene) (PVC/MBS) blends was investigated by means of isothermal thermogravimetry in nitrogen. The total mass loss was determined after 120 min. The kinetic parameters of the degradation process were determined by applying two kinetic models: the model which assumes autocatalytic degradation (Prout-Tompkins) and the model of two-dimensional diffusion. It was established that the thermal degradation at lower degrees of conversion ( $\alpha < 0.20$ ) was well described by the former model, but the latter model was applicable at higher degrees of conversion. The thermal stability of blends at a certain temperature of isothermal degradation depends on the blend composition and the shell/core ratio in MBS, and on the adhesion in the boundary layer in PVC/MBS blends.

**Keywords:** degradation, PVC/MBS blends, thermogravimetry

### **Introduction**

The modification of polymers by different additives is carried out in order to extend the field of application, since the synthesis of new polymers involves long and uncertain work. The addition of modifying agents can exert a considerable influence on the thermal stability of the blend with respect to the original components. The products evolved during the thermal degradation need not have any influence on the rate of degradation, but in most cases they act catalytically or block the degradation processes. Methyl methacrylate-butadiene-styrene (MBS) terpolymer is one of the most effective modifiers of the impact strength of poly(vinylchloride) (PVC) and is added in amounts up to 20%. It also acts as a processing aid. MBS has a characteristic 'shell/core' structure, which consists of a styrene-butadiene core and a styrene-methacrylate shell which is compatible with PVC [1].

The physico-mechanical properties of PVC/MBS blends have been very well investigated [2-5], but relatively few data are to be found on the thermal stability [6, 7]. The reason is probably the difficult preparation of laboratory samples and

the characterization of MBS (as MBS is partly cross-linked, it is insoluble in common organic solvents [4, 8])

In the present work, the isothermal degradation of blends of PVC with MBS of different impact strengths was investigated. On the basis of the thermogravimetric curves, the kinetic parameters of the degradation process were determined (the reaction rate constant, apparent activation energy, pre-exponential factor and compensation parameter  $S_p^*$ ), and used to explain the mechanism of the process at certain degradation degrees.

## Experimental

### *Materials*

The materials were commercially available block polymerized PVC ( $\overline{M}_w = 93\,000$ ) and two MBS samples: one with excellent (MBS<sup>\*</sup>) and the other with very good (MBS<sup>\*\*</sup>) impact strength [9].

### *Preparation of blends*

PVC/MBS<sup>\*</sup> and PVC/MBS<sup>\*\*</sup> blends with compositions 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 were prepared by homogenization of premixed polymer powders, using a laboratory roll mill at 140°C for 1 min. The foils were transparent and about 0.25 mm thick.

### *Thermogravimetric measurements*

The isothermal degradation of the blends was carried out thermogravimetrically (TG) (Perkin-Elmer TGS-2) on  $2.2 \pm 0.1$  mg samples at 230, 240, 250 and 260°C for 120 min under a nitrogen flow of  $30 \text{ cm}^3 \text{ min}^{-1}$ . From the starting temperature (50°C) up to the temperature of isothermal degradation, the samples were heated at a rate of  $80^\circ\text{C min}^{-1}$ .

### *Calculation of kinetic parameters*

Conversion can be defined in thermogravimetric measurements [10]:

$$\alpha = (m_0 - m)/(m_0 - m_f) \quad (1)$$

where  $m$ ,  $m_0$  and  $m_f$  are the actual, initial and final sample mass. The rate of conversion is given by the expression:

$$d\alpha/dt = k(T)f(\alpha) \quad (2)$$

and the dependence of the reaction rate on temperature is given by the Arrhenius equation:

$$k(T) = A \exp(-E_a/RT) \quad (3)$$

where  $k(T)$  is the reaction rate constant,  
 $f(\alpha)$  is a function describing the mechanism of the process,  
 $A$  is the pre-exponential factor,  
 $E_a$  is the apparent activation energy, and  
 $R$  is the general gas constant.

