

Effect of carbon black and fly ash co-fillers content on mechanical and thermal behaviors of styrene butadiene rubber compounds

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Abstract

Fly ash (FA) is produced as a waste byproduct during the burning process of coal in thermal power plants whose cost is primarily associated to cleaning and transportation. It possesses mechanical properties on account of its constituents like silica and alumina. The use of FA as filler in styrene butadiene rubber (SBR) was of researchers' interest to reinforce and/or to reduce product cost. In this article, the physico-mechanical properties of SBR composites with varying amounts viz., 0, 5, 10, 15, 20 and 40 phr of FA contents were investigated. The physico-mechanical properties of the rubber vulcanizates were determined before and after heat aging at 90 °C for 72h. It was observed that fly ash-filled SBR composites were better in mechanical properties such as elongation and resilience. Thermo gravimetric analysis (TGA) studies of the SBR/FA composites have been performed in order to establish the thermal stability and the mode of thermal degradation. TGA thermograms indicate multiple steps of the SBR/FA systems thermal degradation.

Keywords: SBR; fly ash; mechanical behavior; heat ageing; TGA.

Introduction

Fillers are added to rubber for a variety of purposes, of which the most important ones are enhancements in reinforcement, processability and material costs [1]. Fly ash (FA) is a relatively inexpensive by-product, and its usages have the benefit of decreasing environmental problems. Furthermore, FA has been used in industry due to such advantages as low cost, smooth spherical surface and good processability of the filled

materials [2]. Fly ash particles are crystalline compounds of quartz, mullite, hematite and glassy compounds such as silica and other metal oxides. FA particles consist of silicon dioxide similar to silica but with the lower content of silicon dioxide than silica [3]. Fly ash is a waste product generated in very huge quantities (by thermal power stations) posing a problem of disposal. The relevance of this study could help solving the problem of disposal of fly

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ash up to a certain extent, and the polymer industry will get the most economical filler [4]. Attempts have been made to use fly ash purposefully for various applications [5-6], for example, in the chemical field, agricultural field, cement and construction industries, and polymer industries, but very few attempts have been made for its use as a filler in elastomers and plastics [5,6] which could be the largest field for its large-scale use. Even though, carbon black and silica is still well accepted among rubber technologists, the use of some other filler from the natural resources as alternative reinforcing fillers in NR has been carried out to replace silica in rubber compounds [7]. Such fillers include clay, lignin, black rice husk ash (BRHA) and white rice husk ash (WRHA), and cellulose fiber. Recently, Thanunya et al. have investigated the reported effect of fly ash loading on the viscoelastic properties of natural rubber/FA compounds [8].

FA can hardly be considered as filler with a real reinforcement potential because of its much lower structure and surface reactivity. Fly ash, an absolutely low cost inorganic waste product of thermal power stations, continues to pose a hazard and must, thus, be used in applications that help to curb environmental pollution. FA is an interesting filler giving some reinforcements. Moreover, a generation of wealth of data on the effect of FA content on the performance of rubber compounds is of interest in the present investigation [9]. In this study, SBR/FA composites with different compositions have been prepared. Accordingly, this research aimed at investigating the effects of fly ash on the cure characteristics and

physico-mechanical properties of SBR. It is intended to develop a local filler that has a lower cost and is renewable and abundantly available and can be used as a partial substitute for carbon black fillers. The end uses of these resources are of paramount importance for technological growth.

Experimental

Materials

The fly ash particles were obtained from Mae Moh Power Station of KNR Group Co., (Lampang, Thailand). The major chemical constituents of FA are silica (37.6%), alumina (22.4%), calcium oxide (15.1%) and ferric oxide (14.5%). Styrene-butadiene rubber (SBR) was supplied by TSR Corporation, Taiwan.

Compounding of SBR with fillers

Compounding of rubber formulations was carried out in a baby two roll-mixing mill of roll as per ASTM D 3182. The typical recipe which was used to make the SBR/FA composites is given in Table 1. In this investigation, carbon black filler was replaced with the same amount of FA. Rubber was primarily masticated to form a band on the front roll of the mill and the compounding ingredients were sequentially added in the order: ZnO, stearic acid, fillers (carbon black/fly ash), antioxidant, MOR and sulfur. Passing through a small nip of the rolls finally sheeted off the compounded stock. The compounded material was kept in a compression mold, and was cured under pressure and temperature (dimensions of 150 x 150 x 3 mm). The temperature of the compression mold was kept at 140 °C [10,11] and the curing was carried out for 40 min. The molded sheets were subjected to conditioning for 24 hr.

