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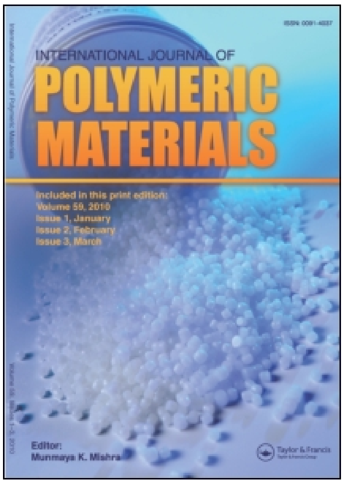

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Polyblends of Polyacrylic Rubber and Fluroelastomer

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Polyblends of Polyacrylic Rubber and Fluroelastomer

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INTRODUCTION

Blending is a process by which one can achieve a compromise between processibility, properties and economy by suitable choice of partners. Polyacrylic rubber is a special rubber, featuring resistance to heat, oil (particularly lubricating oil) and ozone, enjoys increasing demands in automotive and related fields.[1] The use of special heat resistant rubbers like fluroelastomers[2] is a costly affair. Apart from the cost, because of extreme toughness, the fluroelastomers are often faced with processing difficulty. On the other hand the polyacrylic rubber is softer and easy to process. Fluroelastomers cannot blend with general purpose oil resistant rubbers but the presence of polyacrylic rubber can act as an active interphase between the two using a common curative system. Both the polyacrylic rubber and fluroelastomer can be cured with diamine types of curatives and a compromise can be achieved.

We report here the blending of viton-B-50 with Nipol AR-51 in various proportions and their properties before and after high temperature air and oil ageing. Effects of blend ratio on the metal-rubber adhesion was studied to assess suitability in metal-polymer composite application. Based on results, efforts have been made to achieve an intermediate blend properties.

EXPERIMENTAL

Compounding formulation was shown in Table I as a gradual replacement of one polymer by another keeping pure polymer at extreme ends. Fluroelastomer was of viton-B-50 grade from Du Pont, USA and polyacrylic rubber was of Nipol AR-51 grade from Nippon Zeon Co. Ltd., Japan. Firstly, the master batches were made for each elastomer as per formulations given in Table I and then they are blended in various ratios based on 100 Phr total polymer. This is deliberately done in order to get adequate reinforcement from the different kinds of carbon blacks used in two different elastomers.

TABLE I

Compounding formulations

Blend Nos.	A	B	C	D	E	F	G	H	I	J	K
Polyacrylic rubber (Nipol AR-51)	100	90	80	70	60	50	40	30	20	10	0
Fluroelastomer (Viton-B-50)	0	10	20	30	40	50	60	70	80	90	100

Polyacrylic rubber master batch contains: AR-51 - 100 Phr, DIAK -3 -2.5 Phr, MgO - 4.0 Phr, SRF - 30.0 Phr.

Fluroelastomer master batch contains: Vitron-B-50 - 100 Phr, DIAK -3 -2.5 Phr, MgO - 4.0 Phr, MT Black - 30.0 Phr.

The cure characteristics of the blends were studied with the help of Monsanto Rheometer (R-100) at 160°C, 170°C and 180°C. The compounds were then cured up to optimum cure time (t_{90}) at 170°C and the properties were determined on the cured sheet. Ageing was done at 200°C for 48 hours in air oven. Oil aging was done in ASTM oil-3 at 150°C and 200°C for 48 hours. Swelling in toluene is done at ambient in order to study the co-vulcanization following the Kraus[3] plot as

$$V_{r_o}/V_{r_f} = 1 - M\phi/(1 - \phi)$$

where

V_{r_o} = vol. fraction of elastomer in the swollen gel when any dispersed phase is absent

ϕ = vol. fraction of the dispersed phase in the unswollen covulcanizate

M = slope

V_{r_f} = vol. fraction of the elastomer in the swollen gel when dispersed phase is present.