Combination of Eqs (2) and (3) gives

$$d\alpha/dt = Af(\alpha)\exp(-E_a/RT) \quad (4)$$

On integration, the following solution is obtained:

$$g(\alpha) = k(T)t \quad (5)$$

In isothermal degradation, it is assumed that the conversion is proportional to the concentration of undergraded or unreacted sample, or that it is an  $n$ -order reaction:

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

so that the form of Eq. (2) is

$$d\alpha/dt = k(T)(1 - \alpha)^n \quad (7)$$

The differential methods of calculating the kinetic parameters most often use the logarithmic form of Eq. (7), while the integral methods use Eq. (5).

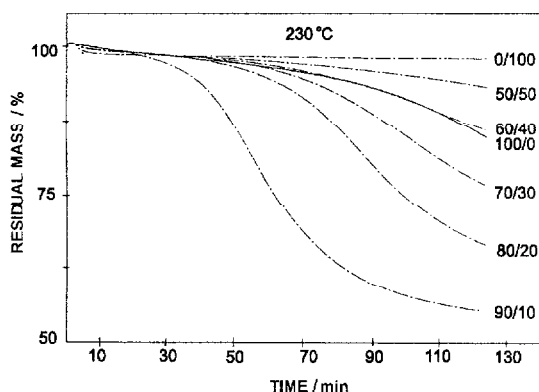


Fig. 1a Isothermal TG curves for PVC/MBS blend at 230°C

For determination of the kinetic parameters of the process of isothermal degradation of PVC/MBS blends, the Prout-Tompkins model was chosen, which assumes autocatalytic degradation [10–12], and also the two-dimensional diffu-

sion model D2 [11]. The Prout-Tompkins model is a modification of the Šesták-Berggren model and is defined as  $f(\alpha) = \alpha/(1 - \alpha)$ .

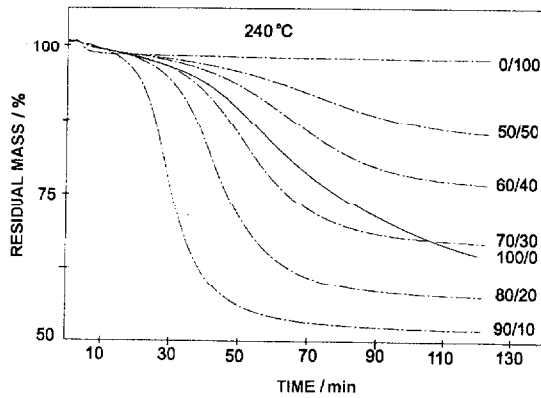


Fig. 1b Isothermal TG curves for PVC/MBS\* blend at 240°C

From Eq. (5), it follows that

$$g(\alpha) = k(T)t = \ln[\alpha / (1 - \alpha)] \quad (8)$$

The integral kinetic equation which uses the D2 model for function  $f(\alpha)$  is

$$g(\alpha) = k(T)t = [(1 - \alpha)\ln(1 - \alpha) + \alpha] \quad (9)$$

From the dependence of  $g(\alpha)$  on  $t$  at several temperatures, the constants are obtained, from which the apparent activation energy and pre-exponential factor are calculated from the Arrhenius equation.

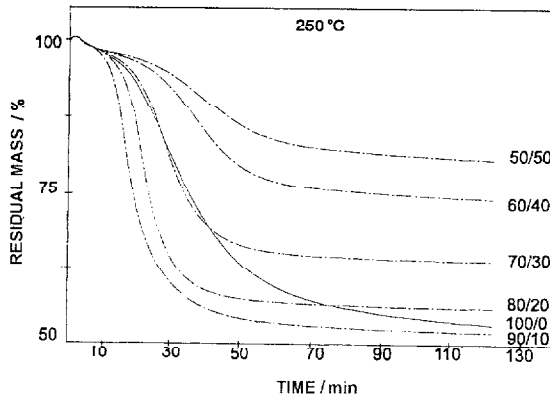


Fig. 1c Isothermal TG curves for PVC/MBS\* blend at 250°C

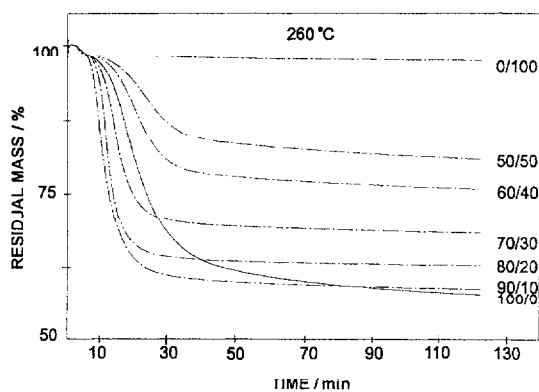


Fig. 1d Isothermal TG curves for PVC/MBS\* blend at 260°C

As the experimental conditions also influence the values of the kinetic parameters, the reactivity of the system can be shown through the compensation parameter  $S_p^* = E_a/\log A$ , though opinions as to its applicability are divided [14, 15].

