Influence of Blend Composition on the Physical, Flame Retardancy, Dielectric, Aging, and Solvent Resistance Properties of Poly[ethylene(vinyl acetate)] and Polychloroprene

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ABSTRACT: Poly[ethylene(vinyl acetate)] (EVAc) has been blended with polychloroprene (CR) to develop a compound for application in the cable industry. Physical, flame retardancy, dielectric, and solvent resistance properties have been investigated for the blends. On air and brine aging, the tensile properties for 50/50 blend remains almost unchanged, though retention in tensile properties is maximum for CR in solvent aging and for EVAc in air aging. 50/50 blend shows substantially lower set and hardness compared to EVAc. The limiting oxygen index of 50/50 blend is found to be higher compared to EVAc, which indicates sufficient inflammable capability of 50/50 blend in atmospheric air. A substantially lower dielectric constant, conductivity with good physical properties, and inflammability of 50/50 blend suggests its suitability for use as a cable sheathing compound. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 551–556, 1999

Key words: EVAc; CR; physical properties; dielectric properties

INTRODUCTION

Polychloroprene (CR), an unsaturated backbone rubber that is highly oil- and flame-resistant finds its use in cable sheathing, sealing, belting, and vibration isolation. However, its service at high temperature is limited due to its oxidative degradation and deterioration of properties on ageing. In order to improve the high temperature properties of CR, it is imperative to blend it with a polymer of saturated backbone.[1,2] Poly[ethylene(vinyl acetate)] (EVAc) was chosen as the blending component due to its versatile characteristics, such as plasticizing action, high aging resistance, and solvent resistance properties.[3] Miscibility of this blend has been studied thermodynamically,[4] spectroscopically,[5] and rheologically.[6] The blends of CR and EVAc are found to be miscible at all compositions. In order to find the suitability of these blends for application in the cable industry, it is required to explore its physical and aging properties,[3,7,8] flammability properties,[9] and dielectrical properties.[10] Keeping this in mind, the present investigation deals with the studies of physical as well as aging and solvent resistance, dielectric, and fire retardancy properties of the blends of CR and EVAc.

EXPERIMENTAL

Materials Used

The details of materials used are given in Table I.

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Table I Materials Used

Material	Specification	Producer
Poly[ethylene (vinyl acetate)], Pilene-2806	Vinyl acetate: 28 wt % Density: 0.96 g/cc MFI: 6 g/10 min	Polyolefin Industries Ltd., India
Polychloroprene, Neoprene-WM1	Specific gravity: 1.23 Mooney viscosity: 40 (ML_{1+4}, 100°C)	Du Pont, U.S.A.
Carbon black (N-110)	CTAB, m^2/g: 127 DBPA, cm^3/100 g: 93 S_f of acetonitrile at 150°C: 1.64	Degussa AG
Dicumyl peroxide, percitol-40	Purity: 40%	Peroxide India Limited
Triallyl cyanurate	Purity: 97% Fusion point: >100°C	Aldrich Chemicals

Sample Preparation

Mixing was carried out in a Brabender Plasticorder (PLE-330) provided with a cam type rotor as per the formulation given in Table II. Thermoplastic EVAc was first melted at 100°C and 60 rpm, then premasticated CR was added, and mixing was allowed to continue for 5 min. Carbon black was then added to the chamber, and mixing continued until a constant minimum viscosity was reached, which indicates proper dispersion of carbon black. Peroxide and other ingredients were added at a lower rotor speed (40 rpm) and temperature (90°C) to avoid scorching under excessive shear. All the samples were molded in a Moore press at 170°C and 10 MPa for 15 min to ensure maximum extent of curing. The mold was cooled with circulation of cold water after molding.

Mechanical Properties

Dumbbell-shaped test samples were punched out from the molded sheets. The thickness of the sample was measured with a bench thickness gauge. The test method described in ASTM-D-412-80 was followed. The test was carried out with a Zwick Universal Testing Machine (UTM-1445) at 25°C and at a crosshead speed of 500 mm/min.

Table II Blend Composition (Wt %)

	Blend Code				
Material	B_1	B_2	B_3	B_4	B_5
EVAc	100	70	50	30	0
CR	0	30	50	70	100

All blends contain 30 phr of carbon black (N-110), 3 phr dicumyl peroxide, and 1 phr triallyl cyanurate.

Hardness

Hardness was tested with a Shore-A durometer according to ASTM-D-2240. The durometer was kept on a stand under a constant load.

