

Influence of Filler–Polymer Interactions on the Cure Mismatch of Dissimilar Polymeric Blends

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ABSTRACT: Cure mismatch between the blends of two dissimilar polymers, poly[ethylene(vinyl acetate)] (EVAc-28, VAc content 28%) and polychloroprene (CR) was investigated through rheometric, mechanical, and dynamic mechanical properties. These studies indicate cure-heterogeneity due to fast curing as well as degradation of CR with dicumyl peroxide (DCP) at 170°C, which facilitates easy liberation of acidic HCl. The low temperature curing of unfilled blends at 145°C reduces the rate of curing as well as liberation of HCl, leading to lower cure heterogeneity and improved physical properties compared to those cured at 170°C. The high specific component of surface energy of carbon black (N110) leads to better filler–polymer interaction with more polar CR and causes lowering in effective occluded volume measured from storage modulus. Carbon black suppresses the cure heterogeneity of the blends and improves their physical properties considerably. CR, which shows higher minimum rheometric torque compared to EVAc-28, is more viscous and hence carbon black incorporation is relatively difficult. This also leads to higher agglomerate structure causing higher networking factor.
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Key words: EVAc-28/CR blends; cure mismatch; carbon black (N110); effective occluded volume

INTRODUCTION

Nowadays polymeric blends of dissimilar character find their application in industry in order to meet the various technological demands. The saturated polymerlike EPDM blended with an unsaturated polymer like natural rubber can greatly improve the rolling resistance without the loss of traction, as well as ozone resistance of natural rubber.¹ When two dissimilar polymers in a blend are co-cured by the action of same curing agent, but at reaction rates which are significantly different for individual polymers, the phenomenon “cure mismatch” will occur, which leads to inferior mechanical and dynamic mechanical properties.^{2–4}

Curatives generally deplete to the more chemically active polymeric phase resulting in cure mismatch or cure incompatibility of the blended polymers. This can be overcome either by arresting depletion of curative^{5,6} or by reducing the chemical reactivity of the more active polymer.^{7,8}

The improvement of the physical properties of the polymers can be achieved with active fillers like carbon blacks. The phenomenon “reinforcement” is directly related to filler–polymer interactions.^{9,10} The measurement of filler–polymer interaction is difficult as it is always associated with polymer crosslink network, filler microdispersion, and polymer occluded within filler. Ayala et al.^{11,12} have been able to measure the filler–polymer interaction eliminating other factors. They measured the interaction parameter y/r , where y is the Young’s modulus in the linear portion of stress–strain plot ($\lambda = 1–3$) and r is the ratio of storage modulus (E') at a lower (1%) and higher

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Table I Materials Used

Material	Specification	Producer
Poly[ethylene(vinyl acetate)] (Pilene-2806)	Vinyl acetate content: 28 wt %	Polyolefin Industries Limited, India
Polychloroprene (Neoprene WM ₁)	Density: 0.96 g/cm ³ M.F.I.: 6 g/10 min Specific gravity: 1.23 Mooney viscosity (ML ₁₊₄ , 100°C): 40	du Pont, USA
Carbon black (N110)	CTAB, m ² /g: 127 BET (N ₂), m ² /g: 140 DBPA, cm ³ /100 g: 93 S _f of acetonitrile at 150°C: 1.64 γ_s^d , MJ/m ² at 150°C: 270.4 I ^{SP} , MJ/m ² of acetonitrile at 150°C: 212.6	Degussa AG
Dicumyl peroxide (PERCITOL-40)	Purity: 40%	Peroxide India Limited
Triallyl cyanurate	Purity: 97% Fusion point: 110°C	Aldrich Chemicals

(25%) double strain amplitude (DSA). The measured interaction parameter emphasizes the strong filler–polymer interaction and reduces the influence of physical phenomena associated with networking.