## Results and discussion

The TG curves of PVC/MBS\* and PVC/MBS\*\* blends (Figs 1 and 2) are S-shaped for all degradation temperatures, which is characteristic for reactions with zero starting rate and for autocatalytic reactions [10, 16]. The degradation of the blends with 10–30% MBS\* begins earlier and the mass loss is greater relative to the 100/0 blend. The mass loss depends on the degradation temperature and the composition of the blends, which is mainly attributed to the dehydrochlorination of the PVC in the blends. The MBS additive destabilizes the PVC in the blends, causing more complete dehydrochlorination. On increase of the temperature, the intensity of the degradation of the blend increases; the effect of temperature is the greatest on the rate of degradation of pure PVC (100/0 blend). After 120 min, the mass loss from the blends, except for the 100/0 blend approaches a constant value, so that the destabilizing influence of MBS on PVC gradually disappears with the rise of temperature (Table 1). A slighter mass loss is observed for PVC/MBS\*\* blends.

From the TG curves, the times for assigned conversions to be reached were determined; these are needed for calculation of the kinetic parameters on the basis of the Prout-Tompkins model and the two-dimensional diffusive model (Figs 3 and 4).

The Prout-Tompkins model describes the kinetic area of the reaction development when the rate of the total process is determined by the rate of chemical reaction. The model is applicable in the area of lower degrees of conversion (Table 2), which indicates an autocatalytic effect: the flow of the inert material and

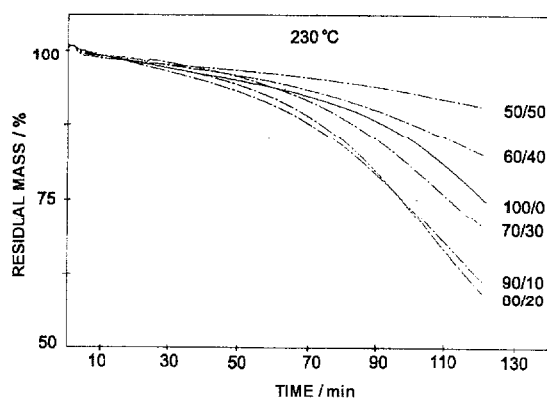


Fig. 2a Isothermal TG curves for PVC/MBS\*\* blend at 230°C

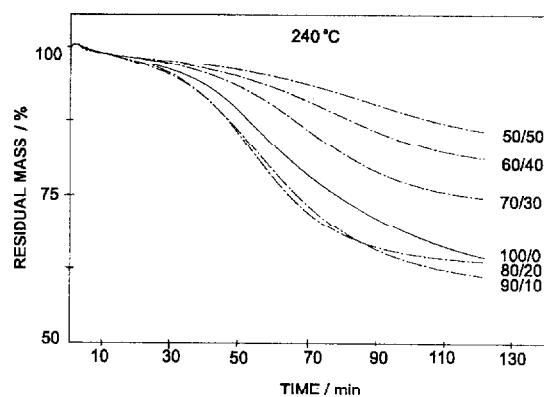


Fig. 2b Isothermal TG curves for PVC/MBS\*\* blend at 240°C

the conditions of the experiment are not sufficient to ensure the thorough elimination of HCl from the reaction medium and in this way to prevent the autocatalytic effect. The disadvantage of this model is that it is derived on the basis of the assumption that the maximal rate of degradation is achieved at a degree of conversion of 0.5, which is not satisfactory for many reactions.

The rate constants of the thermodegradation reaction were determined from the gradient of the linear part of the curves  $g(\alpha)$  vs.  $t$ , as in the example for the PVC/MBS\* 80/20 blend (Fig. 3). The apparent activation energy and pre-exponential factor were then determined from the Arrhenius equation. The kinetic parameters obtained by application of the Prout-Tompkins model are shown in Table 3.

