Acrylic Rubber–Fluorocarbon Rubber Miscible Blends: Effect of Curatives and Fillers on Cure, Mechanical, Aging, and Swelling Properties

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ABSTRACT: The cure characteristics and mechanical properties of gum and filled acrylic rubber (ACM), fluorocarbon rubber (FKM), and their blends of varying compositions were studied both under unaged and aged conditions. The rheometric study showed that optimum cure properties were obtained using a mixed curing system of blocked diamine, hexamethylenediamine carbamate (Diak #1), and ammonium benzoate. From varying the curing agents, the optimum levels of Diak #1 and ammonium benzoate were found to be 1.5 and 2.5 phr, respectively. The addition of different fillers and their loading influenced the cure properties, with increased torque and reduced scorch safety. The gum and filled 50:50 (w/w) ACM–FKM showed overall performance in strength properties. Postcuring improved the strength of all the systems, especially the systems with a higher proportion of FKM. None of the properties changed significantly during aging of the blends. FKM and the blends containing a higher proportion of FKM were affected least by aging. Swelling of the blends was reduced by the addition of fillers. Dynamic mechanical thermal analysis showed a single tan δ peak corresponding to a single phase transition for both cured and filled blends. The storage modulus of the blend increased from the gum blend to the filled blend, indicating the presence of polymer–filler interaction. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1442–1452, 2003

Key words: aging; blends; fillers; mechanical properties; reinforcement; rubber

INTRODUCTION

The demand for high-performance elastomers in situations of high temperature and oil resistance is ever growing. The end users of such polymers in the automobile, aerospace, offshore, and energy-related industries impose stringent product performance standards under elevated temperatures and in hostile chemical environments. Fluorocarbon rubbers of various types are capable of satisfying such demands because of their inherent heat resistance through C—F bonding.[1] On the other hand, acrylic elastomer is preferred for making elastomers that are comparatively lower in cost and superior in oil resistance at moderately higher working temperatures.[2] Recently, we demonstrated that certain acrylic elastomers and fluorocarbon rubbers are thermodynamically miscible,[3] and improved properties of the blends of the gum elastomers were observed as a result of this specific interaction. However, these two polymers use different types of curative package and filler in actual applications.

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Finding common curative and filler system(s) is needed in order to obtain excellent rubber vulcanizate.

The rheological and mechanical properties of gum and filled acrylic rubber (ACM)–fluorocarbon rubber (FKM) blends[4] and a thermoplastic elastomer derived from the blending of ACM–FKM and multifunctional acrylates have been reported in our previous articles.[5] Ashida et al.[6] reported on the morphology and mechanical properties of epoxy-modified acrylic particles for adhesives. Wootthikanokkhan et al.[7] carried out a study on the effect of the curing agent on interfacial adhesion in acrylic rubber–PMMA laminate. Blends of ACM and FKM[8,9] have been reported but without details on curative or filler; however, several articles have taken up the cure behavior of individual rubbers. Vial[10] reviewed acrylic rubbers containing different types of cure site monomers and their cure behavior with different crosslinking agents. Giannetti et al.[11] reported the process of ammonium catalyzed crosslinking, and Jims[12] and Holly et al.[13] studied the effect and properties of curatives on acrylic rubber. A report on diamine-cured acrylic rubber was contributed by Seeger.[14] Likewise, the mechanism of the postcuring of fluoroelastomer was reported by Smith and Perkins.[15] The complete details on the spectrum of fluoroelastomers was reviewed by Ameduri et al.[16] The effects of multifunctional acrylates on radiation curing of fluoroelastomers were discussed by Banik
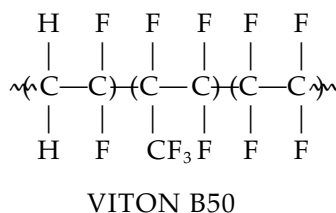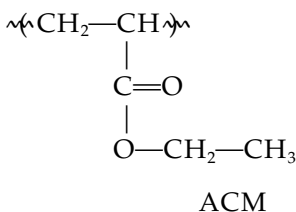
and Bhowmick.[17] However, there has been nothing in the literature on the cure characteristics and mechanical properties of gum and filled blends of ACM and FKM.

This article is centered on the study of the cure characteristics and strength properties of gum and filled ACM, FKM, and their blends of varying compositions. It also will focus on the aging behavior and swelling of these blends, as they are expected to perform at high temperatures and in a hydrocarbon oil environment.

EXPERIMENTAL

Materials

Acrylic rubber (ACM), Nipol AR 51, derived from the polymerization of ethyl acrylate and containing proprietary epoxy cure site monomer [density: 1100 kg/m^3 at 25°C; Mooney viscosity, ML (1 + 4) at 100°C: 55] was obtained from Nippon Zeon Co. Ltd. (Tokyo, Japan). Fluorocarbon rubber (FKM), Viton B 50, a terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene [density: 1850 kg/m^3; Mooney viscosity, ML (1 + 10) at 121°C: 56; 68% F, 1.4% H] and Diak #1 (hexamethylene diamine carbamate) were supplied by DuPont Dow Elastomers, Freeport, TX. Other chemicals listed in the formulation were obtained as laboratory grade from indigenous sources. The molecular structures of ACM and FKM follow:

$$\text{\small\char"223}\text{CH}_2\text{—CH}\text{\small\char"223}$$
$$|$$
$$\text{C}=\text{O}$$
$$|$$
$$\text{O—CH}_2\text{—CH}_3$$

ACM

$$\begin{array}{cccccc} H & F & F & F & F & F \\ | & | & | & | & | & | \\ \text{C—C} & \text{C—C} & \text{C—C} \\ | & | & | & | & | & | \\ H & F & CF_3 & F & F & F \end{array}$$