We have reported earlier¹³ the effect of different fillers having the same surface area and different curatives with varying concentration on the filler–polymer interactions for 1 : 1 homogeneous blends of poly[ethylene(vinyl acetate)] and polychloroprene. This paper reports in detail the influence of filler–polymer interactions on the cure mismatch of EVAc-28 and CR blends containing 30 phr filler (N110) and 3 phr DCP as curative.

EXPERIMENTAL

The details of the materials used are given in Table I.

Sample Preparation

Mixing was carried out in a Brabender Plastimeter (PLE-330) as per the formulation given in Table II. Thermoplastic EVAc-28 was first melted at 100°C and 60 rpm, then premasticated neoprene was added to it. Mixing was carried out for 5 min after which the fillers were added. Mixing was allowed to continue further for another 10 min at the same temperature and rotor speed. At

last, curatives were mixed at 100°C and 40 rpm for another 5 min. The hot mix was passed through a low nip gap two-roll mill to get a sheet.

Rheometric Study

About 10 g of the mix was put on the hot rotor of a Monsanto Rheometer (R-100S) at 170°C with an arc of oscillation of 3° to determine its cure characteristics.

Molding

A part of the mix was molded in a Moore Press at 170°C under 10 MPa for 15 min. After the stipulated time, the mold was allowed to cool with circulation of cold water.

Restriction of Swelling

Samples were extracted to remove any soluble material, then dried, weighed, and immersed in toluene, a good solvent of both EVAc-28 and CR. All the samples were swollen to equilibrium. The weights of swollen samples were periodically checked until the weight maintained a constant value. Finally the samples were deswollen and weighed. The extent of swelling is given by the volume fraction of rubber in the swollen gel and expressed as¹⁴

Table II Blend Composition (wt %)

Material	Blend Code ^a									
	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₉	B ₁₀
EVAc-28	100	70	50	30	—	100	70	50	30	—
CR	—	30	50	70	100	—	30	50	70	100
Carbon black	—	—	—	—	—	30	30	30	30	30

^a All blends contain 3 phr of dicumyl peroxide and 1 phr of triallyl cyanurate.

$$V_r = \frac{(B - FA)\rho_r^{-1}}{(B - FA)\rho_r^{-1} + A_o\rho_s^{-1}} \quad (1)$$

where V_r is the volume fraction of rubber; B , the swollen weight; F , the fraction insoluble; A , sample weight; A_o , the weight of absorbed solvent corrected for swelling increment, ρ_r and ρ_s , the density of rubber and solvent.

Mechanical Properties

Dumbbell-shaped test pieces were punched out from the molded sheets. The thickness of the sample was measured with a bench thickness gauge. The tensile tests were carried out with a Zwick Universal Testing Machine (UTM-1445) at $25 \pm 2^\circ\text{C}$ and at a crosshead speed of 500 mm/min according to the method described in ASTM-D-412-80. Results were plotted through a built-in computer.

Dynamic Mechanical Analysis (DMA)

A dynamic viscoelastometer Rheovibron (DDV-III-EP) of Orientec Corporation, Japan was used for measurement of dynamic mechanical properties at a frequency of 11 Hz. The samples of $70 \times 10 \times 5$ mm were punched out from the sheet. Dynamic mechanical properties were measured in the range of 0.07 to 5% DSA at a temperature of $25 \pm 1^\circ\text{C}$. DSA refers to the ratio of peak-to-peak deformation of the sample to the length of the sample ($2 \Delta L/L$).

RESULTS AND DISCUSSION

Rheometric Studies

Figure 1 shows the plots of variation in the maximum change in rheometric torque ($D_{\max} - D_{\min}$) with % CR content in the filled blends cured at

170°C and unfilled blends cured at 145 and 170°C . D_{\max} and D_{\min} refers to the maximum and minimum torque obtained from the rheometric results. As the difference between maximum and minimum torque is a measure of the extent of cure of the compound, thus Figure 1 indicates the variation of extent of cure with blend composition. For both filled and unfilled compounds cured at 170°C , the extent of cure is found to be minimum for 50/50 EVAc-28/CR blend. Because CR gets cured very fast with DCP compared to EVAc-28, there is cure mismatch leading to heterogeneous curing of the blends. As lowering of the extent or rate of cure reduces cure heterogeneity,^{7,8} 50 : 50 blend shows better cure homogeneity.

