

The Effect of Glycidyl Methacrylate on Mechanical Properties, Morphology, and Thermal Degradation of Recycled Poly(vinylchloride)/Acrylonitrile-Butadiene Rubber Blends

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ABSTRACT

The effect of glycidyl methacrylate (GMA) on mechanical properties, morphology, and thermal degradation of recycled poly(vinylchloride)/acrylonitrile-butadiene rubber (PVCr/NBR) blends was studied. The blends were prepared at 150°C and rotor speed of 50 rpm in an internal mixer. The glycidyl methacrylate was added at 4 php of plastic. The PVCr/NBR (without GMA) blends were also prepared as control samples. It was found that the addition of GMA significantly improved the properties of PVCr/NBR blends. At a similar blend composition, the PVCr/NBR + GMA blends show higher stresses at peak and at 100% elongation (M_{100}) but lower elongation-at-break than PVCr/NBR blends. The scanning electron microscopy (SEM) study of tensile fracture surfaces of the blends indicates that the presence of glycidyl methacrylate increased the interfacial interaction between recycled PVC and NBR phases and thus improved compatibility between PVCr and NBR phases. However, the thermal gravimetry analysis (TGA) of the blends show that the presence of GMA has reduced the thermal stability of PVCr/NBR blends.

Key Words:

recycled poly(vinylchloride);
acrylonitrile butadiene-rubber;
glycidyl methacrylate;
mechanical properties;
thermal degradation.

INTRODUCTION

Blends of rubber and plastic known as thermoplastic elastomers (TPEs) combine the excellent processability characteristics of thermoplastics and the mechanical properties of vulcanized rubber. During the last few years, a large number of studies on

thermoplastic elastomeric blends have been reported [1-5]. However, some of the polymer blends are found to be incompatible. These incompatible blends are characterized by a two-phases morphology, narrow interphase, poor physical and

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chemical interactions across the phase boundaries, and poor mechanical properties [6]. To overcome these problems, it is important to develop a proper control of phase morphology and good interfacial adhesion by the addition or in situ formation of compatibilizers or interfacial agents [7-8]. The effect of addition of block and graft copolymers as compatibilizers in binary polymer blends has been reported by various researchers [9-12]. In our previous work [13], we have reported the comparison between properties of virgin poly(vinylchloride)/acrylonitrile-butadiene rubber (PVCv/NBR) and recycled poly(vinylchloride)/acrylonitrile-butadiene rubber (PVCr/NBR) blends. The results indicate that PVCr/NBR blends show weaker properties (i.e., mechanical properties and swelling resistance) than PVCv/NBR blends. These results were due to the presence of filler and various materials in recycled PVC which reduced the compatibility between the PVCr and the NBR. In this article, the effects of glycidyl methacrylate (GMA) on mechanical properties, morphology, and thermal stability of PVCr/NBR blends were evaluated.

EXPERIMENTAL

Material

Recycled PVC (PVCr) from electrical wires and cables was supplied by Alfasya Jaya Sdn. Bhd. Penang, Malaysia and its inorganic compounds are shown in Table 1. The

Table 1. Inorganic compound of recycled PVC*.

Composition	wt%	Composition	wt%
Al ₂ O ₃	1.7	P ₂ O ₅	0.025
MgO	0.39	SO ₃	0.15
SiO ₂	0.88	K ₂ O	0.023
Cl	20	Fe ₂ O ₃	0.052
CaO	13	CuO	0.19
TiO ₂	0.26	ZnO	0.086
Sb ₂ O ₃	0.21	Br	0.036
PbO	1.2	SrO	0.013
Carbon	61	SnO ₂	0.029
Na ₂ O	0.019		

(*) X-Ray Fluorescence Spectrometer Rigaku RIX 3000

NBR with 34% acrylonitrile content was obtained from Kumpulan Guthrie, Seremban, Malaysia. The higher acrylonitrile content was used in this study, it enhanced the compatibility between PVCr and NBR. The dioctyl-phthalate (DOP) and barium/cadmium stearate, glycidyl methacrylate (GMA), and dicumyl-peroxide (DCP) were obtained from Bayer (M) Penang, Malaysia.