VITON B50

Preparation of the samples

ACM was mixed with FKM in blend ratios of 100:0, 70:30, 50:50, 30:70, and 0:100 (w/w) with and without fillers in a Brabender Plasticorder PLE 330 at 50°C at a rotor speed of 60 rpm. FKM was first introduced in the Brabender to bring the viscosity down. After 1 min ACM was added and mixed with FKM for the next 3 min. Within 2 and 4 min for gum and filled compounds, respectively, the compounding ingredients, listed in Tables I and II, were added in this sequence:

$$Ca(OH)_2 \rightarrow MgO \rightarrow \text{filler} \rightarrow$$

$$\text{ammonium benzoate} \rightarrow DIAK\#1$$

After mixing, the mass was sheeted out at 30°C using a laboratory two-roll mill (6 × 13 in.; Schwabenthan, Berlin, Germany). The samples were then molded in between pieces of aluminum foil in a two-plate hydraulic press (Moore Press, UK) at 170°C at a pressure of 5 MPa. The molding time was adjusted depending on the optimum cure time of the individual mix, as determined from a rheometer. The test specimens were cut from molded slabs approximately 2.0 mm thick using ASTM standard cutting dies. The compression set specimens were molded in order to obtain samples that were circular discs 12.5 mm thick and 50 mm in diameter. The postcuring of test specimens of all mixes was carried out in an oven at 200°C for 6 h.

Measurements

Cure characteristics

Mooney viscosity and Mooney scorch time were measured by a Mooney viscometer (Negretti, Mooney Viscometer Mark III) using ASTM D 1646-97 with a large rotor at 121°C. The cure behaviors were obtained from an oscillating disc rheometer (ODR; Monsanto ODR-100S) at 170°C for 60 min with an oscillating angle of 3°.

Mechanical tests

Tensile and tear specimens were punched out from the molded sheet using ASTM Die-C and ASTM angle tear specimen dies, respectively. The mechanical tests were carried out as per ASTM D412-99 in a universal testing machine (UTM; Zwick-1445) at a crosshead speed of 500 mm/min at 25°C. The average value of three tests for each sample is reported here.

Aging studies

Aging of the samples was performed in an air-circulating oven operated at 175°C for 72 h. Tensile test (ASTM D 412-99) was carried out on a tensile dumbbell test specimen before and after aging to estimate aging resistance.

Compression set

The compression set test was done under a constant strain of 25% according to ASTM D 395-98 method-B at 175°C for 72 h.

TABLE I
Formulation and Comparison of Cure Characteristics and Physical Properties of Gum and Filled ACM, FKM, and Their Blends Before and After Postcuring and Aging

Ingredients (by weight)	ACM	B_1	B_2	B_3	FKM	AF_{30}	$BF1_{30}$	$BF2_{30}$	$BF3_{30}$	FF_{30}
ACM	100	70	50	30	—	100	70	50	30	—
FKM	—	30	50	70	100	—	30	50	70	100
FEF (N550)	—	—	—	—	—	30	30	30	30	30
Ca(OH)$_2$	—	1.8	3	4.2	6	—	1.8	3	4.2	6
MgO	—	0.9	1.5	2.1	3	—	0.9	1.5	2.1	3
DIAK #1	—	0.45	0.75	1.05	1.5	—	0.45	0.75	1.05	1.5
Ammonium benzoate	2.5	1.75	1.25	0.75	—	2.5	1.75	1.25	0.75	—
Cure characteristics										
Mooney viscosity mL (1 + 10) at 121°C	38	41	45	50	56	53	59	66	72	80
Mooney scorch, T_5 (min)	24	22	21	18	17	22	20	19	17	15
ODR, T_{S2} (min)	2	2	2	1.5	1	2	2	1.5	1.5	1
T_{90} (min)	36	27	24	24	8	31	24	22	16	7
M_L (dN.m)	0.05	0.13	0.17	0.23	0.27	0.13	0.27	0.36	0.77	0.58
M_H (dN.m)	0.32	0.38	0.48	0.51	0.71	0.58	0.82	1.07	1.23	1.54
Physical properties (values within parentheses indicate % change of properties after aging at 175°C for 72 h)										
100% Modulus (MPa)	0.3 (21.2)	0.8 (17.3)	1.2 (21.7)	2.1 (12.7)	4.2 (9.5)	1.4 (17.6)	3.1 (18.2)	6.2 (25.4)	7.4 (13.7)	5.8 (6.9)
300% Modulus (MPa)	0.6 (22.8)	2.6 —	3.9 (25.6)	—	—	7.0 (26.2)	—	—	—	—
Tensile strength (MPa)	1.3 (−7.7)	3.4 (−5.9)	5.7 (5.3)	3.8 (−2.6)	6.9 (7.2)	13.2 (−15.2)	10.6 (−3.8)	13.6 (1.5)	11.5 (−1.7)	13.4 (2.2)
Elongation at break (%)	384.0 (−19.0)	361.0 (−29.9)	374.0 (−7.3)	273.0 (−29.7)	225.0 (−4.4)	451.0 (−21.5)	253.0 (−18.2)	242.0 (−7.4)	170.0 (−17.6)	245.0 (−5.7)
Energy to break (kJ/m^2)	1051 (−14.7)	2453 (−4.8)	4450 (−0.5)	1418 (−2.8)	3067 (−1.6)	10070 (−20.4)	5264 (−9.4)	7471 (−0.7)	3650 (−4.5)	7801 (−0.2)
Tear strength (kN/m)	3.5 (−6.1)	10.1 (−3.8)	14.6 (−1.2)	12.2 (−3.5)	11.4 (−1.8)	26.4 (−8.6)	25 (−5.3)	31.4 (−1.5)	23 (−3.6)	28 (−2)
Hardness (Shore A)	32 (6.3)	34 (5.9)	37 (8.1)	42 (4.8)	48 (6.3)	37 (10.8)	52 (5.8)	58 (6.9)	64 (4.7)	73 (2.7)
Hysteresis, 10^{-6} (kJ/m^2) W_1	0.44	1.2	2.18	5.66	9.47	3.16	5.12	9.04	12.4	15.4
W_2	0.22	0.44	0.87	1.53	3.27	0.98	1.74	2.51	3.81	5.55
Compression set at 175°C for 72 h (%)	27.5	44.3	59	64	72	33	56	65.3	70	74
Physical properties after postcuring at 200°C for 6 h										
100% Modulus (MPa)	—	0.8	1.46	2.14	4.3	1.6	4.53	7.5	8.1	6
300% Modulus (MPa)	—	2.4	4.43	—	—	8.85	—	—	—	—
Tensile strength (MPa)	—	3.6	5.7	5.3	7.2	13.2	12.1	13.7	12.6	13.8
Elongation at break (%)	—	406	343	254	217	394	225	250	145	240
Energy to break (kJ/m^2)	—	2984	3841	2938	2846	9129	4769	7541	3547	8009
Tear strength (kN/m)	—	11	15.1	13.1	11.8	27	25.5	31.8	23.8	29.5
Hardness (Shore A)	—	35	39	45	51	41	65	63	65	76