Table 1. Typical formulations of SBR/FA composites

Formulation, phr	1	2	3	4	5	6
SBR	63.9	63.9	63.9	63.9	63.9	63.9
ZnO	3.2	3.2	3.2	3.2	3.2	3.2
St. acid	1.3	1.3	1.3	1.3	1.3	1.3
Antioxidant	0.63	0.63	0.63	0.63	0.63	0.63
Naphthalene oil	3.2	3.2	3.2	3.2	3.2	3.2
Sulphur	1.27	1.27	1.27	1.27	1.27	1.27
MOR	0.95	0.95	0.95	0.95	0.95	0.95
Carbon black	40	35	30	25	20	0
Flyash	0	5	10	15	20	40

Techniques

Cure characteristics of the rubber compounds were measured with the help of a Moving Die Rheometer 2000 (MDR 2000). From the rheographs, cure characteristics such as the extent of curing, scorch time, optimum cure time and cure rate index, of the rubber compound were obtained.

The SBR/FA systems were characterized for physical properties such as surface hardness (shore A and IRHD) and resilience according to ASTM D 2240 and BS 903 methods respectively. The dumb-bell shaped test specimens were punched out from the vulcanized sheet after 24 hr of vulcanization by a tensile specimen cutter. Tensile moduli at 100 and 200 % elongations, tensile strength and percentage elongation at break were measured as per ASTM D 412 using universal testing machine (ZWICK Z 2.5) at room temperature (25 ± 2 °C) and at a uniform speed of separation of 500 mm/min. Tear strength was measured as per ASTM-624 and ASTM-412.

The dumb-bell shaped test specimens were aged as per ASTM D 454 in a hot air aging oven at 90 °C. After aging for 72 hr, tensile behaviors of the specimens have been measured. Surface hardness (Shore A and IRHD) and resilience of the aged

specimen were also measured. The compression set was measured at 120 °C for 70 hr for all samples according to ASTM D 395 method. The swelling studies have been carried out in brake fluid oil as per ASTM D 471 at 70° and 120 °C for 70 hr in TVS girling dot 4 brake fluid.

The chemical resistances of the samples were studied according to ASTM D 543-87 method with 100 mL of 10 % different chemical reagents or pure solvents such as NaOH, HCl, H₂O₂, CH₃COOH, KMnO₄, benzene, toluene, aniline and distilled water. In each case, the previously dried and weighed sample was immersed in different chemical reagents at room temperature for 7 days. After 7 days they were removed, washed with distilled water and surface adhered solvents were removed by pressing them between soft tissue papers. The changes in the surface characteristics and percentage weight are recorded.

The thermal degradation parameters SBR/FA composites were evaluated using DuPont TA Instrument with TGA-Q 50 module. The instrument was calibrated using pure calcium oxalate sample before analysis. About 8-10 mg of sample was subjected to dynamic TGA scans at a heating rate of 20 °C/min in the temperature range of ambient to 800

°C in N₂ atmosphere. The TG curves were analyzed as percentage weight loss as a function of temperature.

Results and discussion

Cure characteristics

Table 2 shows the cure characteristics of the SBR –FA formulations at different filler loadings. It can be seen that the FA filled systems show increasing trend of cure time (T₉₀) with increasing FA loading. The impurities present in FA, may retard the rate of vulcanization of SBR formulations. Hence, SBR/FA compound will take a longer time to vulcanize. From Table 2, it is found that the incorporation of fillers into SBR has decreased the minimum and

maximum torque values. The decrease in minimum torque with FA loading was mainly attributed by filler –filler interaction rather than the rubber-filler interaction [12-14]. As minimum torque is related to viscosity and processability of compounds, the processing compounds become easier with increasing amount of fillers. It is observed that the increasing filler content has slightly increased the scorch time of SBR compounds. This indicates that FA and the impurities present in the filler (compositions) have the ability to reduce the scorch time.