Preparation of the Blends

The formulations of the blends are given in Table 2. Blends of plastics and rubber were prepared at the ratios of 80/20, 60/40, 50/50, 40/60, and 20/80 (wt%), respectively. The glycidyl methacrylate (GMA) concentration was fixed at 4 php of plastic. The PVCr/NBR blends were prepared by melt-mixed in a Haake Rheomix Polydrive R 600/610 at 150°C and rotor speed of 50 rpm. The amounts of DOP and Cd/Ba stearate used in the mixing of the blends were 20 php and 3 php, respectively based on total PVCr content in the all compositions.

The PVCr was initially premixed with stabilizer and plasticizer in a glass beaker for 5 min at room temperature. The PVCr with stabilizer and plasticizer were charged into the mixing chamber together with dicumyl-peroxide (DCP) and glycidyl methacrylate, allowed to equilibrate for 2 min and followed by the addition of NBR. Then mixing was continued until a constant torque was obtained. The total mixing time was 9 min. The compound was removed from the mixer and sheeted on a cold two-roll mill.

Table 2. Formulations of PVCr/NBR blends with glycidyl methacrylate (GMA)*.

Materials	Blend (wt%)				
	1	2	3	4	5
PVCr	80	80	80	80	80
NBR	20	40	50	60	80
Stabilizer ^a	3	3	3	3	3
Plasticizer ^b	20	20	20	20	20
DCP ^c	0.2	0.2	0.2	0.2	0.2
Glycidyl methacrylate ^d	4	4	4	4	4

(a) Ba/Cd stearate; (b) Dioctyl-phthalate (DOP); (c) Dicumyl-peroxide (DCP)

a, b, c, d at php of plastic.

(*) A similar series of PVCr/NBR blends were prepared but without glycidyl methacrylate (GMA)

Compression Moulding and Testing

The samples of PVCr/NBR and PVCr/NBR + GMA blends were compression molded in an electrically heated hydraulic press. Hot-press procedures involved pre-heating at 150°C for 4 min, followed by compressing for 4 min at the same temperature. Tensile tests were carried out by a Testometric tensometer M 500. Tests were done according to ASTM D 412. Dumbbell specimens of 2 mm thickness were cut from molded sheets with a Wallace die cutter S6/1/4.A. Five specimens were used in each case and the median value was selected. Readings of stress at peak, stress at 100% elongation (M_{100}) and elongation at break (E_b) were recorded directly from the digital displays at the end of the each test.

Scanning Electron Microscopy (SEM) Study

Studies on morphology of the fracture surfaces of PVCr/NBR and PVCr/NBR + GMA blends were carried out by using a Leica Cambridge S 360 model scanning electron microscopy (SEM). Surfaces of the sample were coated with a thin gold layer of about 20 nm thickness.

Infrared Spectroscopy Study

The FTIR spectrum was obtained by using a FTIR model Perkin Elmer 2000 series instrument. The spectrum resolution was 4 cm^{-1} and scanning range was from 600 to 4000 cm^{-1} . The samples for FTIR were prepared by using the attenuated total reflectance (ATR) technique and was subjected to FTIR analysis immediately afterwards.

Thermogravimetric (TG) Analysis

Thermal degradation analysis of the PVCr/NBR and PVCr/NBR + GMA blends were carried out using a Perkin-Elmer TGA-7 thermogravimetric analyzer. The weight of each sample was about 10 mg. The weight change of the blends was investigated from room temperature to 590°C at a heating rate of 10°C/min in a nitrogen atmosphere. The first derivative of the thermogravimetric curve was calculated using the in-built software.

RESULTS AND DISCUSSION

Mechanical Properties of Blends

Figures 1 and 2 show the effect of blend composition on stresses at peak and at 100% elongation (M_{100}) of

PVCr/NBR and PVCr/NBR + GMA blends. It can be seen that both properties decrease due to the decreasing of blends rigidity as the NBR composition increases. On the other hand, The increasing of NBR composition in the PVCr/NBR and PVCr/NBR + GMA blends increase the elongation at break, E_b (Figure 3) also.