Restriction of Swelling

For all blends, the volume fraction of rubber in the swollen gel (V_r) has been calculated using eq. (1). Figure 2 shows the plot of $(1 - V_r)$ values of all the samples against blend composition (wt %

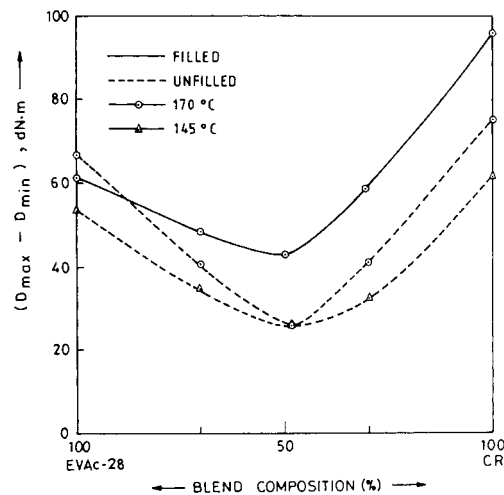


Figure 1 Variation of $(D_{\max} - D_{\min})$ (dN m) with blend composition (%).

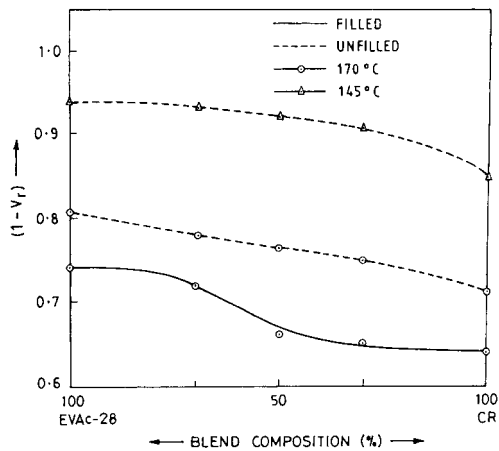


Figure 2 Variation of $(1 - V_r)$ with blend composition (%).

of CR). For the filled blends cured at 170°C, and unfilled blends cured at 145 and 170°C, the $(1 - V_r)$ values are found to decrease with increasing CR content in the blends. But the rate of decrease is much faster up to 50% CR, beyond which the decrease is almost linear for the filled blend. In case of the unfilled blend cured at 170°C the $(1 - V_r)$ values are almost additive, whereas for the same cured at 145°C, $(1 - V_r)$ values are linear up to 50% CR, beyond which they decrease at a higher rate. The highest and lowest values of $(1 - V_r)$ of EVAc-28 and CR indicate their lowest and highest extent of crosslinking.

Mechanical Properties

Variations of mechanical properties with blend composition for the unfilled blends cured at 145 and 170°C and filled blends cured at 170°C are plotted in Figures 3–5. The change in tensile strength (TS), elongation at break (EB) and 100% modulus (M_{100}) with blend compositions for unfilled compounds cured at 170°C are shown in Figure 3. TS decreases with increasing content of CR in the blends and shows an anti-S-shaped relationship with blend composition. This indicates blend heterogeneity¹⁵ which originates from cure-mismatch between EVAc-28 and CR. CR during its curing at 170°C liberates HCl, which in combination with DCP degrades CR and causes microheterogeneity in curing. The microcracks developed due to heterogeneous curing or degradation can propagate at higher elongations and cause lowering in failure properties like TS, etc., with increasing content of CR in the blends. The cure heterogeneity is also evident from the low-