Similarly, swelling in MEK performed in order to study the state of cure. Heat build up was measured with the help of Goodrich flexometer. Compression set was measured at 150°C for 72 hours at 25% deflection. Post curing was carried out both at 170°C and 250°C for 6 hrs. Chemlock-607 was used as bonding agent for studying metal rubber adhesion both before and after aging. Fracture mechanism and adhesion failure were studied with the help of SEM using camscan-series z and E5200 auto sputter coater.

RESULTS AND DISCUSSIONS

Processing and Cure Characteristics of Blends

Viscosity of the blends increases as the polyacrylic rubber is being replaced by fluroelastomer as observed from ML_4 at 120°C and minimum viscosity (T_{min}) at 170°C in Table II. Scorch safety is reduced, both at 120°C and 170°C, as the fluroelastomer content in the blend increases. Cure rate is increased (reflected in decreasing optimum cure time, t_{90} in Figure 1) and the ultimate extent of cure ($T_{max} - T_{min}$) is increased as the polyacrylic rubber is replaced by the fluroelastomers.

TABLE II

Processing parameters and cure characteristics

Blend Nos.	A	B	C	D	E	F	G	H	I	J	K
ML_4 (120°C)	22	24	27	31	35	39	42	46	49	52	54
$MS_{120°C}$ (mins)	39	35	33	29	24	21	18	16	14	12	12
Scorch time (t_2) at 170°C (mins)	8.0	8.0	8.0	7.5	7.0	6.0	5.5	5.0	4.5	4.0	3.0
T_{min} at 170°C	7.0	7.0	7.5	9.0	10.0	11	13.0	16	19.0	22.0	26
t_{90} (mins) at 170°C	45	44	44	42	39	38	36	34	32	32	31
$T_{max} - T_{min}$ at 170°C	19	20	22	24	25	26	27	29	31	32.5	34

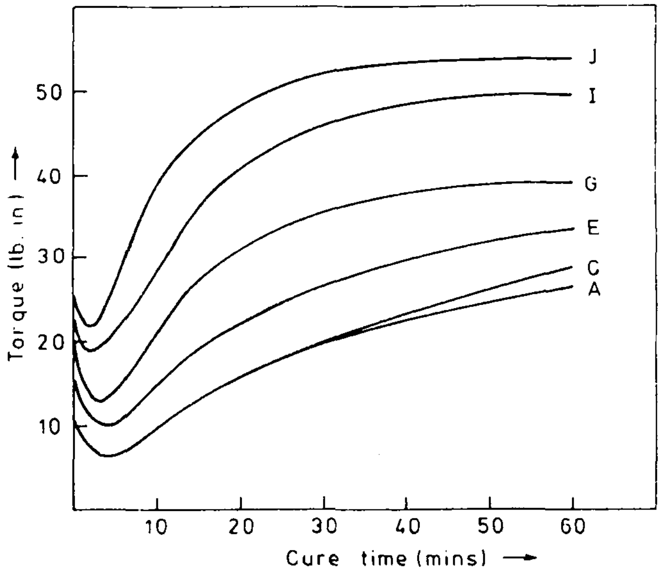

FIGURE 1 Rheograms at 170°C for the blends.

This change in both the processing and curing parameters is prominent after 30% fluroelastomer in the blends. Beyond 30% fluroelastomer the changes are drastic and continued up to its 100% level in the blends.

Figure 2 reveals that the change in optimum cure time with the inverse of temperature follows a straight line plot, the slope of which gives the activation energy of curing. The activation energy of the pure polyacrylic rubber is higher than that of fluroelastomer 50:50 blend exhibit the higher activation energy and lie above the additive average line, although the deviation from additive average value is not significant for the blends up to 30% on each side.

Swelling in Solvents and Oil

Differential swelling in toluene is shown in Figure 3, in which the polyacrylic rubber is soluble. At higher level of polyacrylic rubber, the continuous phase is highly swollen and fluroelastomer the swollen dispersed phase acts as reinforcing filler.