As the NBR content increases, the stiffness and brittleness of the blends decrease gradually with an associated increase in E_b . However, with the similar blend composition, PVCr/NBR + GMA blends show higher stresses at peak and at 100% elongation (but lower elongation-at-break, E_b) than PVCr/NBR blends. This is due to the enhancement in interfacial adhesion between PVCr and NBR phases as shown later in FTIR study. This results in stiffness and brittleness increasing of

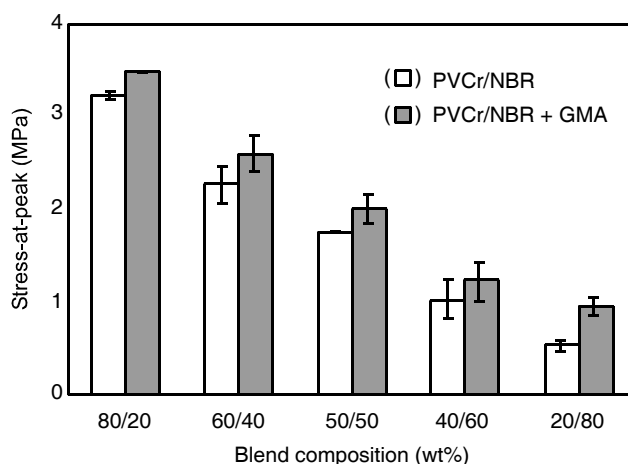


Figure 1. Stress at peak versus blend composition of PVCr/NBR and PVCr/NBR + GMA blends.

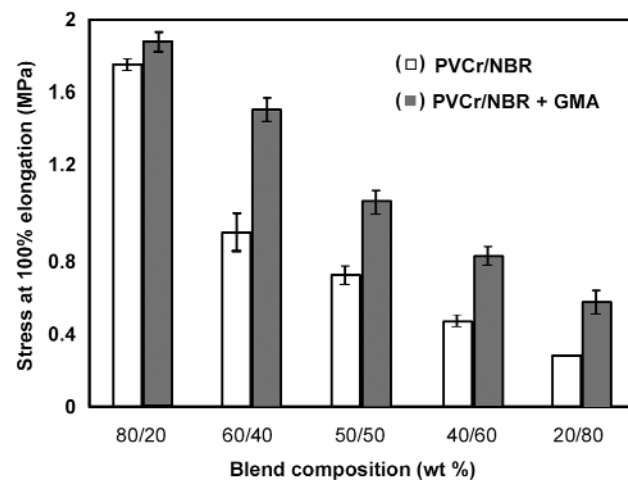


Figure 2. Stress at 100% elongation versus blend composition of PVCr/NBR and PVCr/NBR + GMA blends.

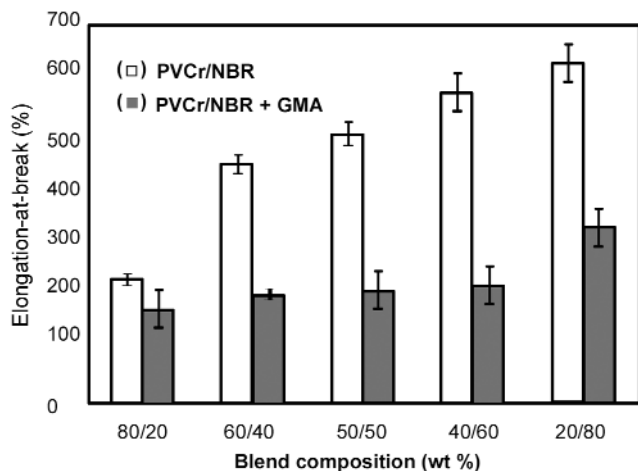


Figure 3. Elongation-at-break versus blend composition of PVCr/NBR and PVCr/NBR + GMA blends.

the blends and reduction of their elongation-at-break, E_b .

Infrared Spectroscopic Studies

Figures 4 and 5 show the spectra of 80/20 (wt%) PVCr/NBR and 80/20(wt%) PVCr/NBR + GMA blends. Both figures exhibit the olefinic C-H stretching frequency just above 3000 cm^{-1} , the $-\text{CH}_2$ bending vibration at above 1431 and 1435 cm^{-1} , the C-O-C stretching, ester vibration at 1274 cm^{-1} , the vibration of CN group at 2237 cm^{-1} from NBR structure, and the C-H out-of-plane bending frequency at 968 cm^{-1} . In both figures the peak centered at 1726 cm^{-1} and 1724 cm^{-1} which represent the carbonyl (C=O) group of aliphatic acid and ester. However, in the spectrum of PVCr/NBR + GMA blends the absence of C-C double bond at 1660 cm^{-1} of glycidyl methacrylate structure might be due to C-C radical of glycidyl methacrylate