Limiting Oxygen Index

The limiting oxygen index was measured according to ASTM-D-2863-77 using a sample of 70 × 7 × 2 mm on a flammability tester (Stanton Redcroft Oxygen Indexer).

Set

The compression set was measured according to ASTM-D-395 under a constant strain at room temperature and at 70°C for 72 h. Tension set properties were measured on putting a dumbbell specimen under a constant strain (100% elongation) on a Zwick universal testing machine (UTM) for 10 min, followed by relaxing it for another 10 min.

Dielectric Properties

The dielectric properties were measured on a GEN-RAD 1620 AP capacitance measuring assembly. The dielectric constant K and the loss factor tan δ were measured with an accuracy of 5% using a frequency of 10 KHz at room temperature (25°C). Silver paste was used as an electrode, applying it on both sides of the circular sample cut from the sheets using a circular die. Conductivity (σ) of the samples in Ω^{-1} cm^{-1} is calculated from the loss factor (tan δ) and the dielectric constant (K) using the following equation[11]:

$$\sigma = f\mathrm{K} \tan \delta \times 10^{-12}/1.8$$

where f is the frequency in Hz, and tan δ is defined as tan $\delta = f \times D$, where D is the dissipative loss.

Aging in Air

Aging of dumbbell samples was carried out in an air oven according to ASTM-D-573 at 70°C for 72 h. Aged samples were tested for tensile properties on a Zwick UTM.

Solvent Resistance

Solvent resistance properties were tested on aging of dumbbell samples in saltwater (brine, 10% salt) at 70°C for 72 h, then the samples were kept in a well-air-circulated oven for 72 h to allow the diffused solvent to come out of the polymer. The dried samples were tested on a Zwick UTM for their mechanical properties.

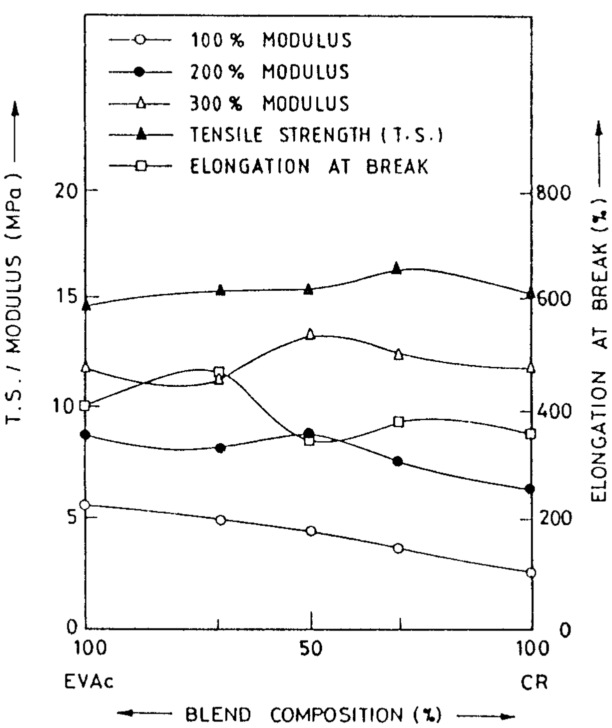

Figure 1 Variation of tensile strength (TS); modulus at 100, 200, and 300% elongation; and elongation at break with blend composition (wt %).

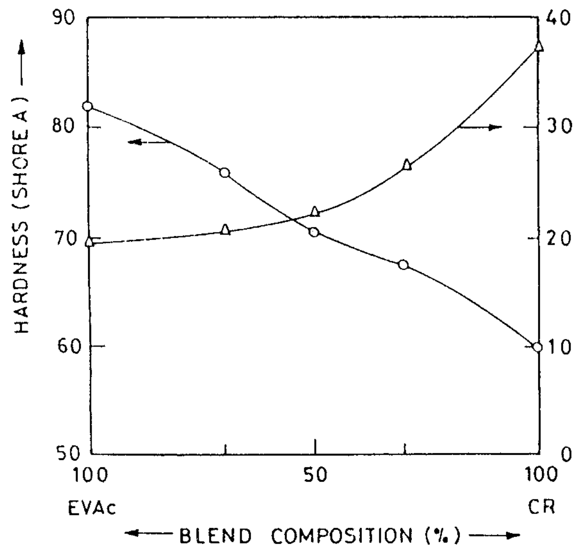

Figure 2 Variation of hardness (Shore A) and limiting oxygen index (% oxygen) with blend composition (wt %).