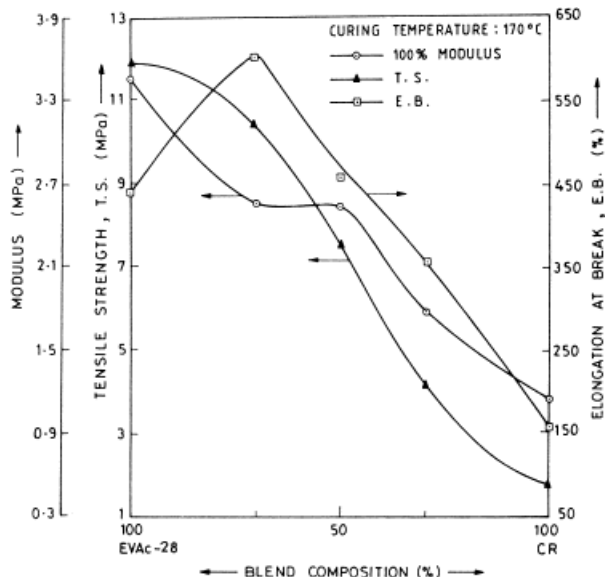


Figure 3 Variation of tensile modulus (MPa), tensile strength, and elongation at break (%) with blend composition (%) for unfilled blends cured at 170°C.

ering in EB with increasing content of CR except for 70 : 30 EVAc-28/CR blend, which shows surprisingly higher EB. The higher EB for 70 : 30 blend may be due to higher physical crosslinking caused by crystalline particles and lower cure-mismatch caused by cocuring of the blended components with DCP. All the modulus values are decreasing with increasing content of CR except that for 50 : 50 blend, which shows higher modu-

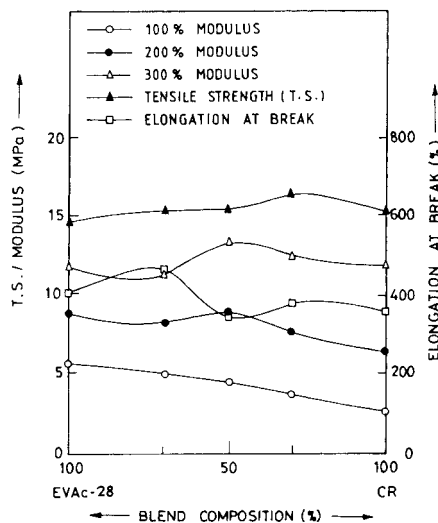


Figure 4 Variation of tensile strength, tensile modulus (MPa), and elongation at break (%) with blend composition (%) for the filled blends cured at 170°C.

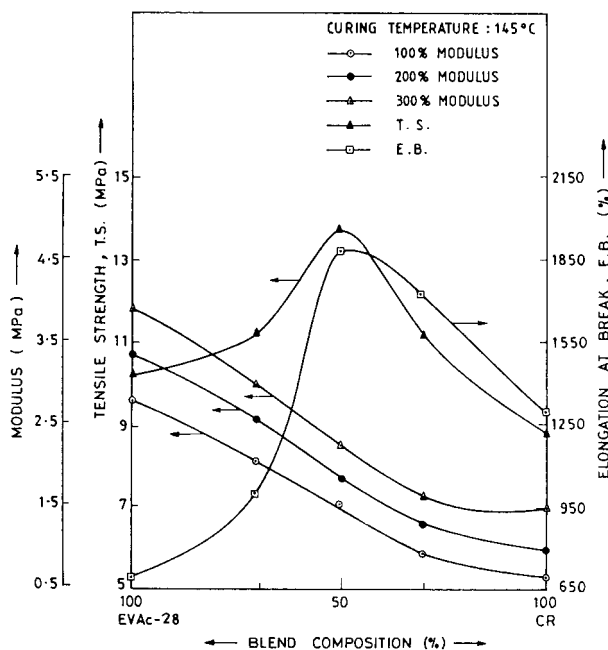


Figure 5 Variation of tensile modulus, tensile strength (MPa), and elongation at break (%) with blend composition (%) for the unfilled blends cured at 145°C.

lus compared to the other blends. EVAc-28, being crystalline, should show higher modulus and with the increase in CR content in the blend, crystallinity decreases, resulting in lowering of modulus. As the cure heterogeneity is minimum for 50 : 50 blend, both phases will be co-cured to a higher extent. The physical crosslinking caused by crystals of EVAc-28 coupled with maximum extent of co-curing of CR causes an increase in modulus for 50 : 50 blend compared to other blends.