For the PVC/MBS\* blend, the reaction rate constant,  $k$ , ranges from  $1.469 \cdot 10^{-2}$  to  $53.614 \cdot 10^{-2} \text{ min}^{-1}$ , depending on the temperature and the blend composition. The values of the constants at all temperatures indicate that the

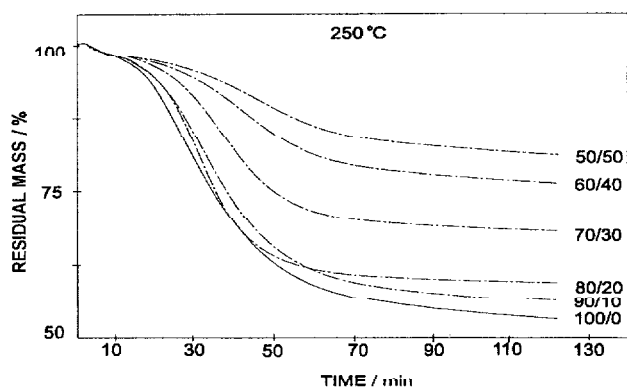


Fig. 2c Isothermal TG curves for PVC/MBS\*\* blend at 250°C

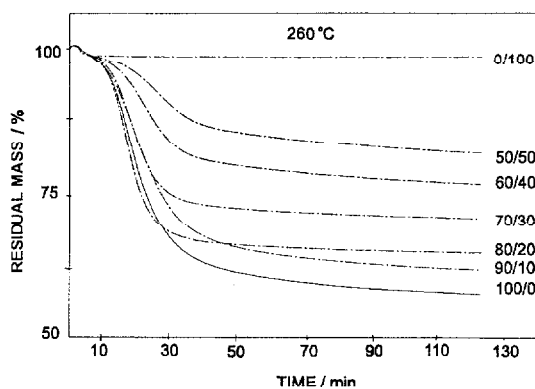


Fig. 2d Isothermal TG curves for PVC/MBS\*\* blend at 260°C

Table 1 Isothermal mass loss of PVC/MBS blends after 120 min

	Temp./ °C	Mass loss/%						
		100/0	90/10	80/20	70/30	60/40	50/50	0/100
PVC/ MBS*	230	15.0	44.7	33.5	23.3	14.2	7.2	2.6
	240	35.6	47.5	42.2	33.3	23.2	14.8	2.8
	250	46.9	48.1	44.1	36.3	26.2	19.6	
	260	50.6	49.5	44.9	38.5	29.5	23.4	3.5
PVC/ MBS**	230	15.0	23.3	24.2	18.1	10.8	5.8	
	240	35.6	38.7	36.3	25.5	19.0	14.3	
	250	46.9	43.7	38.5	31.6	23.3	18.6	
	260	50.6	45.7	18.1	35.1	28.2	22.1	2.4

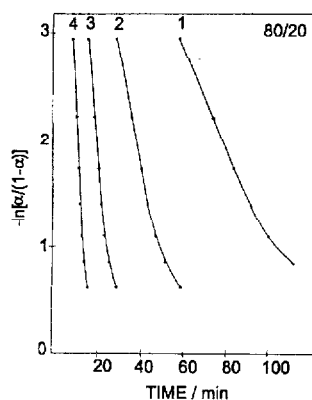


Fig. 3 Applicability of Prout-Tompkins model to isothermal degradation of PVC/MBS\* blend 80/20 at: 1-230°C, 2-240°C, 3-250°C, 4-260°C

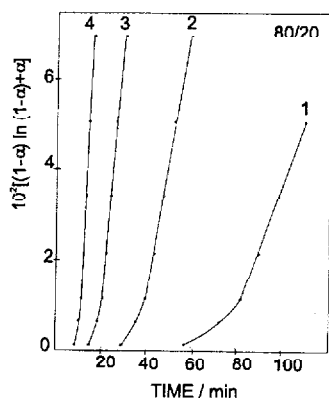


Fig. 4 Applicability of D2 model to isothermal degradation of of PVC/MBS\* blend 80/20 at: 1-230°C, 2-240°C, 3-250°C, 4-260°C

composition 90/10 degrades most rapidly. On increase of the MBS\* ratio from 10 to 50%, the rate constant decreases 5.2-fold on average. The apparent activation energies have different values, and since the pre-exponential factors differ too, the compensation parameters  $S_p^*$  represent the measure of reactivity of the system. The values of this parameter are between the limits 10.38 and 10.86. For PVC, the value of  $S_p^*$  is 10.65. The composition 90/10 gives the lowest value of the parameter, and consequently has the lowest stability.