Swelling

Circular test pieces with a radius of ≈ 20 mm were die-cut from a molded sheet that was 1.5–2.0 mm thick. The accurately weighed samples were immersed in solvents of different solubility parameters at 30°C up to equilibrium swelling, and the swollen samples were weighed accurately and quickly in a glass-stoppered bottle after blotting with a filter pa-per. Volume swelling in percentage was calculated using the following equation.

$$q - 1 = \left(\frac{W_2}{W_1} - 1 \right) \rho_c / \rho_s \qquad (1)$$

where q is the ratio of swollen volume to original volume; $(q - 1)$ is the percentage of volume swell/100;

TABLE II
Comparison of Cure Characteristics and Physical Properties of Filled 50:50 (w/w) ACM–FKM Blend Before and after Postcuring and Aging

Ingredients (by weight)	BI_{30}	$BF2_{10}$	$BF2_{20}$	$BF2_{40}$	$BF2_{50}$	BG_{30}	BS_{30}
ACM	50	50	50	50	50	50	50
FKM	50	50	50	50	50	50	50
ISAF (N220)	30	—	—	—	—	—	—
FEF (N550)	—	10	20	40	50	—	—
SRF (N770)	—	—	—	—	—	30	—
SILICA	—	—	—	—	—	—	30
Cure characteristics							
Mooney viscosity ML (1 + 10) at 121°C	69	58	62	69	75	64	62
Mooney scorch T_5 (min)	18	22	20	17	16	20	20
ODR T_{S2} (min)	1	1.5	1.5	1.5	1	2	2
T_{90} (min)	22	27	25	22	20	28	35
M_L (dn m)	0.22	0.17	0.29	0.50	0.68	0.28	0.32
M_H (dn m)	0.67	0.78	0.92	1.23	1.30	0.94	1.00
Physical properties (values within parentheses indicate % change of properties after aging at 175°C for 72 h)							
100% Modulus (MPa)	6.7 (−1.5)	2.4 (8.3)	3.2 (9.4)	8.2 (1.2)	13.4 (2.0)	6.3 (6.3)	8.1 (8.6)
300% Modulus (MPa)	—	7.94 (1.3)	10.85	—	—	—	—
Tensile strength (MPa)	15.2 (0.0)	9.5 (9.5)	12.7 (−7.1)	14.2 (−3.5)	15.5 (−3.2)	13.5 (1.5)	11.2 (14.3)
Elongation at break (%)	245 (−5.3)	354 (−7.9)	341 (−18.8)	221 (−11.8)	145 (−13.8)	273 (−18.3)	170 (−30.6)
Energy to break (kJ/m²)	8513 (−4.7)	4820 (−13.6)	10286 (−35.8)	9540 (−32.8)	5739 (−18.9)	9821 (−28.0)	4820 (−46.2)
Tear strength (kN/m)	35.2 (−5.2)	20.2 (−7.7)	26.8 (−14.5)	33.2 (−23.8)	39 (−14.0)	31.8 (−18.3)	27.6 (−24.9)
Hardness (Shore A)	60 (4.3)	48 (3.8)	51 (5.5)	63 (4.7)	68 (5.1)	55 (6.3)	60 (4.7)
Hysteresis, 10^{-6} (kJ/m²) W_1	11.21	7.59	18.48	37.95	73.26	8.821	7.079
W_2	3.38	3.96	5.61	11.55	20.46	2.40	1.96
Compression set at 175°C for 72 h (%)	64.1	60.3	62	66	69	61	79
Physical properties after postcuring at 200°C for 6 h							
100% Modulus (MPa)	6.68	3.27	4.24	8.1	12.64	5.81	7.38
300% Modulus (MPa)	—	9.85	11.34	—	—	—	—
Tensile strength (MPa)	15.1	11.6	11.9	13.8	14.9	13.8	12.4
Elongation at break (%)	244	340	323	220	127	270	155
Energy to break (kJ/m²)	8513	4921	9202	6334	4965	8968	4692
Tear strength (kN/m)	34.1	18.7	25.2	31.1	37.5	30.2	24.3
Hardness (Shore A)	63	51	55	65	70	58	66

All blends contain (in phr): $Ca(OH)_2$—3.0; MgO—1.5; Dial #1—0.75; and ammonium benzoate—1.25.

W_1 and W_2 are the weights of the specimen before and after swelling, respectively; and ρ_c and ρ_s are the densities of the specimen and the test solvent, respectively.

An oil swelling study was also carried out in ASTM Oil #3 at 175°C for 72 h according to the ASTM D471-93 procedure. The density of the polymers and the solvents was taken from the standard book for calculation of volume swell.

Diffusion coefficients of selected solvents at room temperature were calculated from the swelling measurements as a function of time, using the following simplified equation.[18,19]

$$\frac{M_t}{M_\infty} = \frac{4}{(\pi)^{1/2}} (Dt/l^2)^{1/2} \qquad (2)$$

where M_t is the weight fraction of the solvent absorbed at time t; M_∞ is the weight fraction of the solvent at equilibrium; l is the initial thickness of the sample; and D is the diffusion coefficient. D can be obtained from the slope of the plot of M_t/M_∞ versus $t^{1/2}/l$.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal properties were evaluated on a DMTA IV (Rheometric Scientific), under tension mode. The experiments were carried out at a frequency of 1 Hz. Measurements were taken from −50°C to 150°C at a heating rate of 2°C/min. The storage modulus and loss tangent (tan δ) were measured for all samples under identical conditions. The data were analyzed on an ACER computer attached to the machine.