Figure 4 shows the variation of TS, EB, and modulus at 100, 200, and 300% elongations versus blend composition for filled system cured at 170°C. TS increases almost linearly with increase in CR content up to 70% CR in the blends. The increasing trend in TS, which is opposite to that observed for unfilled compound, can be explained by the suppression of cure rate caused by the absorption of free radicals generated from DCP by the carbon black (N110) as well as by neutralizing the acid generated during curing.¹⁶ The suppression of cure rate minimizes cure heterogeneity in CR and its blends with EVAc-28. The plot of EB with blend composition shows initial increase at 50% CR followed by subsequent decrease up to 70% CR, as in the case of the unfilled one; whereas EB of CR shows higher values. Thus, EB shows an anti-S-shaped relationship with blend compo-

sition. Higher homogeneity in curing of the blended components causes lowering in EB of 50 : 50 EVAc-28/CR blend compared to that of CR and other blends. Higher EB at 70 : 30 blend can be explained in the same way as that of the unfilled system.

Modulus of the blends at 100% elongation is additive to that of EVAc-28 and CR, whereas 200 and 300% modulus generates S-shaped plots. The decreasing trend in 100% modulus with increasing content of CR is due to lowering of crystallinity, provided it is sufficiently cured. As discussed earlier, $(1 - V_r)$ values of the blends indicate that CR is most tightly cured among the blends. But sufficient curing coupled with physical crosslinking caused by the crystals increases modulus at 100 and 200% elongations of EVAc-28 and EVAc-28 rich blends compared to CR. But at 300% elongations, CR shows much higher modulus compared to EVAc-28. This is due to the tremendous crystallizing ability of CR at higher elongations. 50 : 50 blends show higher tensile modulus due to a synergistic effect of miscibility of blends.

Tensile strength, elongation at break, and modulus at 100, 200, and 300% elongations of the unfilled blends cured at 145°C are plotted against blend composition in Figure 5. Tensile strengths of the blends are much higher compared to their additive values due to the synergistic effect caused by the miscibility of the blends of EVAc-28 and CR.¹⁷ This effect is maximum at 50% CR, blending what leads to maximum TS. The tensile values of CR and their blends are much higher compared to those cured at 170°C. This may be due to better cure compatibility of EVAc-28 and CR, and also due to lesser cure heterogeneity of CR. All the modulus plots indicate lowering in modulus on increasing the CR content in the blends. This is due to lowering of crystallinity and hence reduction in physical crosslinking. Modulus values obtained from 145°C curing are lower in comparison with those obtained by curing at 170°C. This is due to a lower amount of crosslink density of all blends cured at a lower temperature of 145°C, which is also evident from the results of the swelling studies. The changing trend in EB is similar to that of TS.

Dynamic Mechanical Properties

The storage modulus values at 1 and 5% DSA for all blends cured at 170°C are reported in Table III. The storage modulus is higher for all compounds at low DSA, which decreases to a mini-

Table III Storage Modulus, f_d , and Interaction Parameter

Compound Code	$E'_{0.01}$ (MPa)	$E'_{0.05}$ (MPa)	f_d^a	r	Y/r
B ₆	51	37.7	0.53	1.35	4.2
B ₇	31	22.4	0.38	1.38	3.6
B ₈	25.5	18.3	0.37	1.39	3.2
B ₉	14	10.1	0.24	1.41	2.6
B ₁₀	11	7.0	0.03	1.57	1.6

^a f_d calculated from relative storage modulus (E'_i/E'_e) at 5% DSA; E'_e for compounds B₁, B₂, B₃, B₄, and B₅ are 17, 10.7, 7.2, 4.9, and 3.8 MPa, respectively.

imum value at very high DSA. According to Payne and Whittaker,¹⁸ the augmentation of storage modulus at low strain amplitude is due to a networking effect, which is mainly physical in nature depending on the morphology of carbon black. With increase in DSA, more and more secondary structures (floculates/agglomerates) break down and rubber occluded in the structure comes out. Thus, hydrodynamic volume of carbon black decreases, which causes lowering in storage modulus at higher DSA (>1%).¹⁹ With further increase in DSA (5%), most of the secondary structures break down and only near-constant hydrodynamic volume of primary structure gives rise to a minimum storage modulus.