The constants of the reaction rates for PVC/MBS\*\* blends have values from  $1.533 \cdot 10^{-2} \text{ min}^{-1}$  to  $23.980 \cdot 10^{-2} \text{ min}^{-1}$ . The ratio of the highest and lowest values of the constants is on the average 2.3. The values of the constants show that the composition 80/20 is the most unstable. However, PVC (10.65) has the lowest



$S_p^*$  value, followed by the composition 80/20 (10.67). The stability of the blends rises with increasing MBS\*\* ratio (Table 3).

**Table 2** Applicability of kinetic models to isothermal degradation of PVC/MBS blends

PVC/ MBS*	Degree of conversion, $\alpha$		PVC/ MBS**	Degree of conversion, $\alpha$	
	Prout-Tompkins	D2		Prout-Tompkins	D2
100/0	0.05–0.15	0.15–0.30	100/0	0.05–0.15	0.15–0.30
90/10	0.05–0.20	0.20–0.35	90/10	0.05–0.15	0.20–0.30
80/20	0.05–0.20	0.15–0.35	80/20	0.05–0.15	0.15–0.30
70/30	0.05–0.15	0.15–0.25	70/30	0.05–0.15	0.15–0.20
60/40	0.04–0.12	0.10–0.12	60/40	0.04–0.10	0.10–0.12
50/50	0.04–0.10	0.07–0.12	50/50	0.04–0.07	0.10–0.12

The kinetic model of two-dimensional diffusion D2 is satisfied at higher degrees of conversion, in the area of the greatest rates of conversion (Table 2). This indicates that the process of mass transfer is responsible for the rate of thermal degradation, since the rate of the chemical reaction is high.

**Table 3** Kinetic parameters for isothermal degradation of PVC/MBS blends according to the Prout-Tompkins model

Model	Prout-Tompkins				$E_a/$ kJ mol <sup>-1</sup>	$A/$ min <sup>-1</sup>	$S_p^*$	
	Temp/°C	230	240	250				260
		10 <sup>2</sup> k/min <sup>-1</sup>						
PVC/MBS*								
100/0	2.450	5.368	12.677	20.600	161.30	1.41·10 <sup>15</sup>	10.65	
90/10	7.947	17.618	29.711	53.614	139.25	2.59·10 <sup>13</sup>	10.38	
80/20	4.757	10.315	22.659	50.002	174.62	6.26·10 <sup>16</sup>	10.40	
70/30	3.619	7.212	14.022	31.202	158.87	1.09·10 <sup>15</sup>	10.56	
60/40	2.545	4.578	8.240	16.301	136.70	3.83·10 <sup>12</sup>	10.86	
50/50	1.469	2.858	6.516	11.618	156.19	2.39·10 <sup>14</sup>	10.86	
PVC/MBS**								
100/0	2.450	5.368	12.677	20.600	161.30	1.41·10 <sup>15</sup>	10.65	
90/10	2.888	5.842	10.732	17.444	133.63	2.24·10 <sup>12</sup>	10.82	
80/20	3.287	6.385	12.202	23.980	146.89	5.75·10 <sup>13</sup>	10.67	
70/30	3.024	4.397	8.754	19.122	138.13	5.83·10 <sup>12</sup>	10.82	
60/40	2.115	3.367	6.399	13.061	135.39	2.33·10 <sup>12</sup>	10.96	
50/50	1.533	2.618	5.266	9.564	137.65	2.86·10 <sup>12</sup>	11.05	

The model is valid in a narrow range of conversions as the degradation occurs in the whole mass of a sample, not only on the surface. The application of the D2 model for the PVC/MBS\* blend is shown in Fig. 4. The kinetic parameters are determined as described by the Prout-Tompkins model, and are shown in Table 4. For the PVC/MBS\* blend, the values of the compensation parameter range from 10.11 to 11.12.  $S_p^*$  for the composition 100/0 is 10.32; the lowest  $S_p^*$  value was obtained for the composition 90/10, and the highest for the 60/40 blend. Except for PVC, the highest reaction rate constants for the PVC/MBS\*\* blend were calculated for the composition 80/20. The values of the constants varied from  $1.926 \cdot 10^{-2}$  to  $60.012 \cdot 10^{-2} \text{ min}^{-1}$ . The maximal average ratio of the constants is 8.1. The compensation parameter indicates that, besides PVC, the composition 80/20 is the most unstable.