RESULTS AND DISCUSSION

Choice of cure system

According to a survey of the literature, fluorocarbon elastomers (FKM) containing vinylidene fluoride as a
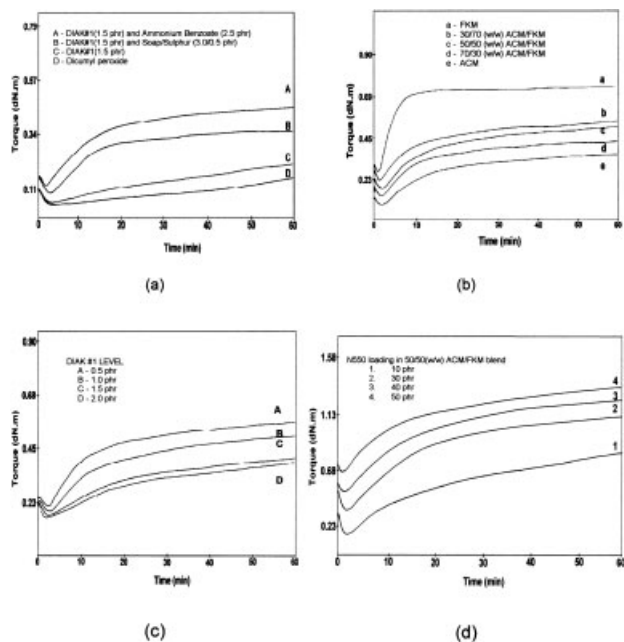
Figure 1 Rheograph of ACM, FKM, and their blends: (a) comparison of cure characteristics of 50:50 (w/w) ACM–FKM blend using different cure systems; (b) effect of blend ratios on cure characteristics of ACM–FKM blends with a mixed cure system containing Diak #1 (1.5 phr) and ammonium benzoate (2.5 phr); (c) variation in level of Diak #1 with a constant level of ammonium benzoate with 50:50 (w/w) ACM–FKM; (d) effect of carbon black on cure characteristics of 50:50 (w/w) ACM–FKM blend cured with a mixed cure system containing 1.5 phr Diak #1 and 2.5 phr ammonium benzoate.

cure site group were crosslinked mainly by blocked diamines and dihydroxy alcohol with an accelerator containing phosphonium ions.[1] On the other hand, acrylic rubber (ACM) was cured depending on the nature of the reactive cure sites.[10–12] An ACM-containing chlorine reactive group was cured mostly by a soap–sulfur system, and a reactive epoxy group was crosslinked by many agents, including diamines, ammonium salt of aromatic acid, and dicarboxylic acids.

In the present study, because both ACM and FKM are involved, several curing agents were tried with a representative 50:50 (w/w) ACM–FKM blend, and the results of such systems are represented in the rheograph curves in Figure 1(a). A combination of a soap–sulfur system with curative number 50 (bisphenol AF) did not raise the torque to an appreciable level and was not included in the figure. Peroxide curing increased the torque only after a long period of time and was not adequate for complete crosslinking of the rubber. A mixed cure system consisting of Diak #1 (hexamethylenediamine carbamate) and a soap–sulfur system showed a better cure graph than the peroxide. The trial of the diamine cure system (Diak #1) alone showed a good increase in torque up to a maximum

torque of 0.36 dN/m. However, the molded sheet showed shrink marks and appeared leathery. This curing agent may show preferential curing of the blend by crosslinking the FKM through migration into the fluorocarbon rubber rather than the acrylic rubber. Mastomatteo et al.[20] also have reported on this kind of migration of crosslinking ingredient into one of the phases of ethylene–propylene–diene rubber (EPDM)/styrene–butadiene rubber (SBR) blend because of the difference in polarity. We observed a similar migration of curatives for many other blends.[21,22] Hence, using Diak #1 alone as a curative for a blend containing ACM–FKM is not sufficient. Mixed curatives containing Diak #1 and ammonium benzoate at 1.5 and 2.5 phr levels were tried. The cure curve of this mixed cure system shows [Fig. 1(a)] the highest torque in all the selected cure systems, and the molded sheet does not show any defects such as shrink mark. Therefore, the balance of the current study on mechanical and dynamic mechanical thermal analysis was carried out on samples cured by a Diak #1–ammonium benzoate mixed curing agent. The ODR curves of the blends of varying compositions are shown in Figure 1(b). Among all the cure curves, ACM occupied the lower position with minimum M_L and M_H and had a higher optimum cure time (Table I). M_L and M_H values of the blends were gradually increased with an increasing proportion of FKM. Finally, the observed maximum torque for pure FKM also showed the lowest optimum cure time. It also can be seen from Figure 1 that the difference in M_H values between pure FKM and the blends with varying compositions was very large, indicating the effect of ACM on reducing the compound viscosity. The results for the blends lay between the values of the control polymers.