The storage modulus of unfilled compounds at 5% DSA and filled compounds at 1% and 5% DSA are plotted against blend compositions in Figure 6. All three plots show a decrease in E' with increasing content of CR in the blends. The higher storage modulus of EVAc-28 is due to physical crosslinking caused by crystals. As the amount of CR is increased in the blend, crystallinity of EVAc-28 experiences a sharp drop of up to 30% CR contents; thereafter crystallinity decreases gradually. Crystallinity of EVAc-28 almost disappears on 70% CR blending.¹⁷ On the other hand, heterogeneity in curing is maximum for CR and minimum for 50 : 50 blend in comparison to the other two blends. The above trend of crystallinity and cure heterogeneity is also reflected in the plot of E' with blend composition, as E' sharply decreases on blending with 30% CR, followed by a gradual decrease of up to 70% CR, while CR itself shows the lowest storage modulus. In comparison to the unfilled system, the filled one shows a much higher rate of decay of E' on 30% CR blending, which is even higher for filled compound at 1% DSA compared to that at 5% DSA. From the plot,

it is evident that carbon black-filled 50 : 50 blend shows relatively higher storage modulus at 1 and 5% DSA compared to the other two blends. This relative comparison is done from their additive values.

Networking Factor (r) and Interaction Parameter (Y/r)

Considering machine limitation, networking factor (r) is taken as the ratio of storage modulus at 1% and 5% DSA. The interaction parameter (Y/r) is calculated from the tensile modulus at 100% elongation (Y). Carbon black (N110), whose surface characteristics are reported in Table I, indicates that both specific and dispersive components of its surface are higher. In a suitable environment, one or both of them can be operative. For CR, an unsaturated hydrocarbon rubber, the dispersive component of N110, will play a much more active role; whereas for EVAc-28, a saturated polymer having a polar pendent group (vinyl acetate), the specific component will have a greater role on the filler–filler interactions. Thus, carbon black inclusions will lead to higher networking. The values of the networking factor (r) and interaction parameter (Y/r) are reported in Table III.

Figure 7 shows that the interaction parameter (Y/r) is much higher for EVAc-28, indicating better dispersion, and decreases linearly with an increase in CR content in the blends. Y/r decreases in the region of 0–30 and 70–100% CR, but the decreasing rate is very slow and generates a hump

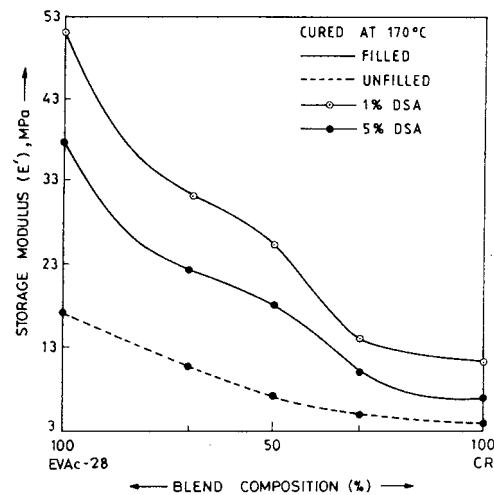


Figure 6 Variation of storage modulus, E' (MPa), with blend composition (%).

