

Effects of Dynamic Vulcanization and Glycidyl Methacrylate (GMA) on Mechanical Properties, Swelling Index and Morphology Properties of Recycled Poly(vinyl chloride)/Acrylonitrile Butadiene Rubber (PVCr/NBR) Blends

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ABSTRACT

Polymer blends with varying amounts of recycled Poly(vinyl chloride) (PVCr) and Acrylonitrile Butadiene Rubber (NBR) have been developed to produce Thermoplastic Elastomers (TPEs). The effects of dynamic vulcanization and Glycidyl Methacrylate (GMA) on mechanical properties, swelling index and morphology properties of the blends were studied. The blends were prepared using a Haake Rheomix at 150°C and rotor speed of 50rpm for 11 minutes. It was found that, dynamic crosslinking has enhanced the stress at peak, stress at 100% elongation and swelling resistance of dynamically vulcanized PVCr/NBR + GMA blends compared to PVCr/NBR blends. The introduction of cross-link into the elastomer phase and better compatibility between PVCr and NBR are responsible for the enhancement of mechanical properties of dynamically vulcanized PVCr/NBR + GMA blends as evidence from the Scanning Electron Microscopy (SEM) of extracted surfaces of the blends.

Keywords : Acrylonitrile butadiene rubber; recycled poly(vinyl chloride); glycidyl methacrylate

INTRODUCTION

Poly(vinyl chloride) (PVC) is an extensively used thermoplastic materials because of its valuable properties, such as superior mechanical and physical properties, high chemical, and abrasion resistance and widely utilized in durable applications, e.g. for pipes, window profile, house siding, wire cable insulation and flooring. Acrylonitrile Butadiene-rubber (NBR)/poly(vinyl chloride) blends is miscible physical mixture of commercial importance. NBR can acts as a permanent plasticizer for PVC applications

as in electrical wires and cables coating, wrapping film for the food industry, conveyor belts, domestic application, etc. Dynamically vulcanized Thermoplastic Elastomer (TPEs) have been widely used because of their technical advantages in processing as well as their versatile end use properties [1]. It is obvious that in thermoplastic elastomers, dynamic vulcanization of the rubber has improved the mechanical, thermal and impact properties (compared to those of uncured or slightly crosslinked composition) [2-5]. Some of the blends however, incompatible [6-8]. To improve the mechanical properties of these blends, it is important to develop a proper control of phase morphology and good interfacial adhesion by using compatibilizing agents. Compatibilization was achieved by the in situ formation of an interfacial agent and dynamic vulcanization, i.e. vulcanization of rubber phase in blends during mixing of polymer blends to improve the properties of immiscible polymer blend through stable morphology and good interfacial adhesion. In situ compatibilization of polyamide 6/ natural rubber blends with maleic anhydride, whereas our previous works [10-12] used Acrylic Acid (AAc) and Maleic Acid (MAc) as compatibilizers in recycled Poly (vinyl chloride)/Acrylonitrile Butadiene Rubber (PVCr/NBR) blends. We have also reported [13] the effect of maleic anhydride (MAH) on properties of recycled Poly (vinyl chloride)/ Acrylonitrile Butadiene Rubber (PVCr/NBR) blends. It was found that, for Maleic anhydride (MAH) compatibilized blends, the increase in tensile strength is due to the increased dipolar interaction between the PVCr-MAH and NBR phases, which cause an increase in interface adhesion between PVCr and NBR phases. Here, we report the effects of dynamic vulcanization and glycidyl methacrylate on mechanical properties, swelling index, and morphology properties of PVCr/NBR blends.

EXPERIMENTAL

Materials and Methods

Recycled PVC (PVCr) from electrical wires and cables was supplied by Alfasya Jaya Sdn. Bhd. Penang, Malaysia and the compositional analysis of recycled PVC is shown in Table 1. NBR with 34% acrylonitrile content was obtained from Kumpulan Guthrie, Seremban, Malaysia. The Dioctyl-phthalate (DOP), Glycidyl Methacrylate (GMA), dicumyl peroxide, barium/cadmium stearate, stearic acid, zinc oxide, Tetramethyl Thiuram Disulphide (TMTD), Dibenzothiazyl Disulphide (MBTS), and sulphur were obtained from Bayer (M) Penang, Malaysia.