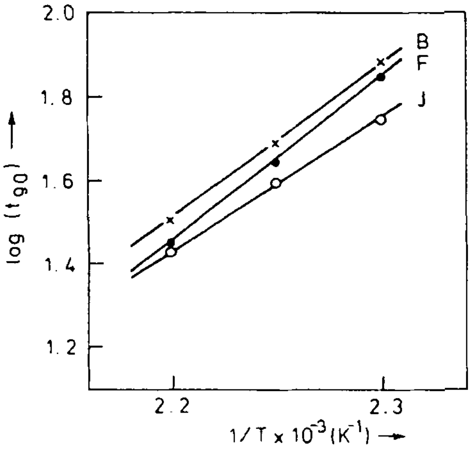

FIGURE 2 Variation of log (t_{90}) with inverse absolute temperature.

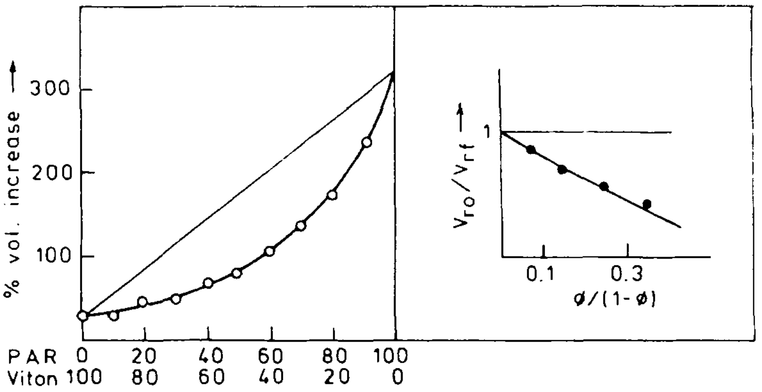

FIGURE 3 Swelling of blends in toluene at ambient.

If the interfacial bonds are formed during covulcanization the lightly swollen dispersed phase will restrict the swelling of the highly swollen continuous phase below the additive average line. The negative slope of the plot V_{r_o}/V_{r_f} against ($\phi/1 - \phi$) will also suggest the covulcanization. Left portions of Figure 3 reveal that the volume swell for the blends lies well below the additive average line suggesting the swelling restriction. The right portion of Figure 3 also confirms the above view as 'M' becomes appreciable and straight line lies below the unity line suggesting strong interfacial bonds causing swelling restrictions.

Swelling in ketonic solvent like MEK has been shown in Figure 4. This reflects the effect of crosslinking on the volume swell. Polyacrylic rubber with lowest crosslinking exhibits higher amount of swelling. The volume swell decreases with the increase of fluroelastomer in the blend which in turn increases the crosslinking in the blend systems. Deswelled sample has the surface cracks and layers like separation within the blend ratio of 70:30 and 30:70. Swelling in polar oil like ASTM oil 3 has been studied at elevated temperature and is represented graphically

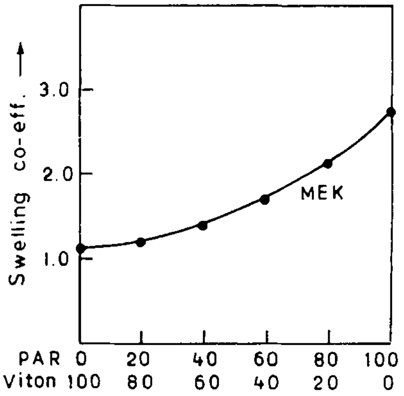

FIGURE 4 Swelling of blends in MEK at ambient.

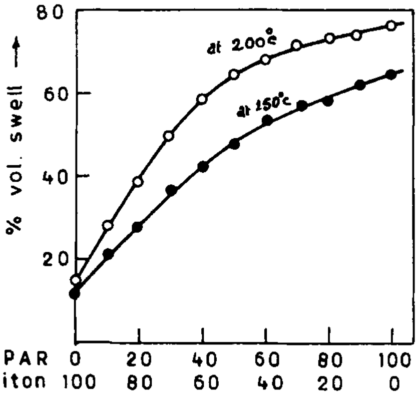

FIGURE 5 Swelling of blends in ASTM oil 3 at 150°C and 200°C.

in Figure 5. As shown in the Figure 5, the polyacrylic rubber swells more than the fluroelastomers at both the temperatures. Swelling decreases as the polyacrylic rubber is being replaced by fluroelastomer. The effect of temperature is more in the case with polyacrylic rich blends. There are two distinct steps in the variation of swelling with blend ratio as observed in Figure 5. First, there is slower rate of decreasing volume swell up to 50% of fluroelastomer, beyond which the volume swell decreases at a faster rate. These two steps are more prominent at the higher temperature of testing especially around 50:50 blend ratio. Here again, the layer like separation exists for the blends in the middle region at the high temperature of swelling in oil.