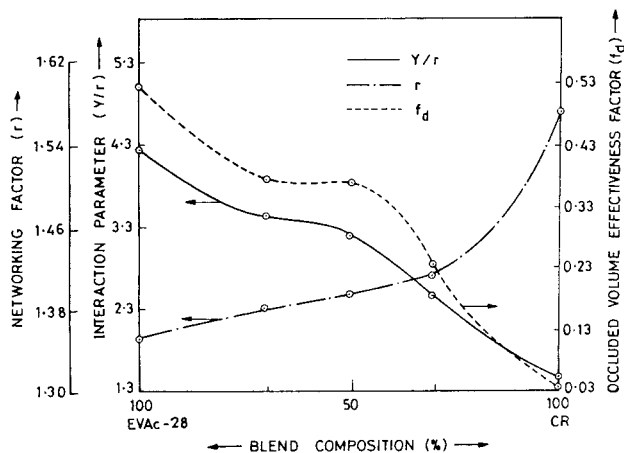


Figure 7 Variation of networking factor (r), interaction parameter, and occluded volume effectiveness factor with blend composition (%).

at around 50% CR in the blends, indicating better black-polymer interaction at this blend composition. Whereas the plot for networking factor (r) in Figure 7 indicates lower networking of EVAc-28 compared to that of CR. As CR is more viscous compared to EVAc-28, as evident from the minimum rheometric torques, carbon black, having a high dispersive component of surface energy, can easily be incorporated in EVAc-28 at 100°C, and forms lesser and smaller agglomerates. This is the reason for a lower networking factor of EVAc-28 compared to CR. With increase in CR content in the blends, the networking factor increases almost linearly up to 70% CR, beyond which it increases asymptotically.

Occluded Volume Effectiveness Factor (f_d)

Medalia²⁰ first proposed that the structure of carbon blacks as characterized by their DBP absorption value is related to polymer-occluded volume of filler, which is shielded against deformation. The effective immobilization of a portion of polymer acting as a part of the filler rather than the polymer matrix increases the effective volume of filler beyond the value calculated from the mass and density of filler. The occluded volume effectiveness factor, f_d , has been given by Medalia²⁰ as

$$f_d = \frac{(V_{eff} - \phi)}{(\phi' - \phi)} \quad (2)$$

where ϕ is the volume fraction of carbon black,

($\phi' - \phi$) is the actual occluded volume calculated from dibutyl phthalate absorption (DBPA) value as

$$(\phi' - \phi) = \phi(\text{DBPA} - 21.5)/68.26 \quad (3)$$

and V_{eff} is the effective polymer-occluded volume fraction of the filler calculated from relative modulus by Medalia²⁰ as

$$V_{eff} = (-2.5 + \{6.25 + 56.4[E_f/E_g - 1]\}^{1/2})/28.2 \quad (4)$$

The filler parameters like surface activity, structure, anisometry, etc. influence the effective filler volume (V_{eff}), which is also dependent on operating variables like strain and temperature.

The occluded volume effectiveness factor (f_d) calculated from the relative storage modulus (E'_f/E'_g) of the blends cured at 170°C is reported in Table III and plotted against %CR content in the EVAc-28/CR blends in Figure 7. The value of f_d decreases with increase in CR content, but the rate of decrease is much higher in the regions of 0–30% and 70–100% CR. The values of f_d are calculated at higher DSA (5%), taking into account the aggregate structure, because at higher DSA, most of the agglomerates are broken down into aggregates. The specific component of surface energy of carbon black plays a dominant role leading to chemical interaction between black and polymer through the surface active functional groups of black, and the polar groups present in the polymer.²¹ As CR is more polar compared to EVAc-28, it is more interactive to carbon black and thus generates more compact filler-polymer aggregates. These are the reasons for lower and higher f_d values of CR and EVAc-28, respectively. The crystals already present in EVAc-28 can act as solid inclusions. As CR content is increased in the blend, the crystallinity goes down severely at 30% CR blending and it is minimum for 100% CR.¹⁷ With increased CR content in blends, the filler-polymer interaction increases, leading to more compact filler aggregates within which polymers are occluded. These are the reasons for a higher rate of decrease in f_d in the region of 0–30% and 70–100%.