RESULTS AND DISCUSSION

Physical Properties

Variation of the tensile properties of the samples with blend composition are shown in Figure 1. Modulus and tensile strength decreases with increasing content of CR. This is due to their lowering of crystallinity. CR has tremendous ability to crystallize at a higher strain. This crystallizing ability is higher in the blends up to 50% CR due to the presence of some crystals, which initiates crystal growth at higher elongation. That is the reason for higher modulus at 50% CR blending. Tensile strength goes on increasing with increasing content of CR in the blends except that of CR, which, due to higher cure heterogeneity,[12] fails at relatively lower elongation and shows lower stress.

The variation of hardness and the limiting oxygen index (LOI) with blend composition are shown in Figure 2. Hardness decreases with increasing content of CR in the blends. Thermoplastic EVAc shows higher hardness due to presence of crystals, and, as the crystallinity decreases with increasing content of CR, the hardness also decreases. EVAc shows lower LOI, whereas CR shows very high LOI due to liberation of HCl at higher temperatures. As the amount of CR increases in the blends, LOI increases linearly up to 50% CR, beyond which the LOI value increases sharply. The LOI values of the blends containing more than 50% CR indicate higher stability with

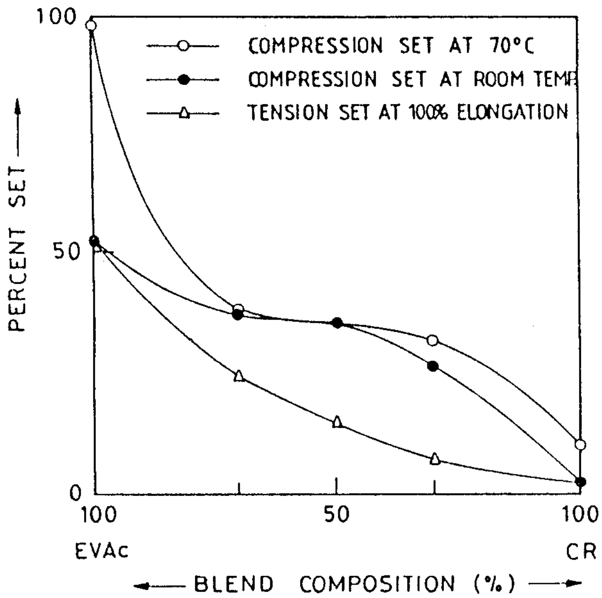

Figure 3 Variation of compression set (%) at 70 and 25°C (room temperature) and tension set (%) at 100% elongation with the blend composition (wt %).

respect to flammability at normal atmospheric conditions.

The variation of tension set at 100% elongation and the compression set at both room temperature and 70°C with weight % of CR in the blends are shown in Figure 3. For all these cases, the compression set of thermoplastic EVAc is much higher, whereas the compression set of elastomeric CR is very low; and with increasing content of CR, set properties go on decreasing. The rate of decrease in compression set is much higher in the region of 0–30 and 70–100% CR generating concave plot with respect to blend composition.

The plots of dielectric loss (tan δ), dielectric constant, and conductivity with weight percent of CR in the blends are shown in Figure 4. Chloro groups adjacent to double bonds present in CR are highly polarizable compared to the acetate groups of EVAc.[13] This is the reason for a lower dielectric constant, a higher dielectric loss, and higher conductivity of CR compared to EVAc. Both conductivity and the dielectric constant decrease with increasing content of CR in the blends up to 70% CR, beyond which both these properties increase with different rates, and conductivity shows a sudden increase with a very high rate. In the region of 0–30% CR, lowering of the dielectric constant is very sharp compared to the lowering of conductivity. The loss tangent of EVAc increases on blending with 30% CR, beyond which it decreases up to 50% CR, followed by its increase. Interestingly, all these properties does not follow the additive rule and show negative deviation with respect to their additive values. EVAc and CR in their blends undergo dipolar interactions[6]; thus, the number of free polar groups, like olefinic and chloro groups of CR and acetate groups of EVAc, get reduced while interacting with surface polar groups of carbon black. Thus, the dispersive centers[14] of carbon black get reduced, causing a reduction in the conductivity of the blends.