To fix the level of amine curative, the amount of Diak #1 was varied from 0.5 to 2.5 phr in relation to the FKM rubber at a constant level of ammonium benzoate (the variation in ammonium benzoate level in relation to ACM was optimized and found to be 2.5 phr). Figure 1(c) shows the rheograph of the 50:50 (w/w) ACM–FKM blend containing different levels of Diak #1. It can be seen that the increase in Diak #1 level increased the M_L (minimum torque) and M_H (maximum torque) and decreased T_{s2} (scorch time) and optimum cure time. At a 0.5 phr level the blend underwent partial curing, as shown by the leathery nature of molded sheet. For levels above 2.0 phr the compound became too "scorchy" and could not be processed. The mechanical properties of the gum blends of 50:50 (w/w) ACM–FKM cured with different levels of Diak #1 (not shown in the table) also suggest that maximum properties were reached at 1.5 phr. Therefore, all succeeding experiments were carried out at a 1.5 phr level of Diak #1 and a 2.5 phr level of ammonium benzoate. This mixed curative system
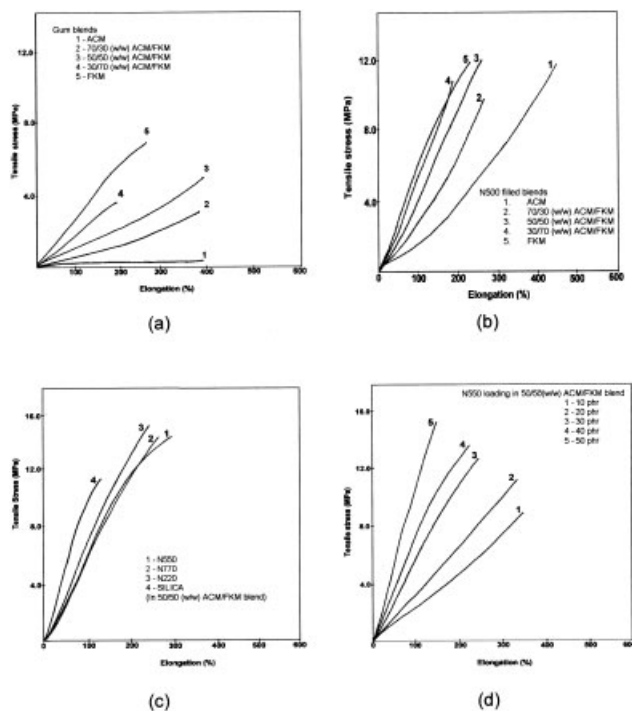
Figure 2 Stress–strain curves of ACM, FKM, and their blends with different compositions: (a) variation of blend ratio (gum blends); (b) variation of blend ratio (30 phr N550 filled blends); (c) 50:50 (w/w) ACM–FKM blends containing different types of fillers; (d) effect of carbon black (N550) loading on 50:50 (w/w) ACM–FKM blend.

helped in getting the optimum properties of the blends.

The effect of different levels of carbon black (N550) in 50:50 (w/w) ACM–FKM on cure characteristics is represented in Figure 1(d). An increase in filler level increased the M_L and M_H values from 0.17 and 0.78 dN/m, respectively, for 10-phr filled blends to 0.68 and 1.30 dN/m, respectively, for 50-phr filled blends, respectively (Table II). This implies that increasing the level of carbon black will increase the minimum viscosity of the compound through filler–polymer interaction. The presence of a larger amount of carbon black reduced the t_{90}, indicating an accelerating effect of the filler. Among different carbon blacks, N220 imparted a higher M_H and N770 a lower torque, signaling differences in the reinforcing characteristics of different carbon blacks.

Stress–strain characteristics

Response to stress–strain behavior by a polymer predicts most of its mechanical performance. Such behaviors are dependent on many factors such as temperature, strain rate and mode of application. The stress–strain curves of gum and filled ACM, FKM, and their blends are represented in Figure 2(a–d). All the curves

show the true elastic behavior of the rubbers. Gum ACM showed a very low stress level and modulus even at relatively higher deformation [Fig. 2(a)]. The low level of stress can be attributed to the low energy requirement for stretching crosslinked polymer chains formed through pendant functional group because of lower crosslink density (reported later). On the other hand, FKM shows a higher level of stress on deformation, which was nonsigmoidal. The values of the blends with varying compositions fell between those ACM and FKM. The 30:70 (w/w) ACM–FKM blend showed a lower level of strain at break compared to that of the individual rubbers. This may be a result of FKM at higher proportions taking up the curatives and starting the crosslinking faster than ACM, resulting in two phases: one highly crosslinked and the other possibly acting as flaw for the other.

The effect of filler on stress–strain behavior of filled ACM–FKM blends with varying compositions is depicted in Figure 2(b). On the addition of carbon black (N550), the acrylic rubber showed tremendous improvement in its deformation behavior, with a low stress requirement for the initial strain, followed by higher level of stress at higher deformation with a corresponding increase in modulus. This indicates that carbon black has a reinforcing effect on elastic behavior of acrylic rubber by forming a rubber–filler network. Although FKM showed a similar trend, the extent of increase was not as high as that of ACM, showing a lower reinforcing effect by the same carbon black with fluorocarbon rubber. The stress–stain curves of the blends with varying compositions fall between those of ACM and FKM, approximately following the additive rule of mixing.

A comparison of stress-deformation curves of a 50:50 blends to which various types of filler had been added indicates that a filler with large particle sizes required a higher stress level for a given strain [Fig. 2(c)]. The following order of stress at break was observed from the stress–strain curves

$$N220 > N550 > N770 > Silica$$

The stress–strain curves of 50:50 (w/w) ACM–FKM filled with different levels of N550 is represented in Figure 2(d). By increasing the level of carbon black, the strain level was reduced at a given stress because of limited extensibility. The higher the filler loadings, the higher the filler–polymer and filler–filler networks will be and the lower the deformation capacity. The reduction in the strain level was a result of interparticle aggregation of the filler, which resisted the chain extensibility of the polymer chains. Highly filled blends require more stress to attain the same level of deformation of the gum system.
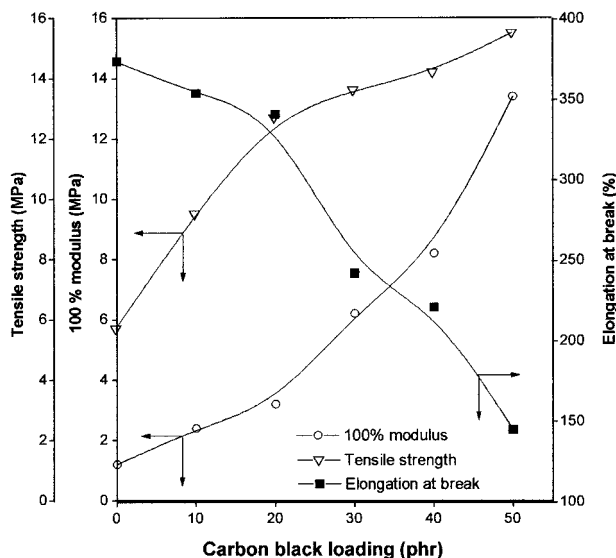
Figure 3 Effect of carbon black loading on mechanical properties of 50:50 (w/w) ACM–FKM blend.