Metal-Blend Adhesion

Adhesion strength has been shown in Figure 6 both before and after aging as a function of blend ratio. There is very marginal change in adhesion value for the blend ratio of 80:20 at the both ends. Before aging the adhesion strength decreases as the fluroelastomer content increases, attains a minimum at around 50:50 and then increases. Adhesion strength with polyacrylic rubber is slightly higher than

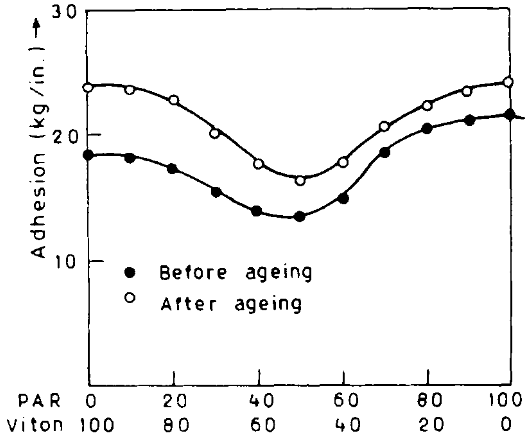

FIGURE 6 Metal blend adhesion before and after ageing.

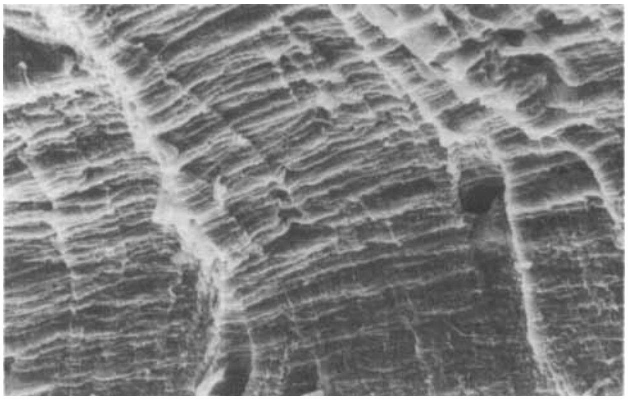

FIGURE 7 SEM fractogram for adhesion failure for blend A (100×).

that with fluroelastomer. There are two types of failure mode that have been observed throughout the entire blend systems.[4,5] At both the ends up to 70:30 ratio the adhesion bond failure is observed which has been confirmed by solvent swelling technique. Within the range of 70:30 and 30:70 the cohesive failure occurs i.e., failed in the rubber layer leaving a thin layer of rubber on the metal plate. The failed rubber samples have been scanned in order to find out the mode of failure and are shown in Figures 7–9. For the polyacrylic rubber (Figure 7), there is slight tendency of stick-slip type failure having surface cracks. In the case of fluroelastomer (Figure 8) the intermittent adhesion failure, most erratic in nature has been observed. However, in the case of 50:50 blend the smooth rubbery failure (Figure 9) has been experienced.

For all the blends adhesion strength increases on ageing, as shown in Figure 6, although to a different extent depending on the blend ratio. After ageing the fluroelastomer exhibits a higher bond strength than the polyacrylic rubber. Here again the blends around 50:50 ratio exhibit lower bond strength. Ageing does not change the mode of failure as observed by SEM studies of the failed rubber samples.

FIGURE 8 SEM fractogram for adhesion failure for blend K (100×).