**Table 4** Kinetic parameters for isothermal degradation of PVC/MBS blends according to the D2 model

Model	D2				$E_a /$ kJ mol <sup>-1</sup>	A/ min <sup>-1</sup>	$S_p^*$
	Temp/°C	230	240	250			
		10 <sup>2</sup> k/min <sup>-1</sup>					
<b>PVC/MBS*</b>							
100/0	–	10.516	30.388	60.012	195.90	$9.77 \cdot 10^{18}$	10.32
90/10	24.884	62.002	69.166	125.345	110.30	$8.03 \cdot 10^{10}$	10.11
80/20	14.173	30.789	65.358	133.175	166.18	$2.53 \cdot 10^{16}$	10.13
70/30	–	16.010	32.668	72.712	169.92	$3.12 \cdot 10^{16}$	10.30
60/40	2.752	4.888	6.907	13.303	112.71	$1.38 \cdot 10^{10}$	11.12
50/50	–	2.091	4.723	8.949	163.56	$9.56 \cdot 10^{14}$	10.92
<b>PVC/MBS**</b>							
100/0	–	10.516	30.388	60.012	195.90	$9.77 \cdot 10^{18}$	10.32
90/10	–	15.561	29.516	39.466	104.85	$7.76 \cdot 10^9$	10.60
80/20	–	16.182	35.824	57.916	143.59	$7.02 \cdot 10^{13}$	10.37
70/30	–	6.847	16.612	33.626	178.95	$1.16 \cdot 10^{17}$	10.49
60/40	–	3.081	6.218	13.484	165.78	$2.28 \cdot 10^{15}$	11.79
50/50	–	1.926	4.034	7.895	158.62	$4.48 \cdot 10^{14}$	10.83

Both kinetic models are valid in a more extensive area of conversional degrees for the PVC/MBS\* blend as compared with the PVC/MBS\*\* blend. The values of the reaction rate constants reveal that the PVC/MBS\*\* blends are thermally more stable. This is confirmed by the values of the compensation parameter, which are higher for all PVC/MBS\*\* blends. A larger parameter value generally means a lower reactivity of the system [16]. Such differences in thermal sta-

bility of blends are probably a consequence of the different shell/core ratio in MBS. In the PVC/MBS\* blend, due to the greater ratio of the styrene-butadiene component (higher impact strength), the adhesion in the boundary layer or compatibility is lower; this was also demonstrated by earlier DSC research on glass transition characteristics [17, 18].

This improves the autocatalytic effect of HCl, which is retained in the PVC phase. At the same time, the retarded diffusion of the chlorine radical reduces the possibility of the stabilizing interaction of the styrene-methyl methacrylate component and PVC [19, 20]. However, as the thermal stability inside one series of blends is improved by a higher ratio of MBS, it can be supposed that such a stabilization effect does exist.

## Conclusions

The isothermal degradation of PVC/MBS in nitrogen gave S-shaped curves, characteristic of autocatalytic reactions. The mass loss from the blends is a consequence of the process of dehydrochlorination of PVC. This confirms the applicability of the Prout-Tompkins model for  $\alpha < 0.20$ . In the area of the highest rates of degradation, the rate of the chemical reaction is controlled by the process of mass transfer. The values of the kinetic parameters, expressed through  $S_p^*$ , indicate that the PVC/MBS\*\* blends are more stable than the PVC/MBS\* blends. The thermal stability of the blends rises, while the difference in stability of the two systems decreases with increase of the amount of MBS in the blends. This is explained by the stabilizing interaction of the components in the blends and by the difference in compatibility of the PVC/MBS\* and PVC/MBS\*\* blends.

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