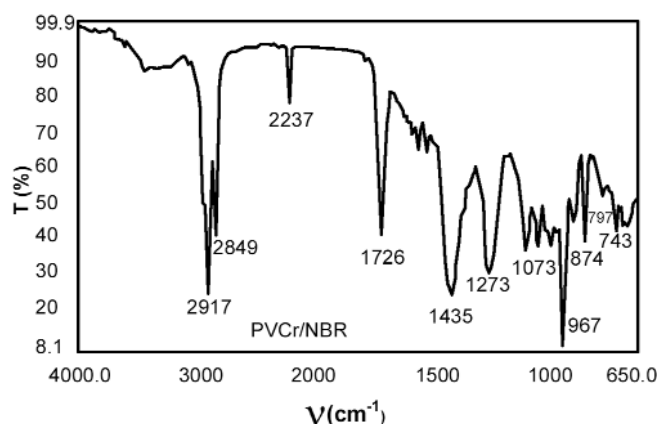


Figure 4. IR Spectrum of PVCr/NBR blend.

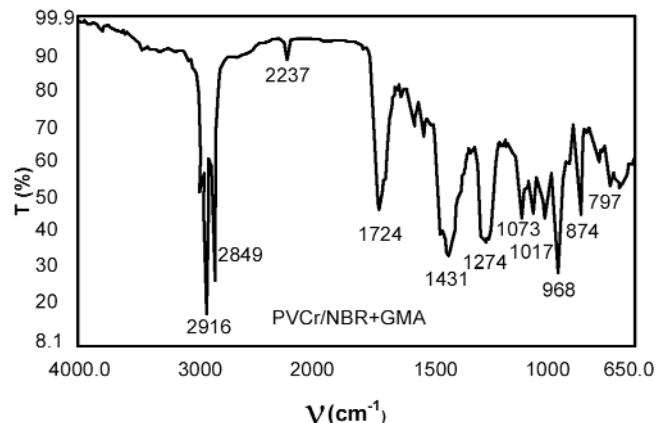


Figure 5. IR Spectrum of PVCr/NBR + GMA blend.

(GMA) which grafted with PVCr and improved the interfacial adhesion between PVCr and NBR.

Figure 6 shows the reaction mechanism of GMA grafted recycled PVC with NBR which occurred during melt mixing. According to Bucknall [14], an increase of interfacial adhesion suppressed production of void or flaws in the blends, which might grow into cracks. The increased interfacial adhesion enables the deformation to occur easily in the cross-section and facilitates shear yielding.

Morphology Properties of Blends

Figures 7a-7c and 8a-8c show the comparison of tensile fracture surfaces of PVCr/NBR and PVCr/NBR + GMA at 80/20, 50/50, and 20/80 (wt %), respectively. It can be seen in all these figures that as the NBR composition

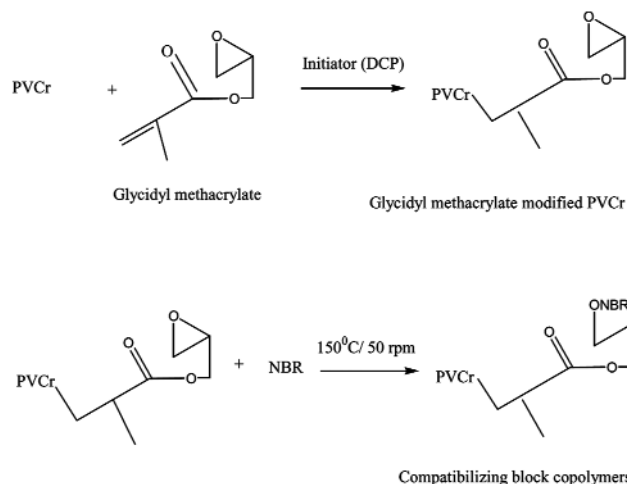
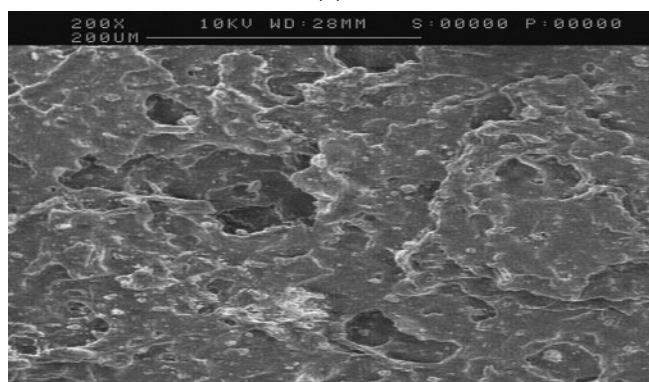