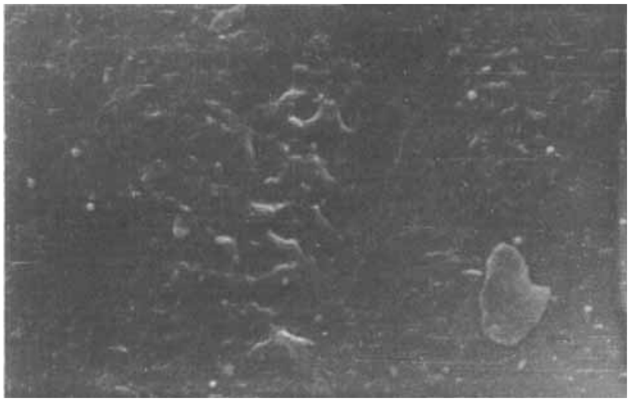

FIGURE 9 SEM fractogram for adhesion failure for blend F (100×).

Physical Properties both Before and After Ageing

Both before and after ageing properties are given in Table III. Replacement of polyacrylic rubber with fluroelastomer increases the modulus and thereby hardness and decreases the elongation at break. The observation is in the line with the rheometer study ($T_{max} - T_{min}$) of ultimate extent of cure, in Table II. Tensile strengths of blends are less than the pure polymers. Polyacrylic rubber is having more tensile strength than the fluroelastomer and decreases gradually as the blend ratio approaches 50:50 from both ends. Compression set is better for pure polymers than the blends although the state of cure has improving tendency. Heat build up is increased as the polyacrylic rubber is replaced by the fluroelastomer and around 50:50 ratio the sample cracks. Polyacrylic rubber, however, shows lower heat build up than the fluroelastomer. This may be attributed to the high hardness and low elongation at break for fluroelastomer rich blends.

Number of cycles required for 100% cut growth has been taken as a measure of cut growth rate as shown in Table III. As observed the rate of cut growth is more for the blends than that for pure polymers. Fluroelastomer is having higher cut

TABLE III

Physical properties before and after ageing

Blend Nos.	A	B	C	D	E	F	G	H	I	J	K
Modulus (200%) (kg/m^2)	30	32	35	42	52	64	86	90	99	104	110
Tensile strength (kg/cm^2)	140	129	107	90	82	79	88	98	105	126	132
Elongation at break (%)	500	460	410	380	310	210	210	220	230	240	240
Hardness (°A)	50	52	54	60	64	70	75	76	78	79	80
Compression set (%) (before post curing)	18	—	28	—	34	36	32	—	25	—	20
Compression set (%) (after post-curing)	21	—	30	—	34	35	30	—	20	—	12
Heat build up (ΔH, °C)	25	—	30	—	35	38	47	—	34	—	30
Cut growth (Kc^s) (100%)	1.4	—	1.26	—	1.02	0.89	0.99	—	1.14	—	1.22
Percentage change in physical properties after ageing at 200°C for 48 hrs.											
Tensile strength	−10	−14	−14	−16	−20	−28	−30	−20	−18	−16	−16
Modulus (200%)	+30	+32	+26	+21	—	—	—	—	—	—	—
Elongation at break	−20	−26	−31	−36	−38	−42	−40	−37	−30	−24	−18
Percentage change in physical properties after ageing in ASTM-3 oil at 150°C for 48 hrs.											
Tensile strength	−40	−38	−40	−42	−45	−41	−36	−29	−21	−18	−16
Modulus (200%)	−31	−30	−28	−32	−35	—	—	—	—	—	—
Elongation at break	−27	−25	−21	−24	−28	−29	−26	−20	−16	−17	−15

growth rate than the polyacrylic rubber. This may be due to the low viscosity of the polyacrylic rich blends where high flexibility offers lower cut growth rate. Very high cut growth rate near 50:50 may be due to probable phase separation. Effect of postcuring on the compression set values has been found out and shown in Table III. As observed, the postcuring of the vulcanizates lowers the compression set values for all the systems. Lower temperature postcuring is beneficial for polyacrylic rich blends and higher temperature postcuring is favorable for fluroelastomer rich blends.