CONCLUSION

The dissimilar character of EVAc-28 and CR shows cure mismatch to a minimum extent for 50/

50 EVAc-28/CR blend during curing with dicumyl peroxide compared to the other blends. The cure heterogeneity in CR and its blends with EVAc-28 is greatly suppressed when they are either filled with carbon black (N110) or cured at a lower temperature (145°C). This is evident from the improvement in tensile strength properties of the carbon black filled and unfilled compounds cured at 170 and 145°C, respectively. The cure compatibility of the filled compound is due to high filler-polymer interactions and the higher free radical scavenging capability of carbon black. The lower amount of free radical generation at 145°C reduces the extent of cure, which is evident from the rheometric as well as swelling studies. The lower extent of cure causes lowering in cure mismatch, thereby improving mechanical properties. The relatively higher viscosity of CR, which is evident from higher minimum rheometric torque, leads to a higher networking factor. The high specific component of surface energy of carbon black leads to better filler-polymer interaction, giving rise to lower effective occluded volume measured from the storage modulus. The higher storage modulus of EVAc-28 is due to enhancement of total crosslink density caused by physical crosslinking of crystals in combination with the peroxide curing.

REFERENCES

1. A. Y. Coran, *Rubber Chem. Technol.*, **61**, 281 (1988).
2. M. M. Sain, I. Hudec, J. Beniska, and P. Rosner, *Rubber Chem. Technol.*, **61**, 747 (1988).
3. V. A. Shershnev, *Rubber Chem. Technol.*, **55**, 537 (1982).
4. E. H. Andrews, *J. Appl. Polym. Sci.*, **10**, 47 (1966).
5. P. J. Corish and B. D. W. Powell, *Rubber Chem. Technol.*, **47**, 481 (1974).
6. T. Inoue, E. Shomura, T. Ongizawa, and K. Miyasaka, *Rubber Chem. Technol.*, **58**, 837 (1985).
7. M. E. Woods and J. A. Davidson, *Rubber Chem. Technol.*, **49**, 112 (1976).
8. R. F. Bauer and E. A. Dudley, *Rubber Chem. Technol.*, **50**, 35 (1977).
9. G. Kraus, *Rubber Chem. Technol.*, **51**, 297 (1978).
10. S. Wolff, M. J. Wang, and E. H. Tan, *Kautsch. Gummi Kunstst.*, **47**, 102 (1994).
11. J. A. Ayala, W. M. Hess, F. D. Kistler, and G. A. Joyce, *Rubber Chem. Technol.*, **64**, 19 (1991).
12. J. A. Ayala, W. M. Hess, A. O. Dotson, and G. A. Joyce, *Rubber Chem. Technol.*, **63**, 747 (1990).
13. P. P. Kundu and D. K. Tripathy, *Polymer Networks and Blends* (to appear).
14. A. K. Bhowmick and D. Mangaraj, in *Rubber Products Manufacturing Technology*, A. K. Bhowmick, M. M. Hall, and H. A. Benarey, Eds., Marcel Dekker, Inc., New York, 1994, p. 317.
15. J. Furukawa, *J. Appl. Polym. Sci.*, **51**, 187 (1994).
16. L. G. Hernandez, A. Rodriguez Diaz, A. Marcos Fernandez, and C. Chamorro Anton, *Kautsch. Gummi Kunstst.*, **47**, 715 (1994).
17. P. P. Kundu, B. K. Samanta Roy, and D. K. Tripathy, *Polymer Networks and Blends*, **5**, 11 (1995).
18. A. R. Payne and R. E. Whittaker, *Rubber Chem. Technol.*, **44**, 440 (1971).
19. A. I. Medalia, *Rubber Chem. Technol.*, **51**, 436 (1978).
20. A. I. Medalia, *Rubber Chem. Technol.*, **45**, 1171 (1972).
21. S. Wolff and M. J. Wang, *Kautsch. Gummi Kunstst.*, **47**, 17 (1994).