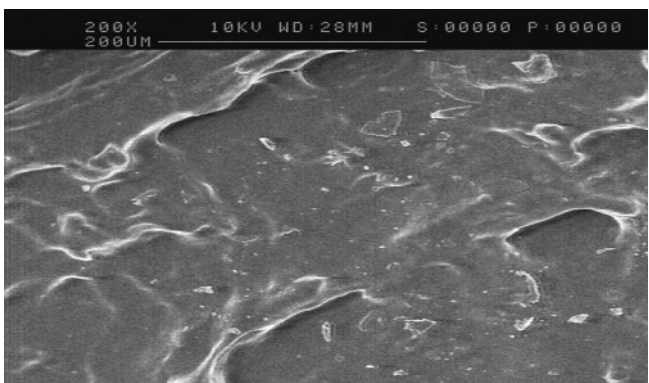
Figure 6. Illustration of reaction mechanism of GMA-grafted PVCr with NBR.



(a)



(b)

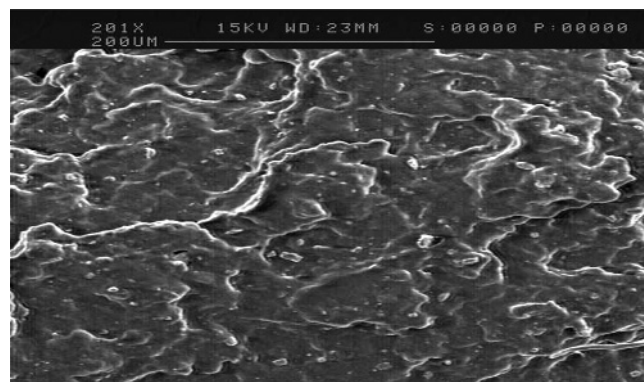


(c)

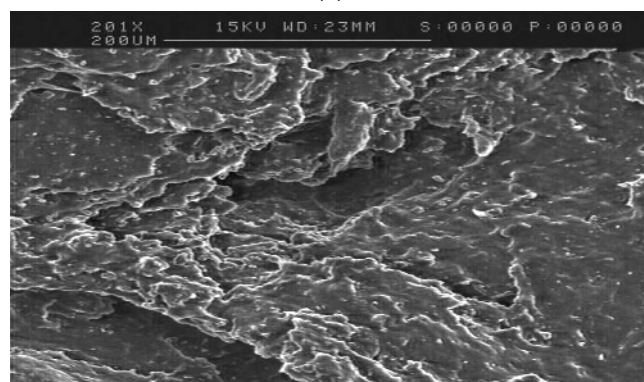
Figure 7. Scanning electron micrographs of tensile fracture surfaces of PVCr/NBR blends: (a) 80/20, (b) 50/50, (c) 20/80.

increases, the nature of failure surface changes from rough failure surface into smooth failure surface. However at a similar blend composition, the PVCr/NBR + GMA blends show better strength with many tear lines and more homogeneous blends than PVCr/NBR.

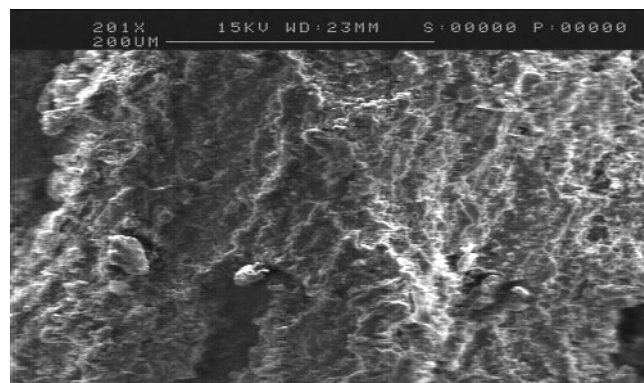
Figure 7a shows a coarse and unstable particle structure and an uneven distribution of the dispersed NBR phase. This indicates low adhesion between phases, given rise to poor stress transfer across the interface. However, in the presence of GMA (Figure 8a)