Table 2. Cure characteristics of fly ash loaded SBR formulations

Properties	Fly ash content (phr)				
	0	5	10	15	20
T _{s2}	3.7	4.0	4.95	5.14	5.5
T _{s90}	9.4	9.8	10.1	10.4	10.9
M _L	3.2	2.8	2.3	1.9	1.5
M _H	22.0	19.5	19.3	17.9	15.7

Physico-mechanical properties

Surface hardness

The measured physico-mechanical properties such as surface hardness, tear strength and tensile behaviors of FA loaded SBR composites are nominated in Table 3. The obtained surface hardness of SBR/FA composites lies in the range 73-56 IRHD and 73-54 Shore A. Surface hardness values monotonically decrease with an increase in FA content. This result clearly indicates that FA is not a good reinforcing filler.

Resilience

There was a total increase in resilience as there was increase in FA

content in SBR systems. Resilience is slightly increased as the carbon black (CB) content decreases or the FA content increases. This result clearly indicates the poor interaction between SBR and FA than SBR and CB. The resilience depends on the behavior of particulate fillers in the compounds. The rubber-filler physical interactions and chemical anchorage established during processing and compounding, apparently at the expense of some degree of rubber-rubber and filler-filler interactions, may result in some degree of disentanglement of the rubber chains which is expected to grow in prominence with decrease in carbon black loading. These types of

interactions induce more elasticity. The impact of such chain disentanglement is clearly exhibited in the observed rising trend in resilience rate with decrease in carbon black loading [15].

Tear strength

SBR/carbon black system has tear strength of 42.5 and a gradual and significant reduction in tear strength from 38.4 to 22.8 with increase in FA content from 5 to 40 phr was noticed. This result clearly indicates that the interaction between rubbers to FA is poorer than rubber to carbon black.

Tensile strength

SBR/CB (without FA filler) and SBR/FA (without CB) systems have the tensile strength of 23.5 and 1.8 MPa, respectively. It is worth mentioning that the result clearly indicates the non-reinforcing behaviour of FA filler in SBR matrix. From Table 3, it was observed that the tensile strength of the composite drastically decreased as we witnessed increase in fly ash content and it lies

in the range 1.8 - 23.5 MPa. This was not unexpected because, at a low volume fraction of the filler, the matrix material was in large quantity, so that all filler particles were capable of being completely wetted by the matrix material while at higher volume fractions of the filler the matrix (i.e., elastomer) it was incapable of wetting the filler. This resulted in heterogeneity in the composites leading to deterioration of properties. From the table it was found that a slight reduction or retain in the tensile strength values up to 10 phr resulted in FA loading in SBR matrix. The percentage elongation at break for SBR/CB system is 357 %. A significant increase in percentage elongation at break for FA filled SBR systems were noticed. However, there is no systematic variation in percentage elongation with reference to filler composition. The impurities present in FA filler may act as chain extender and contribute to improve in elongation.

Table 3. Effect of fly ash content on the mechanical properties of SBR/FA composites

Fly ash content (phr)	Tensile strength (MPa)	Elongation at break (%)	Tensile Modulus (MPa)		Surface Hardness		Resilience (%)	Tear strength
			@ 100 %	@ 200 %	IRH D	Shore A		
0	23.5	357	5.6	12.2	73	73	54	42.5
5	23.3	404	4.6	10.1	73	71	50	38.4
10	19.0	387	4.1	8.8	71	69	52	34.5
15	18.5	428	3.3	7.0	69	67	57	28.3
20	12.2	435	2.4	4.9	66	64	64	22.8
25	1.8	368	1.1	1.1	56	54	61	-

Table 3 showed the effect of filler on modulus at 100 and 200 elongations for SBR/FA composites. It was observed that modulus at both elongations of composites were drastically reduced with increase in FA filler. This was rather surprising,

as fillers are customarily added to enhance the modulus. Generally, the presence of load bearing or dissipating microelements with their phase boundaries leads to a decrease in micro stress concentration. At higher volume fraction of filler,

stresses tend to initiate local rupture at micro domain boundaries. However, these are too small to cause fracture on a microscopic scale. Thus, cracks are limited by micro in homogeneity and cannot proceed very far without encountering modulus changes diverting their path and reducing their energy. It is also observed that the modulus increased after aging for all composites. It is believed that the poor filler to SBR interaction reduces the tensile properties of SBR/FA compounds. A significant reduction in tensile modulus with increase in filler content is expected as FA doesn't have strong polymer-filler interactions, which do not restrict the mobility of SBR.