Table 1 Inorganics residue in recycled PVC measured by X-Ray Fluorescence Spectrometer Rigaku RIX 3000.

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		

Preparation of the Blends

The formulations of the blends are given in Table 2. Blend ratio of plastic to rubber was fixed as 80/20, 60/40, 50/50, 40/60, and 20/80 (wt%). Sulphur concentration was fixed at 0.6phr of rubber. The PVCr/NBR blends were prepared by melt-mixing in a Haake Rheomix Polydrive R 600/610 at 150°C with a rotor speed of 50rpm. The amount of DOP and Cd/Ba stearate used for the mixing of the blends were 20php and 3php, respectively based on total PVCr content in all compositions. The PVCr was initially pre mixed with stabilizer, plasticizer and GMA in a glass beaker for five minutes at room temperature. The compounded PVCr was charged into the mixing chamber, equilibrate for two minutes and then NBR was added. Zinc oxide and stearic acid were added at six minutes and curing agents (sulphur + accelerator) were added at seven minutes of mixing. Mixing was then continued until a constant torque was obtained. The total mixing time was eleven minutes. The compound was removed from the mixer and sheeted on a cold two-roll mill. For PVCr/NBR blends, the zinc oxide, stearic acid and curing agents and GMA were not added during mixing.

Compression Molding

The samples of blends were compression molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 150°C for four minutes, followed by compressing for four minutes at the same temperature. Tensile tests were carried out with Testometric tensometer M 500. Tests were done according to ASTM D412. Dumbbell specimens of 2mm 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 calculated. Reading 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 each test.

Table 2 Formulations of dynamically vulcanized PVCr/NBR + GMA blends.

Materials	Blends (wt %)				
	I	II	III	VI	V
PVCr	80	60	50	40	20
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
GMA ^d	4	4	4	4	4
ZnO ^e	3	3	3	3	3
Stearic acid ^f	1.5	1.5	1.5	1.5	1.5
Dibenzothiazyl disulphide (MBTS) ^g	X	X	X	X	X
Tetramethyl thiuram disulphide(TMTD) ^h	X/3	X/3	X/3	X/3	X/3
Sulphur	X	X	X	X	X

a, b, c, d at php of plastic

e, f, g, h at phr of rubber

X= 0.6 phr of rubber

*A similar PVCr/NBR blends were prepared but without the addition of ZnO, stearic acid, MBTS, TMTD, sulphur and GMA.

Swelling Test

Determination of the swelling index of the blends was carried out according to ASTM D471. The test pieces of the blends of the dimension 30mm x 5mm x 1.5mm were weighted using an electrical balance and this was considered to be original weight. The test pieces were immersed in toluene at room temperature for 46 hours, respectively. The test pieces were then removed from the toluene, wiped with tissue paper to remove excess toluene from the surface, and weighted (swollen weight). The swelling index of the blends was calculated as follows :

$$\text{Swelling index} = \frac{\text{swollen weight}}{\text{original weight}} \quad (1)$$

Scanning Electron Microscopy Studies

The blends were characterized with the help of a Scanning Electron Microscopy (SEM) (Leica Cambridge S 360 model). The morphology of the samples was examined after solvent extraction for 24 hours at room temperature using dichloromethane to extract the NBR from the blend. The samples were then finally dried. Surfaces of the samples were coated with a thin gold layer of about 20nm thickness prior to scanning.

Figures 1 and 2 show the stress at peak and stress at 100% elongation (M_{100}) of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends. It can be seen that, as the NBR composition increases, the stress at peak and M_{100} decrease as

a result of decreasing blends rigidity. The increasing of NBR composition in both blends increases the elongation at break, E_b (Figure 3). As the NBR content increases, the stiffness and brittleness of the blends decrease gradually with associated increase in elongation at break. However, at a similar blends composition, dynamically vulcanized PVCr/NBR + GMA blends have higher stress at peak and stress at 100% elongation but lower elongation at break than PVCr/NBR blends. This is due to the increased of cross-link density in dynamically vulcanized PVCr/NBR + GMA blends. The better stress at peak and M_{100} of vulcanized PVCr/NBR + GMA over PVCr/NBR blends is due to the enhancement in interfacial adhesion between PVCr-GMA-NBR phases.