(a)



(b)



(c)

Figure 8. Scanning electron micrographs of tensile fracture surfaces of PVCr/NBR + GMA blends: (a) 80/20, (b) 50/50, (c) 20/80.

there is a better dispersion of NBR. The more evenly distribution of NBR in the PVC matrix indicating improvement in compatibility between recycled PVC and NBR. The presence of many tear lines on the tensile fracture surfaces of PVCr/NBR + GMA blends (Figures 8a-8c) indicates the effect of increased interaction between phases, thus improving compatibility and consequently enhance the stresses at peak and at 100% elongation of PVCr/NBR blends.

Table 3. IDT, $T_{50\%}$, FDT, and total weight loss of PVCr/NBR and PVCr/NBR + GMA blends obtained by TGA.

Blend composition (wt%)	IDT (°C)	$T_{50\%}$ (°C)	FDT (°C)	Total weight loss (%)
80/20 PVCr/NBR	201.10	374.99	587.51	71.95
50/50 PVCr/NBR	201.12	465.12	587.36	78.57
20/80 PVCr/NBR	201.40	469.43	587.20	85.80
80/20 PVCr/NBR + GMA	201.18	428.61	587.13	72.91
50/50 PVCr/NBR + GMA	201.25	462.18	587.07	79.84
20/80 PVCr/NBR + GMA	201.46	467.23	587.04	85.92

(IDT): Initial decomposition temperature; ($T_{50\%}$): Decomposition temperature at 50% of weight loss;

(FDT): Final decomposition temperature.

Thermogravimetric Analysis

Thermogravimetric analysis enables us to study the various loss of mass caused by a rise in temperature of the samples. Degradation occurs and the mass remaining decreases as the temperature increases. Figure 9 shows the typical thermogravimetric degradation of PVCr/NBR + GMA blends in the temperature range of 25-600°C. For all blends composition, the degradation of PVCr/NBR and PVCr/NBR + GMA blends, which were started at 27°C completed at 590°C.

Table 3 shows the initial decomposition temperature (IDT), decomposition temperature at 50% of weight loss ($T_{50\%}$), final decomposition temperature (FDT), and total weight losses of PVCr/NBR and PVCr/NBR+ GMA blends. It can be seen that at the similar blend ratio the total weight loss of PVCr/NBR+GMA is higher than PVCr/NBR blends. This indicates that the presence of GMA has reduced the thermal stability of the PVCr/NBR blends.

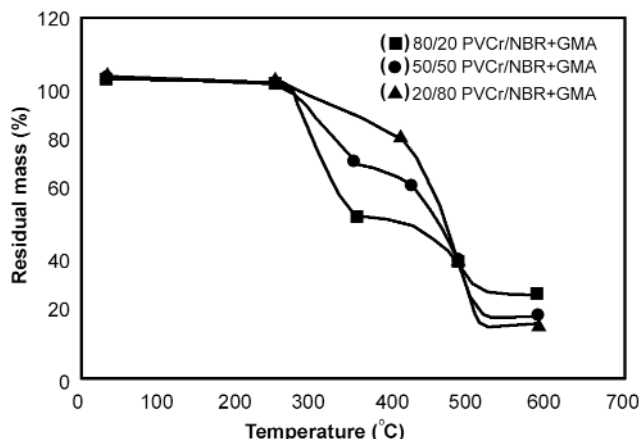


Figure 9. TG Thermograms of PVCr/NBR + GMA blends.

A similar trend was observed by Qiao et al. [15], who reported that the compatibilizer has a decreasing influence on thermal stability of the composite materials.

CONCLUSION

The presence of GMA increases the stresses at peak and at 100% elongation (M_{100}) of PVCr/NBR blends but lowers the elongation-at-break, E_b . FTIR and SEM results show the evidence of enhancement in interfacial adhesion between phases of recycled PVC and NBR by the addition of glycidyl methacrylate (GMA).

However, the presence of GMA has reduced the thermal stability of PVCr/NBR blends.

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