Mechanical properties

The performance of any product is easily judged by its strength properties. Tensile failure is regarded as catastrophic tearing by the growth of crack-initiated flaws. Tensile properties can be improved by dissipating most input energy in the form of heat through an irreversible molecular process (i.e., lowering the elastic energy for the breaking of the polymer network). Strain-induced crystallization is one such process. Noncrystalline polymers such as ACM and FKM are unable to dissipate the stored energy through strain-induced crystallization. This is attributed to the inherent weakness of these polymers. The poor mechanical strength of cured gum ACM is a result of the presence of a bulky ester group in the pendant position, which prevents crystallization. On the other hand, gum FKM also shows poor strength because of the presence of vinylidene fluoride, which destroys the crystallites of poly(tetrafluoroethylene) or poly(hexafluoropropylene), the constituents of fluoroelastomer.

Blending of ACM with FKM alters the molecular arrangement through the formation of weak dipole–dipole type of bonding and hence increases the strength above the additive rule of blending as explained in our earlier work.[3] A similar observation was made for the cured blends of gum and filled ACM–FKM blends. Table I shows the mechanical properties of the gum and N550 filled ACM and FKM and their blends. The tensile strength and modulus at 300% elongation of the gum blends were increased on incorporation of FKM into the blend. The gum 50:50 blend showed maximum strength among the blends. This was true also for elongation at break of the blends.

The reinforcing effect of carbon black can be seen in the individual rubbers and their blends with uniform increase in tensile strength and reduction in elongation at break. ACM shows (Table I) drastic improvement in modulus at 300% elongation and tensile strength, from 0.6 MPa and 1.3 MPa, respectively, for the gum compound, to 7.0 MPa and 13.2 MPa, respectively, for the 30-phr N550–filled compound. The tear strength also increased, from 3.5 kN/m for gum ACM to 26.4 kN/m for the filled compound. The 50:50 blend showed the maximum improvement for most properties for both the gum and filled compounds. The increase in tensile strength and reduction in elongation of a filled system can be explained by the saltation mechanism[23] (detachment and reattachment of polymer chains with carbon black particles) and energy dissipation through a breakdown of agglomeration, high viscous flow from filler–polymer chain entanglement, and slippage of rubber molecules along the filler surface.[24,25]

The reinforcing effects of various fillers and different loadings of N550 on tensile and tear properties of ACM–FKM blends are shown in Table II. Among different fillers N220 showed the highest tensile strength, followed by N550, with the lowest strength observed for the silica-filled blend. The small particle size and large surface area of N220 provides a greater possibility of polymer–filler interaction and consequent molecular slippage. These processes enhance the energy dissipation and hence the strength. At the same time chain extensibility of a polymer is reduced, leading to less elongation.

Figure 3 depicts the effect of carbon black loading on the tensile properties of the N550-filled 50:50 (w/w) ACM–FKM blend. An increase in filler loading increased tensile strength, from 5.7 MPa, for the gum
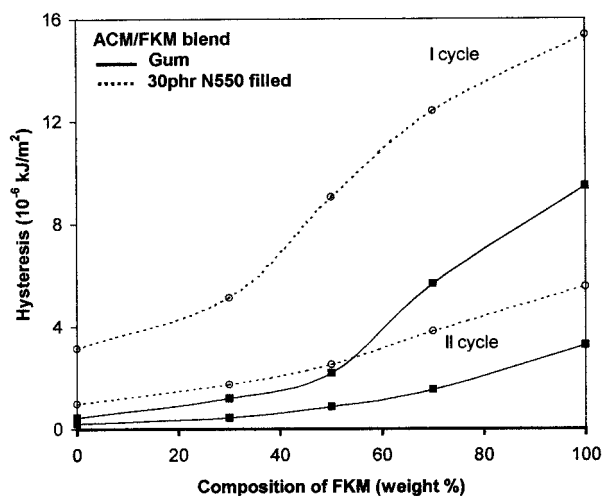

Figure 4 Comparison of hysteresis loss of gum and filled ACM, FKM, and their blends.
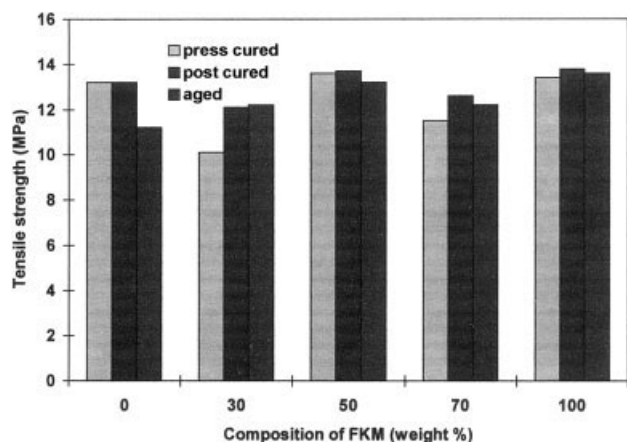
Figure 5 Comparison of tensile strength of cured, post-cured, and aged 50:50 (w/w) ACM–FKM blend containing 30 phr N550.

compound, to 15.5 MPa, for the 50-phr loaded compound, and decreased elongation at break, from 384% to 145%. The nature of the curve shown in Figure 3 indicates that the reinforcing effect at a higher loading is much smaller. Because this experiment was limited to a maximum 50-phr filler level, a decreasing trend at higher loadings could not be obtained.

Hysteresis

Hysteresis is a measure of energy dissipated by a material during cyclic deformation. The portion of mechanical energy input not recovered is essentially converted to heat.[26] Figure 4 shows the effect of filler loading on hysteresis of the ACM–FKM blend. The values for other systems are shown in Tables I and II. On increasing FKM content in the blend, the hysteresis loss increased and reached a maximum value for gum FKM. This implies that FKM is able to dissipate more stored energy than ACM, which is inherently weak. The hysteresis loss of the N550 filled 50:50 blend shows that an increase in filler loading increases hysteresis loss and that the effect is highest in the first cycle, as seen in Figure 4. The highly filled 50:50 blend showed the largest hysteresis loss.