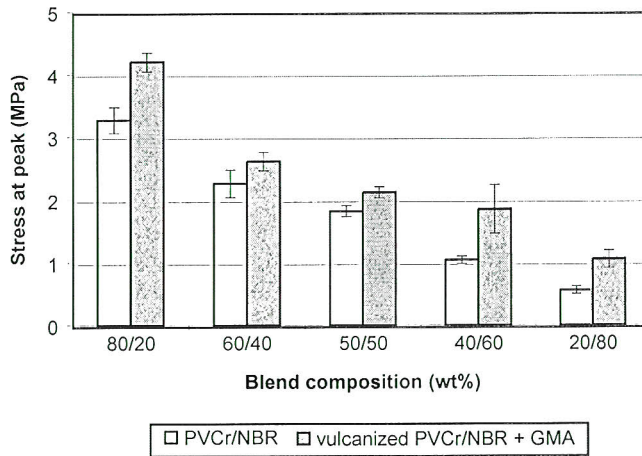


Figure 1. Stress at peak vs. blend composition of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends.

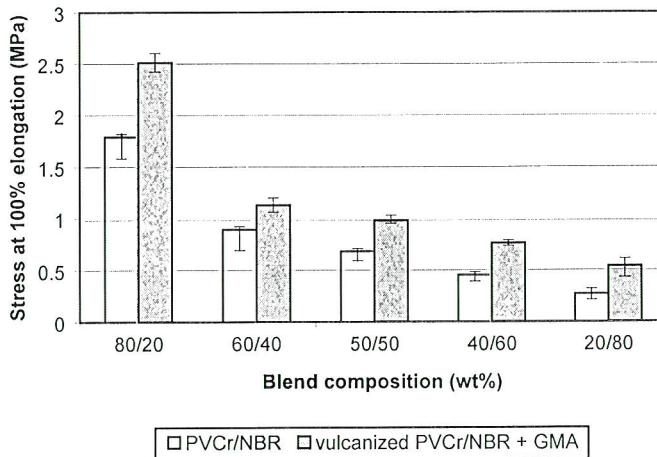


Figure 2. Stress at 100% elongation vs. blend composition of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends.

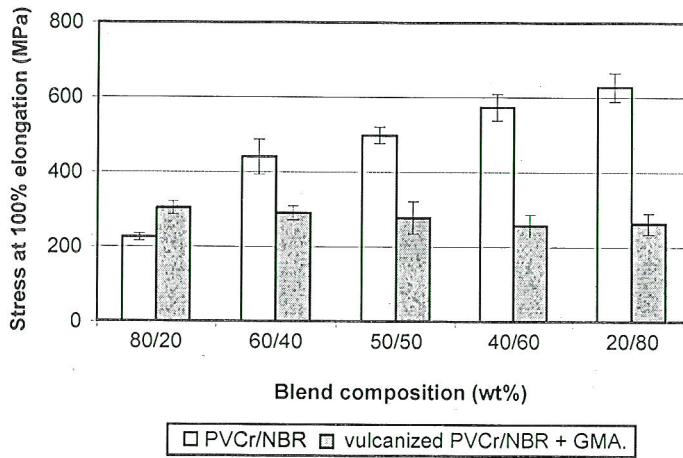


Figure 3. Elongation at break vs. blend composition of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends.

Swelling Behaviour

Table 3, shows the effect of blend composition on swelling index of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends. It can be seen in Table 3 that the swelling index increases with increasing NBR composition. Swelling index is a good indication of the extent of crosslinking as the extent of swelling is an inverse function of the increase in crosslinking. At a similar blend composition, swelling index of dynamically vulcanized PVCr/NBR + GMA blends is lower than PVCr/NBR + GMA blends. As the crosslink density in dynamically vulcanized PVCr/NBR + GMA increases, the blends become stiffer and less penetrable by the toluene.