Air Aging

Tensile properties of air-aged samples, along with their corresponding variation in percent with respect to the unaged samples, are plotted in Figure 5. Modulus, tensile strength (TS), and elongation at break (EB) show the same trend as those of unaged samples on their variation with blend compositions. On aging, EVAc shows the maximum amount of retention in modulus as the change is positive. The retention of properties (modulus, TS, and EB) decreases as the amount of CR increases in the blends, with the exception of 100% CR and the 50/50 blend at 100% modulus. As the unaged 50/50 blend shows maximum improvement in properties compared to the other blends, higher retention for the 50/50 blend is justified. The decrease in retention properties with increasing content of CR in the blends is due to the proneness of unsaturated CR to aerial oxidation at an elevated temperature (70°C).

Solvent Resistance

The plots for the tensile properties and the percentage of change on aging in brine at 70°C with

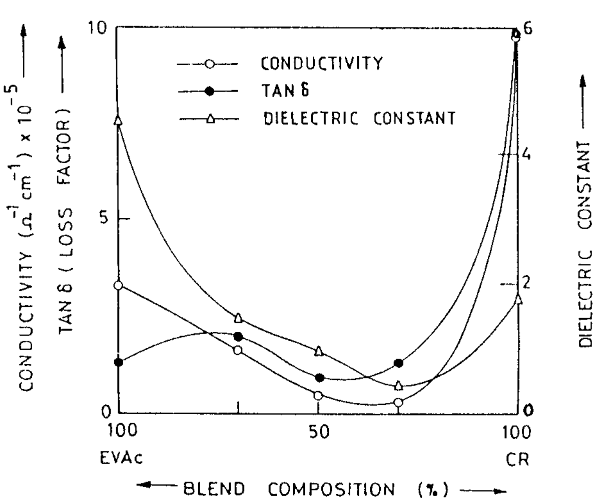

Figure 4 Variation of conductivity, loss tangent, and dielectric constant with the blend composition (wt %).

blend compositions are shown in Figure 6. The modulus plot shows almost same trend as that of unaged samples. EVAc shows higher elongation at break and lower tensile strength compared to the 70/30 EVAc–CR blend. The change in modulus and TS on brine aging is minimum, and the retention is maximum for 100% CR. The retention is minimum for 100% EVAc. Retention increases with an increasing amount of CR in almost all cases except for the 100 and 200% moduli, which show a decrease in the region of 0–30% CR. Almost all properties show higher retention at the

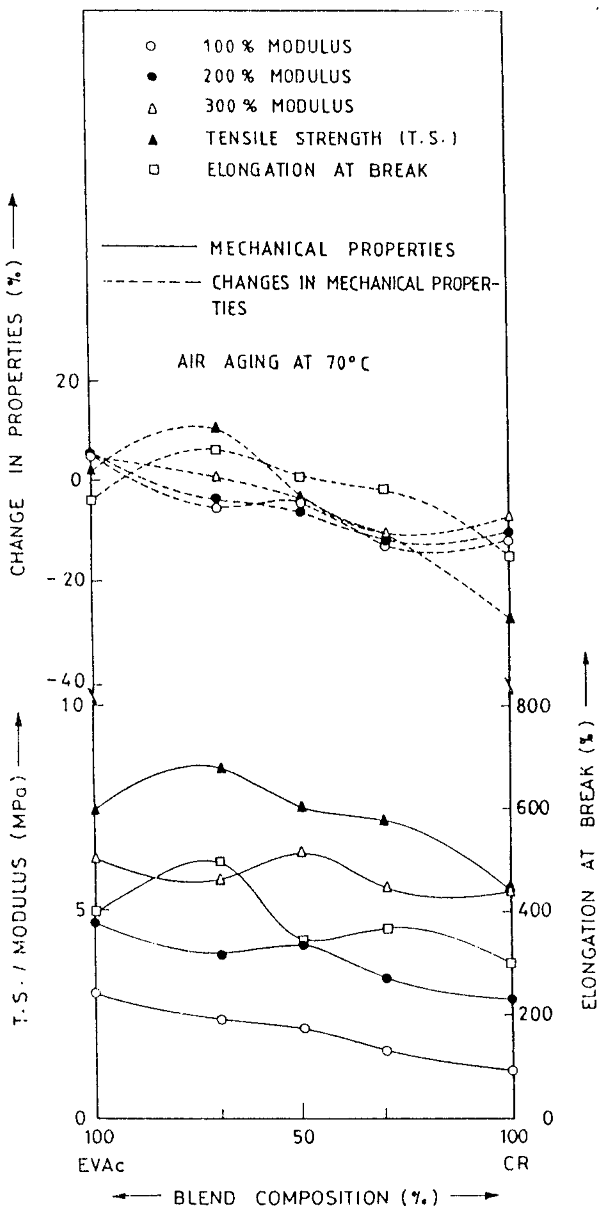

Figure 5 Variation of tensile properties on air aging at 70°C and their percentage of changes with blend composition (wt %).

