

Thermal Analysis of Elastomer Composites

D. K. SETUA, G. N. MATHUR

Defence Materials and Stores Research and Development Establishment, DMSRDE Post Office, G.T. Road, Kanpur 208013, India

Received 20 December 1999; accepted 29 January 2000

ABSTRACT: Thermal analysis of polychloroprene elastomer composites was carried out. Addition of reinforcing fillers such as precipitated silica (Vulcasil-S), carbon black (FEF N-550), and short silk fiber led to significant changes in the degradation pattern, depending on their reinforcement and adhesion ability with the elastomer matrix. Attempts were made to correlate the variations of thermal properties with the surface chemistry and the reinforcement characteristics of these fillers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 646–651, 2001

Key words: thermal analysis; elastomer composites; reinforcing fillers

INTRODUCTION

Polychloroprene rubber (CR) is used in a variety of applications because of its inherent characteristics like weather and chemical resistance, thermal stability, and very good physicochemical properties. Setua and Dutta¹ and Setua and De² reported on their studies on the mechanical properties and failure characteristics of CR vulcanizates using silica, carbon black, and short silk fibers as the reinforcing fillers. It was observed that the extent of reinforcement depends on the nature of the filler, processing conditions, and type of bonding between the fiber and the rubber. In subsequent publications, Setua³ reported scanning electron microscopy studies on thermooxidative aging of CR and also reviewed the short fiber reinforcement of rubber composites comprising natural rubber, nitrile-butadiene rubber, styrene-butadiene rubber, and CR.⁴ Thermoanalytical techniques such as differential scanning calorimetry, thermogravimetric analysis (TGA), and dy-

namic mechanical analysis on the influence of compatibilizing agents on the adhesion and thermal stability of binary blends of isobutylene-isoprene copolymer and CR was recently reported by Pandey et al.⁵

In this article we report the results of TGA and differential thermal analysis (DTA) of unfilled and silica, carbon black, or short fiber filled CR composites. The effect of the addition of different bonding systems on the extent of adhesion and its effect on the thermodegradation characteristics of the composites were also studied.

EXPERIMENTAL

The formulations of the mixes are given in Table I. Mixing was done in a conventional laboratory open mill (150 × 330 mm) at 30–40°C according to ASTM D 15-70. The nip gap, mill roll speed ratio, sequence of the addition of different ingredients, and time of mixing were the same for all the mixes. The compounds were vulcanized to their respective optimum cure times as determined by a Monsanto rheometer (R-100) at 150°C. The details of preparation of the compos-

Correspondence to: D. K. Setua (kwcho@postech.ac.kr).

Journal of Applied Polymer Science, Vol. 79, 646–651 (2001)
© 2000 John Wiley & Sons, Inc.

Table I Formulations of Mixes

	Mixes				
	A	B	C	D	E
Polychloroprene ^a	100	100	100	100	100
MgO	4	4	4	4	4
PBNA ^b	2	2	2	2	2
Silica ^c	—	—	40	10	—
Carbon black ^d	—	40	—	—	10
Process oil	—	4	—	—	1
Cohedur RK ^e	—	—	—	10	10
Silk fiber ^f	—	—	—	20	20
Stearic acid	0.5	0.5	0.5	0.5	0.5
Cohedur A ^g	—	—	—	3.2	3.2
ZnO	5	5	5	5	5
TMTM ^h	1	1	1	1	1
DOTG ⁱ	0.5	0.5	0.5	0.5	0.5
Sulfur	0.5	0.5	0.5	0.5	0.5

^a Neoprene rubber (WM-1 grade, Du Pont).

^b Phenyl β -naphthalamine.

^c Vulcasil-S (Digussa).

^d Semireinforcing carbon black (FEF N-550).

^e A condensation product of resorcinol and formaldehyde (Bayer Ltd.).

^f Mulberry type obtained as waste in filatures (Indian Silk Industries).

^g Methoxymethyl melamine (Bayer Ltd.).

^h Tetramethyl thiuram monosulfide.

ⁱ Di-ortho-totyl guanidine.

ites are described in a previous publication.⁶ In the case of short silk fiber filled compounds (mixes D and E), the fibers were first chopped to 6-mm length. The shear force during mixing caused breakage of the fibers. A fall in the mean aspect ratio (average length to diameter ratio) from its original value of 500–85 that was due to mixing was observed by dissolving the fiber filled compounds in chloroform, followed by extraction of the fibers and examination of the fiber length distribution with an optical microscope (Leitz model HM-Pol).