Hysteresis loss of carbon-black-filled rubber has been attributed to[27] (1) the molecular friction accompanying deformation of gum phase, (2) detachment at the carbon black–polymer interphase, which is dependent on the surface area of the filler, and (c) the breakdown of particles of carbon black.

Effect of postcuring

The mechanical properties of postcured samples are shown in Tables I and II. As ACM could not be postcured at a temperature of 200°C for 6 h, its property

change is not reported here. However, the blends containing ACM could be postcured, and postcuring increases the tensile strength of FKM as well as the blends to different magnitudes. The gum blends containing a higher proportion of FKM showed more changes in strength properties compared to the other blends. Postcuring and elongation at break could not be correlated, as there was a mixed trend for the blends. In fact, tear strength was increased in all cases. The percent change in the properties of filled ACM and the blends containing a higher proportion of ACM was greater than that of filled FKM, which was the least affected after postcuring.

The effect of filler types and loading also showed there was some increase in the strength properties and decrease in elongation. Postcuring of ACM and FKM completed the process of vulcanization to the maximum level. During press curing reaction products such as water generated from the following reaction inhibited the vulcanization process and hence the lower level of strength.[13]

$$MgO + 2HF \rightarrow MgF_2 + H_2O \qquad (3)$$
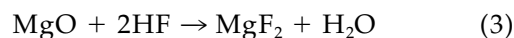
During postcuring evolved water is removed easily in an open-air atmosphere. The comparison of tensile strength of cured and postcured N550 filled ACM–FKM blends containing different levels of FKM is shown in Figure 5. It can be seen that the effect of postcuring on tensile strength was the minimum for neat polymers and the 50:50 (w/w) blend, whereas the 70:30 and 30:70 (w/w) blends showed an increase in tensile strength because of the completion of the curing reaction during postcuring. However, there was only marginal change in other properties for all the neat polymers and their blends.

Effect of aging

Aging of polymers normally reduces its useful properties. However, saturated polymers are affected to a lesser extent than olefinic rubbers that contain a dou-

TABLE III
Swelling Data of Gum and Filled ACM, FKM, and Their Blends (Values Are Represented by % swell)

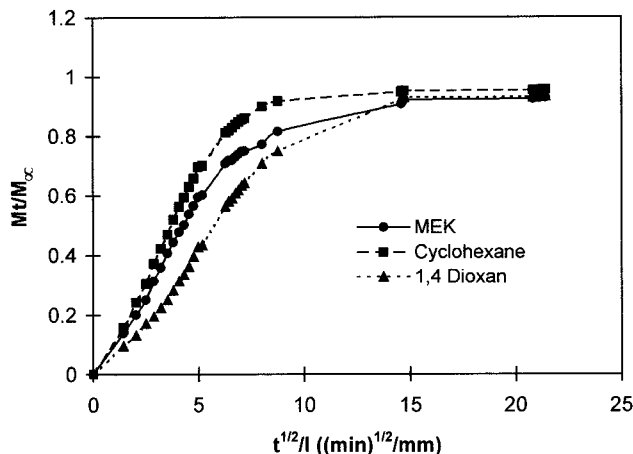| Samples	Methyl ethyl ketone	1,4-Dioxan	Cyclohexane	ASTM oil #3
ACM	685	957	13	6
B_1	445	527	10	9
B_2	299	341	10	5
B_3	284	295	4	5
FKM	194	135	2	2
AF_{30}	267	377	12	5
$BF2_{30}$	176	197	5	5
FF_{30}	114	89	2	1

Figure 6 Plot of M_t/M_∞ against $t^{1/2}/l$ for 50:/50 (w/w) ACM–FKM blend.

ble bond, which acts as a reactive site for aging. Tables I and II show the aging results for ACM, FKM, and their blends. Aging did not alter the mechanical properties to a great extent. This is primarily because the rubbers involved in this work were basically high-temperature-resistant materials, and the conditions under which aging tests are performed are not very severe. The main objective of doing the aging study was to determine if the blends prepared from ACM and FKM were resistant to standard aging tests. The results show that the blends of various compositions had same heat resistance, about that of the individual rubbers (Fig. 5). Comparing the thermal resistance properties, it was found that ACM and the blends containing a higher proportion of ACM were affected to a greater extent than the FKM version. It is surprising that the gum and the filled 50:50 blends showed an increase in tensile strength after aging.

Compression set

The results of the compression set experiments are depicted in Tables I and II. They show that FKM was undergoing maximum set under both conditions. On the other hand, ACM showed minimum set. The blends showed values in between those of ACM and FKM depending on the proportion of ACM. The high compression set of FKM is a result of diamine curing, which normally yields more set.[13]

Swelling studies

The swelling data of the rubbers and their blends in three different solvents are presented in Table III. Gum acrylic rubber had the highest swelling, more than 900% in 1,4-dioxan and 685% in methyl ethyl ketone (MEK). This is because of the similar solubility

parameters of the solvents and the rubber. On the other hand, FKM did show swelling but to a lesser extent, with a maximum value of 194% in MEK and 137% in 1,4-dioxan. Increasing the FKM ratio in the blend gradually reduced the percent swelling. No blend showed a lower swelling value than FKM. This may be because of the slight difference in the solubility parameter between MEK and FKM and 1,4-dioxan and FKM.