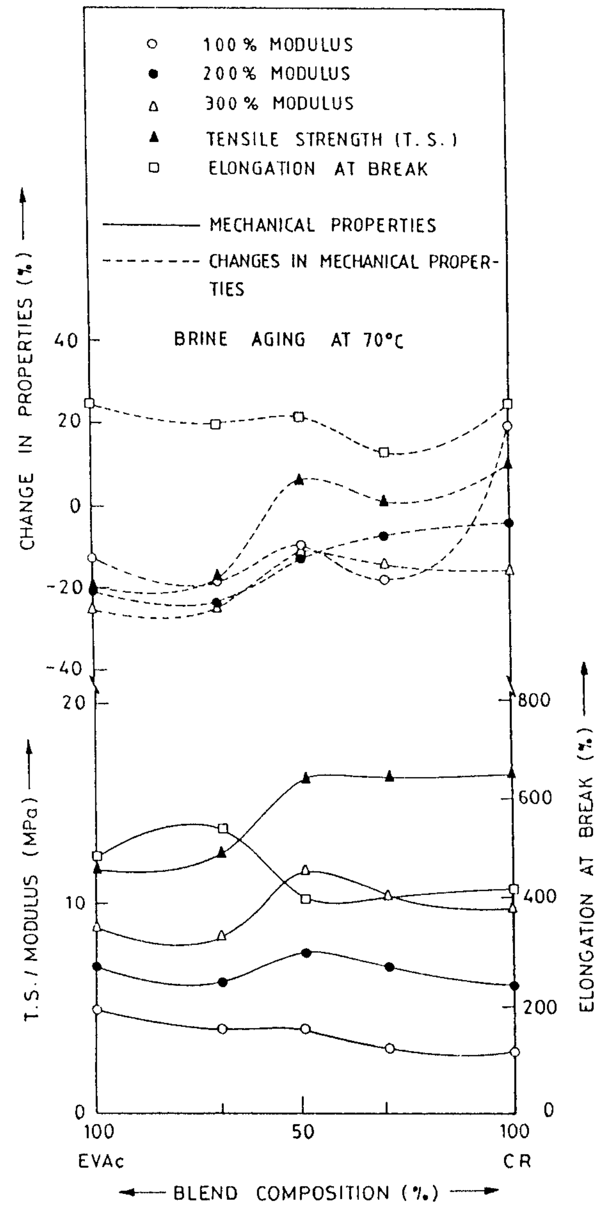

Figure 6 Variation of tensile properties on brine aging at 70°C and their percentage of changes with blend composition (wt %).

50/50 blend compared to the other two blends. Elongation at break shows enhancement on brine aging. The increment in length is due to the plasticizing action of absorbed water molecules. Saltwater (brine) being polar, it can diffuse very slowly into the hydrocarbon polymers. Polar groups present in EVAc and CR can enhance absorption of diffused molecules. The samples are dried for sufficient time such that the diffused solvent molecules can come out. Polar saltwater may solubilize the crystals present in EVAc or act as defects in crystal lattices. These defects or lower crystallinity is the reason for lower retention in properties of EVAc and its blends with CR compared to 100% CR. The 50/50 blend shows higher retention in properties compared to the other 2 blends.

CONCLUSION

The 50/50 blend shows higher modulus and lower elongation compared to the other blends. The properties of the 50/50 blend remain almost unchanged on aging in air and brine at 70°C. The retention in properties on brine and air aging of CR is maximum and minimum due to its comparative higher polarity and unsaturation, respectively. Set properties, as well as the hardness of CR, is substantially low compared to 100% EVAc. The higher limiting oxygen index of the 50/50 blend indicates its substantial inflammable capability in atmospheric oxygen compared to 100% EVAc. Dielectric constant and conductivity are lowest for the 30/70 EVAc–CR blend. But the 50/50 blend with its lowest dielectric loss factor, comparable conductivity, and dielectric constant with respect to 30/70 blend is expected to have overall improved dielectric properties.

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