The tensile strength, elongation at break, modulus, and tear strength of the composites were measured in a Zwick tensile testing machine at room temperature ($30 \pm 2^\circ\text{C}$). The rate of separation of the grips for the above tests was adjusted to 500 mm/min. ASTM procedures were adopted in the determination of other mechanical properties (heat buildup in a Goodrich flexometer, abrasion in a Du Pont abrader, and hardness with a Shore A durometer).

Thermal analyses of the composites were carried out in a Paulik–Paulik Erday MOM derivetograph. The initial weight taken for each mix was

120 mg, and TGA sensitivity was kept constant at 500 mg. The DTA sensitivity was kept fixed at 1/5 for all the mixes. The rate of heating in each case was maintained at $10^\circ\text{C}/\text{min}$. The results were plotted in the instrument itself as a function of time and were then converted into temperature functions.

RESULTS AND DISCUSSION

Physicomechanical Properties

Table II gives the physicomechanical properties of the composites. The hardness and heat buildup of the vulcanizates increased with the addition of fillers. Fiber filled composites (mixes D and E) showed maximum hardness while the silica filled vulcanizate (mix C) showed maximum heat buildup. The addition of reinforcing fillers and short fibers increased the tear resistance, and the highest increase was noted in the silica filled composite (mix C). The increase in tensile strength was maximum in the silica (mix C) while addition of fiber (mixes D and E) lowered the tensile strength. Elongation at break was decreased on

Table II Physicomechanical Properties of Composites

	Mixes				
	A	B	C	D	E
Hardness (Shore A)	50	74	82	92	90
Tear strength (kN/m)	21.5	40.8	77.7	46.6	43.0
Tensile strength (MPa)	14.85	19.76	22.42	11.45	9.61
Elongation at break (%)	910	450	940	25	30
Heat buildup for 20 min at 50°C (°C)	21	32	56	41 (18)	39 (15)
Compression set at 400-lbs constant stress (%)	15	7	18	7	9
Abrasion loss (mL/h)	4.19	1.23	1.65	1.83	1.98

The values in the parentheses indicate the time of failure (min) of the test specimen in Goodrich flexometer testing.

the addition of carbon black (mix B) and short fibers (mixes D and E) fillers. However, the silica filled composite (mix C) showed high elongation at break due to slippage of the polymer chains on the filler surface.^{7,8} For similar reasons the set property was poor in mix C. The abrasion loss decreased with the addition of filler, and the effect was maximum for mix B.

Relative Efficiency of Silica and Carbon Black in Adhesion Between Short Fibers and Rubber

Table I shows that mix D contains 10 phr of silica along with the Cohedur RK-Cohedur A bonding system. Mix E contains 10 phr of carbon black in place of the silica. A comparison of the physico-mechanical properties of mixes D and E showed that the former led to a higher tensile strength, tear strength, abrasion loss, and compression set, and almost similar hardness, heat buildup, and elongation at break properties. These imply a lower level of fiber-rubber adhesion in mix E compared to mix D. Use of the Cohedur RK-Cohedur A-silica bonding system would therefore be preferable to the Cohedur RK-Cohedur A-carbon black bonding system for designing of the short fiber-rubber composites.

Thermal Analyses Results

Figures 1 and 2 show the DTA and TGA plots of the composites, respectively. Table III shows the summary of the DTA peaks and corresponding weight losses for different composites. The gum rubber vulcanizate of mix A showed a small endothermic peak in the temperature range of 120–180°C with a peak minimum at 160°C. This was due to molecular rearrangement of the long chain

polymeric molecules in this temperature region to achieve a more ordered configuration, leading to a neat entropy decrease. The small weight loss of 6.25% was due to loss of the rubber chemicals (e.g., antioxidant, stearic acid, etc.) used for the preparation of the vulcanizate. After this endothermic process the vulcanizate experienced exclusions of small molecules like Cl_2 and HCl from the rubber moiety, which was an exothermic pro-