Table 3 Data of swelling index of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends in toluene for 46 hours.

Blend composition (wt %)	Swelling index
80/20 PVCr/NBR	1.70 ± 0.05
50/50 PVCr/NBR	2.86 ± 0.08
20/80 PVCr/NBR	5.12 ± 0.14
Vulcanized 80/20 PVCr/NBR + GMA	1.58 ± 0.01
Vulcanized 50/50 PVCr/NBR + GMA	2.20 ± 0.09
Vulcanized 20/80 PVCr/NBR + GMA	3.30 ± 0.09

Figure 4 and Figure 5 show the extracted surfaces of PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA blends at 80/20, 50/50, and 20/80 (wt%). As the NBR composition increases, the extracted surface indicates the weak cross-link and the formation of large holes due to the extracted NBR from PVCr/NBR blends and dynamically vulcanized PVCr/NBR + GMA. At a similar blend composition, it can be seen that, dynamically vulcanized PVCr/NBR + GMA blends (Figure 5 (a-c)) show more difficult to extract NBR from PVCr/NBR + GMA blends than PVCr/NBR blends. This is due to the crosslinking formation in NBR phase and the better interaction between PVCr and NBR as a result of glycidyl methacrylate addition.

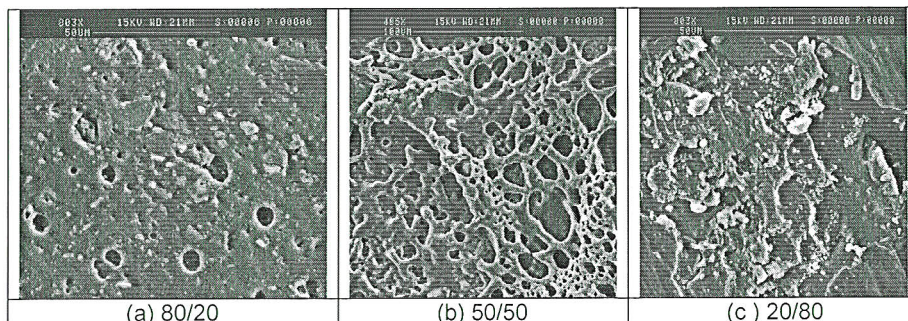


Figure 4. (a-c) SEM micrographs of extracted surfaces of PVCr/NBR blends. (a) 80/20, (b) 50/50, (c) 20/80.

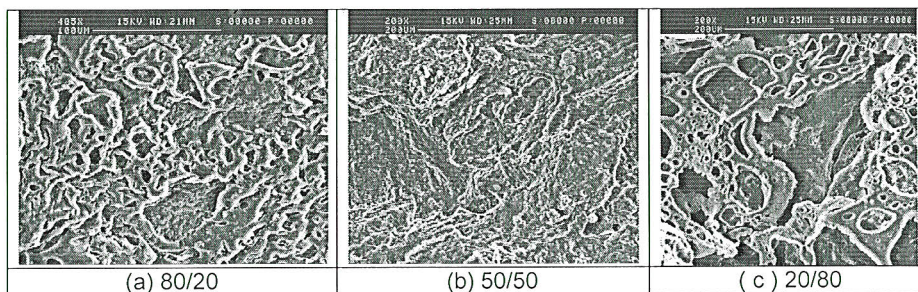


Figure 5. (a-c) SEM micrographs of extracted surfaces of dynamically vulcanized PVCr/NBR + GMA blends. (a) 80/20, (b) 50/50, (c) 20/80.

CONCLUSIONS

The dynamic vulcanization system and the addition of glycidyl methacrylate significantly improved the mechanical properties of PVCr/NBR blends as evidences by higher stress at peak and stress at 100% elongation. Morphological study of extracted surfaces indicates that dynamically vulcanized PVCr/NBR + GMA blends have better interfacial adhesion, swelling resistance, and more compatible than PVCr/NBR blends.

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