The reinforcing effect of filler on solvent swelling is clearly seen from the reduction of percent swelling of N550 filled ACM, FKM, and 50:50 (w/w) blend. Fillers interact with rubbers and form a considerable amount of bound rubber through a filler–polymer network, which resists the penetration of solvent molecules into the network, thereby reducing the swelling. The excellent oil resistance of both ACM and FKM and their blends was evident from the very low level of swelling of these rubbers in ASTM #3 oil. FKM showed less than 2% swell, whereas ACM had about a 5%–6% swell. All the blends showed less than 5% swell except the 70:30 blend, which was a little higher. Figure 6 depicts the diffusion coefficient (*D*) curves of the 50:50 (w/w) ACM–FKM blend in three different solvents. The diffusion coefficient was calculated for the solvents from the slope of the curve. 1,4-Dioxan had the highest *D*, followed by MEK. The cyclohexane had a very small D coefficient because of the large difference in the solubility parameter between the blend and the solvent.
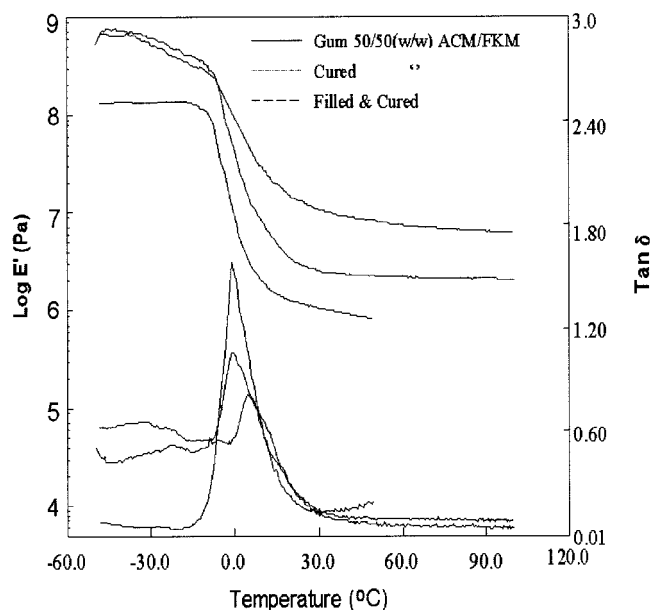

Figure 7 Temperature dependence of storage modulus (E′) and loss tangent (tan δ) of neat and cured gum and filled 50:50 (w/w) ACM–FKM blends at 1-Hz frequency.

Dynamic mechanical thermal analysis

Figure 7 shows the temperature dependence of storage modulus, E′, and loss tangent (tan δ) of the uncured and the cured blends of 50:50 (w/w) ACM–FKM with and without filler over the temperature range of −50°C to 150°C. The loss tangent peaks, corresponding to glass-transition temperature of unfilled blends and of both cured and uncured gum blends were observed at −1.0°C and 0°C, respectively. The individual polymers showed lower glass-transition (T_g) temperatures, and their blends with different compositions showed higher T_g because of a specific interaction, as we explained in our earlier work.[3] However, the corresponding peak for the filled system was observed at 5°C, with reduction in the loss tangent value, indicating the influence of filler on the T_g of the blend. The effect of curing and the addition of filler were also seen with increasing storage modulus values at all measured temperatures because of the restricted mobility of the polymer chain through crosslinking and polymer–filler networking, respectively.

CONCLUSIONS

A study of the cure characteristics and mechanical properties, aging, and swelling resistance of ACM, FKM, and their blends was carried out. The following conclusions were drawn:

1. Among various crosslinking agents, a combination of Diak #1 and ammonium benzoate yielded good cure characteristics with higher scorch safety. The use of Diak #1 alone resulted in preferential curing of FKM phase because of a faster cure reaction between diamine and vinylidene fluoride through dehydrofluorination.
2. The curing of the gum blend of 50:50 (w/w) ACM–FKM suggests that optimum cure is reached at 1.5 phr of Diak #1 at a constant level of ammonium benzoate. Higher loading of Diak #1 lowered the scorch safety and produced an uneven cure rate between ACM and FKM. The addition of ACM to FKM rubber decreased both M_L and M_H and increased the scorch safety of FKM because of the dilution effect of the less viscous ACM. The effect of different levels of carbon black (N550) in the filled 50:50 (w/w) ACM–FKM on cure characteristics indicated that an increase in filler level increased the minimum viscosity of stock and raised the maximum torque because of the accelerating and reinforcing effect of carbon black.
3. The stress–strain behavior values of the blends with varying compositions fell between ACM and FKM following the additive rule of mixture. However, the 30:70 (w/w) ACM–FKM blend showed a lower level of strain at break compared to that of the individual rubbers. A comparison of stress-deformation curves of the filled 50:50 blend showed the reinforcing capability of different carbon blacks depending on their particle size. Smaller-particle-size carbon black showed a higher stress level for a given strain, proving the higher reinforcing effect. By increasing the level of carbon black, the strain level was reduced at a given stress as a result of the dilution effect of diminishing volume fraction of polymer molecules. The rupture of filler polymer network during stressing may also reduce the strain level.
4. The tensile and tear properties of the 50:50 (w/w) ACM–FKM blends showed strength above the additive rule, indicating the presence of some kind of interaction between two rubbers through a dipole–dipole type of attraction. ACM drastically improved its strength properties on the addition of carbon black because of the reinforcing effect of carbon black through filler–polymer interaction. The 50:50 blend showed the maximum improvement in all measured properties for both gum and filled compounds, suggesting maximum interaction between filler particles and the polymers at this blend ratio.
5. The effect of blend compositions and filler loading on hysteresis of ACM–FKM blends indicates that either increasing either the FKM content in the blend or the carbon black level increases the hysteresis loss. Reinforcement is a result of labile filler–polymer associations that permit creep and frictional energy dissipation. Detachment of the polymer–filler interface also contributes to the hysteresis loss.
6. Postcuring does not considerably change all properties. However, gum blends containing a higher proportion of FKM showed more changes in strength properties than did other blends. This is because the curing reaction of fluororubber by diamine generates water molecules, which hinder the complete curing of FKM. Postcuring for an extended period of time at a higher temperature removes water. The percent change in the properties of the filled ACM and the blends containing a higher proportion of ACM was larger compared to that of FKM because of the acidic nature of carbon black, which delays the curing of ACM.
7. Thermal resistance of ACM and blends containing a higher proportion of ACM were affected to some extent during aging because of the poor thermooxidative stability of ACM compared to

FKM, which showed a higher thermal stability as a result of the presence of C—F linkage.

8. Lower swelling was achieved by adding reinforcing filler for all systems. The reinforcement of rubber by filler through filler–polymer interaction increased the physical crosslink density, which prevented the penetration of solvent molecules into the rubber matrix. The oil resistance of both ACM and FKM and their blends in ASTM #3 oil were comparable and had low values of oil swelling because of the polar nature of both rubbers.

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