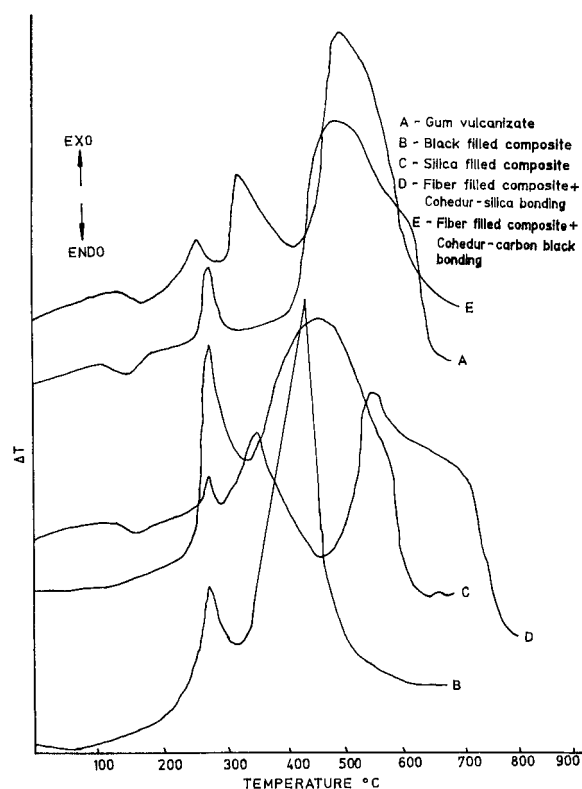


Figure 1 DTA plots of the elastomer composites.

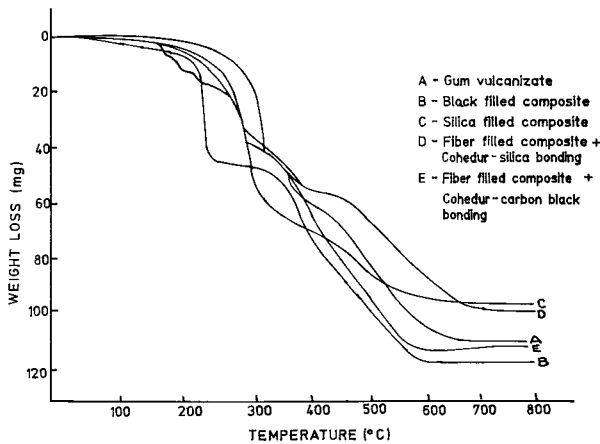


Figure 2 TGA plots of the elastomer composites.

cess. Formation of the peak in the temperature region between 180 and 320°C with a maximum at 280°C and a corresponding weight loss of 42.5% were therefore observed. After 320°C the vulcanizate showed the beginning of combustion in the presence of oxygen. The presence of a broad exothermic peak in the temperature range of 380–500°C with a maximum at 440°C and corresponding weight loss of 93.7% supported the above conclusion.

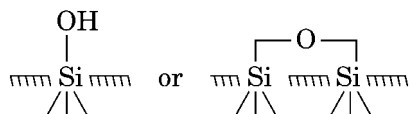
When carbon black was added to the compound (mix B), because of the lower particulate size, it was assimilated into the rubber chains and thus produced a reinforcing effect as a result of polymer–filler interaction. The presence of the filler also caused immobilization of the polymeric chains and thereby restricted the molecular rearrangements at lower temperature. Therefore, mix B showed no endothermic peak as observed in the gum rubber vulcanizate of mix A. However, the carbon black catalyzed the process of molecular elimination and combustion reactions of the rubber and produced an exothermic peak in the temperature range of 180–320°C with maximum at 280°C. The higher weight loss for mix B (42.5%) that was due to the loss of ingredients and elimination of small molecules and the combustion of a part of the carbon black in this temperature range were observed. The final combustion peak in the temperature range of 320–500°C (maximum at 410°C) was due to total combustion of the polymer and the carbon black with a corresponding weight loss of 93.75%.

As had been observed for carbon black, incorporation of fine particulate silica in mix C also resulted in the absence of the endothermic peak

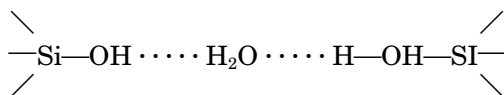
Table III Characteristic Degradation Peaks and Corresponding Weight Losses of Mixes

Mixes	Peak Position	Weight Loss (%)	Peak Position	Weight Loss (%)	Peak Position	Weight Loss (%)	Peak Position	Weight Loss (%)
A	Endo. peak at 120–180°C (min. 160°C)	6.25	Exo. peak at 180–320°C (max. 280°C)	42.5	Exo. peak at 380–500°C (max. 440°C)	93.70		
B	—	—	Exo. peak at 180–320°C (max. 280°C)	53.12	Exo. peak at 320–500°C (max. 410°C)	93.75		
C	—	—	Exo. peak at 180–340°C (max. 280°C)	46.87	Exo. peak at 340–600°C (max. 460°C)	81.00		
D	Endo. peak at 140–200°C (min. 140°C)	6.25	Exo. peak at 200–320°C (max. 270°C)	31.25	Exo. peak at 300–450°C (max. 360°C)	46.87	Exo. peak at 450–650°C (max. 550°C)	82
E	Endo. peak at 180–210°C (min. 170°C)	9.38	Exo. peak at 210–280°C (max. 240°C)	30.25	Exo. peak at 280–440°C (max. 340°C)	53.12	Exo. peak at 440–600°C (max. 500°C)	90.62

at the lower temperature region. However, unlike carbon black, silica did not undergo combustion; rather, it started an elimination of water molecules bound to the surface at increased temperatures. The surface of silica has two kinds of end groups:



It also has bound water in the form of



The increase in temperature caused elimination of these water molecules. A weight loss of 46.57% associated with an exothermic peak in the temperature range of 180–340°C with a maximum at 280°C corresponds to the weight loss due to the loss of ingredients, the elimination of small molecules from the rubber chains, and simultaneous elimination of water molecules from the surface of the silica. In mix C the silica remained unaffected and only the polymer underwent total combustion unlike that of mix B where the carbon black and the polymer both experienced total combustion. The final weight loss of mix C was therefore less than that of mix B; and because the silica did not catalyze any polymer combustion, the peak maximum was found to be shifted toward a higher temperature. The final weight loss of mix C was also less than that of mix A because of the decrease in the total volume fraction of rubber for the former compared to that of the latter.

From Table II it is also evident that the dry bonding system Cohedur A–Cohedur RK–silica offered better adhesion and strength properties between the silk fiber and the rubber matrix in their composition (mix D) compared to the adhesion offered by Cohedur A–Cohedur RK–carbon black (mix E). The average size of the short fibers in the vulcanizates was larger compared to the particulate fillers (e.g., carbon black and silica), and they did not prevent any molecular rearrangement of long chain polymer molecules at lower temperatures. Therefore, mix D showed an endothermic peak in the temperature region of 140–200°C and a weight loss of 6.25% that was due to loss of ingredients as observed in mix A.

Silk fiber also contains many functional groups like —CH₂OH, —NHCO, and —NH₂ on its surface and these were eliminated at higher temperatures. The exothermic peak in the temperature range of 200–320°C with a total weight loss of 31.25% thus resulted. Another exothermic peak in the temperature range of 300–450°C (maximum at 360°C) corresponds to a partial oxidation of the fiber and the polymer, leading to a net weight loss of 46.87%. A broad exothermic peak in the temperature range of 450–650°C corresponds to the total combustion of both the fiber and the rubber with a total weight loss of 82%.

As observed in mix D, mix E containing carbon black and silk fibers showed a small endothermic peak in the temperature range of 180–210°C with a minimum at 170°C. The exothermic peak in the temperature range of 210–280°C and the weight loss of 30.25% were due to eliminations of small molecules from the polymer and the fiber. Another exothermic peak in the temperature range of 280–440°C (maximum at 340°C) and a weight loss of 53.12% were due to weight losses of oxidation of a part of the fiber and the rubber and were also due to combustion of the carbon black. However, because of the lower adhesion between the fiber and the rubber, this exothermic peak maximum occurred at a lower temperature (i.e., 340°C compared to 360°C in mix D). For obvious reasons, mix E showed a higher weight loss than mix D in this temperature region. The final exothermic peak in the temperature range of 410–600°C with a peak maximum at 500°C corresponds to complete combustion of the carbon black, polymer, and fibers. As expected, the total weight loss of 90.62% was higher than that observed in mix D containing inert silica filler.

CONCLUSIONS

1. Addition of either reinforcing fillers (carbon black or silica) or short fibers in combination with a proper bonding system could enhance the thermal stability of the elastomer composites.
2. Polymer chain mobility in the initial stages of increasing temperatures up to ≈200°C is restricted because of the addition of the particulate fillers (carbon black or silica) with small particle and agglomerate size contrary to unfilled or short fiber filled composites.

3. An attempt was made, probably for the first time, to correlate physicochemical properties and filler–matrix adhesion with the thermodegradation characteristics of the elastomeric composites.

REFERENCES

1. Setua, D. K.; Dutta, B. *J Appl Polym Sci* 1984, 24, 3097.
2. Setua, D. K.; De, S. K. *J Mater Sci* 1985, 20, 3357.
3. Setua, D. K. *Polym Degrad Stabil* 1985, 12, 169.
4. Setua, D. K. In *Polymeric Materials: New Renewable Resources*; Sperling, L. H., Carraher, C., Eds.; Plenum: New York, 1985; Vol. 6, p 275.
5. Pandey, K. N.; Debnath, K. K.; Rajagopalan, P. T.; Setua, D. K.; Mathur, G. N. *J Therm Anal* 1997, 49, 281.
6. Setua, D. K.; De, S. K. *Rubber Chem Technol* 1983, 56, 808.
7. Wagner, M. P. *Rubber Chem Technol* 1976, 49, 703.
8. Fetterman, M. R. *Rubber Chem Technol* 1976, 46, 927.