Effect of high temperature air ageing and the high temperature oil aging on the mechanical properties are shown in Table III. Blends are having the poor ageing characteristics than that of pure polymers. Especially for the blends within the range of 70:30 and 30:70 region. Up to 30% of polyacrylic rubber in fluroelastomer and vice-versa the ageing performance does not change appreciably. Similar is the observation for oil resistance, which is better for fluroelastomer rich blends than the polyacrylic rich blends. The blends within 70:30 and 30:70 ratio has more deteriorating effects towards high temperature oil aging.

The fracture mode of the blends has been studied by SEM on the tensile fractured surface,[6] shown in Figures 10–12 for blends C, F and I respectively. As high level

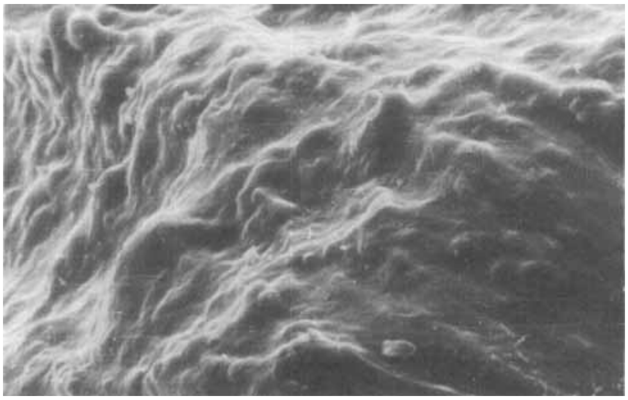

FIGURE 10 SEM fractogram for tensile failure for blend C (100×).

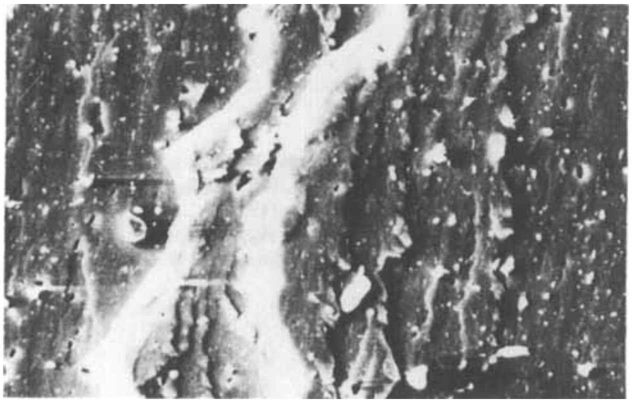

FIGURE 11 SEM fractogram for tensile failure for blend F (100×).

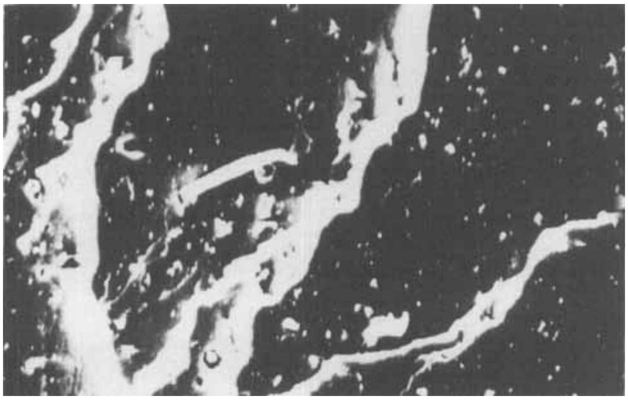

FIGURE 12 SEM fractogram for tensile failure for blend I (100×).

of polyacrylic rubber (blend C, Figure 10), where the viscosity is low, the rough surface and curved tear lines are prominent. Whereas at higher level of fluroelastomers (blend I, Figure 12) the flow of matrix is restricted and cracks appear on the fractured surface and brittleness increases. At the 50:50 (blend F, Figure 11) deep cracks appear accompanied by cavitation which is irregular in shape, may be responsible for lower tensile strength.

CONCLUSION

Although the state of cure is improved as the polyacrylic:fluroelastomer ratio decreases, most of the properties decrease drastically within the range of 70:30 and 30:70 blend ratio. Phase separation is very much prominent around 50:50 ratio especially under dynamic applications. Maximum 25 percentage replacement of each polymer by the other can be utilized for high temperature and oil environments.

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