Effect of heat ageing on tensile behaviors

The effect of heat ageing on mechanical performance of SBR/FA systems has been studied. The measured tensile properties and surface hardness values after heat ageing of SBR/FA composites is

tabulated in Table 4. The tensile strength and percentage elongation at break after heat ageing lies in the range 1.7- 21.0 MPa and 154-195%, respectively. A slight reduction in tensile strength and a drastical reduction in percentage elongation after heat ageing were noticed. However, from Table 4, it was found that a significant improvement in tensile modulus at 100 and 200 % elongation and surface hardness of the composites after heat ageing were observed as it was expected. This can be attributed to an increase in crosslink density of vulcanized rubber after heat ageing.

The measured compression set at 120 °C for 70 hr and for all samples is tabulated in Table 4. From the table, it was noticed that the compression set value for SBR/CB is 55 and for SBR/FA systems it lies in the range 52.3 – 68.9. This result indicates a marked improvement in compression set values with increase in FA content.

Table 4. Effect of heat ageing on mechanical properties of SBR/FA composites

Fly ash content (phr)	Tensile strength (MPa)	Elongation at break (%)	Tensile Modulus (MPa)		Surface Hardness +1.5		Resilience	Compression set @120 °C/70hr
			@ 100 %	@ 200 %	IRHD	Shore A		
0	21.0	195	9.5	20.8	82	80	55	56.9
5	20.9	241	7.4	16.1	80	78	57	52.3
10	18.1	247	6.0	13.2	78	76	61	56.2
15	14.1	260	4.8	10.5	76	74	64	64.0
20	10.6	230	4.2	9.0	74	72	70	60.6
40	1.7	154	1.7	2.9	62	60	72	68.9

Swelling behaviors in brake fluid

The effect of FA content on the swelling behaviors of SBR/FA compounds in brake fluid has been measured at 70 and 120 °C for 70 hr. The obtained results were tabulated in Table 5. From the table, it was

noticed that at 70 °C all the samples show a slight increase in weight due to swelling, however, at 120 °C, all the samples exhibit a reduction in weight. This may be due to a higher temperature brake fluid which extracts some of the uncrosslinked or

low molecular weight ingredients present in the SBR formulation. This result indicates that swelling

behaviour is sensitive to temperature of measurement.

Table 5. Effect of volume swelling in brake fluid of SBR/FA composites

Fly ash content (phr)	Volume swell	
	@70 °C/70hr	@120 °C/70hr
0	0.61	-0.38
5	0.44	-0.70
10	0.24	-1.16
15	0.30	-0.77
20	0.61	-1.09
40	0.95	-0.20

Chemical resistance

From Table 6, there was almost no significant changes in the physical appearance of fly ash filled SBR in the chemical reagents under investigated except samples immersed in KMnO₄ solution and organic solvents. This result indicates that fly ash filled SBR is moderately resistant to dilute acids and alkalis. From the table, a slight change was noticed in the weight for the samples exposed in HCl, NaOH, aniline, CH₃COOH and water. However, prominent swelling of fly ash filled SBR was noticed in

organic solvents such as benzene and toluene. This is due to the fact that benzene and toluene can penetrate into the core of fly ash filled SBR with less resistance. A pronounced change was observed in weight for the specimens exposed to KMnO₄ solution. Fly ash filled SBR was degraded in the oxidation media. Based on these observations it can be concluded that the chemical resistivity depends on the structure and morphology of the fly ash filled SBR and nature of the chemical reagents.

Table 6. Change in weight of fly ash filled SBR after exposure to different chemical reagents for 7 days

Fly ash content (phr)	% Change in weight for 7 days at room temp. for various chemical reagents									
	NaOH (10%)	HCl (10%)	CH ₃ CO OH (10%)	FAS (10%)	KMnO ₄ (10%)	Benzene	Aniline	Toluene	H ₂ O	
0	1.9	3.7	6.9	1.3	D	155	16.5	152	1.2	
5	1.8	4.4	7.0	1.2	D	169	16.7	158	1.8	
10	1.3	4.0	7.4	1.3	D	169	16.8	162	2.2	
15	1.2	5.1	8.1	1.4	D	176	16.9	168	1.9	
20	1.6	5.7	8.9	1.4	D	196	17	183	2.0	
40	1.8	7.2	9.8	1.1	D	271	18	268	2.3	

Thermal stability

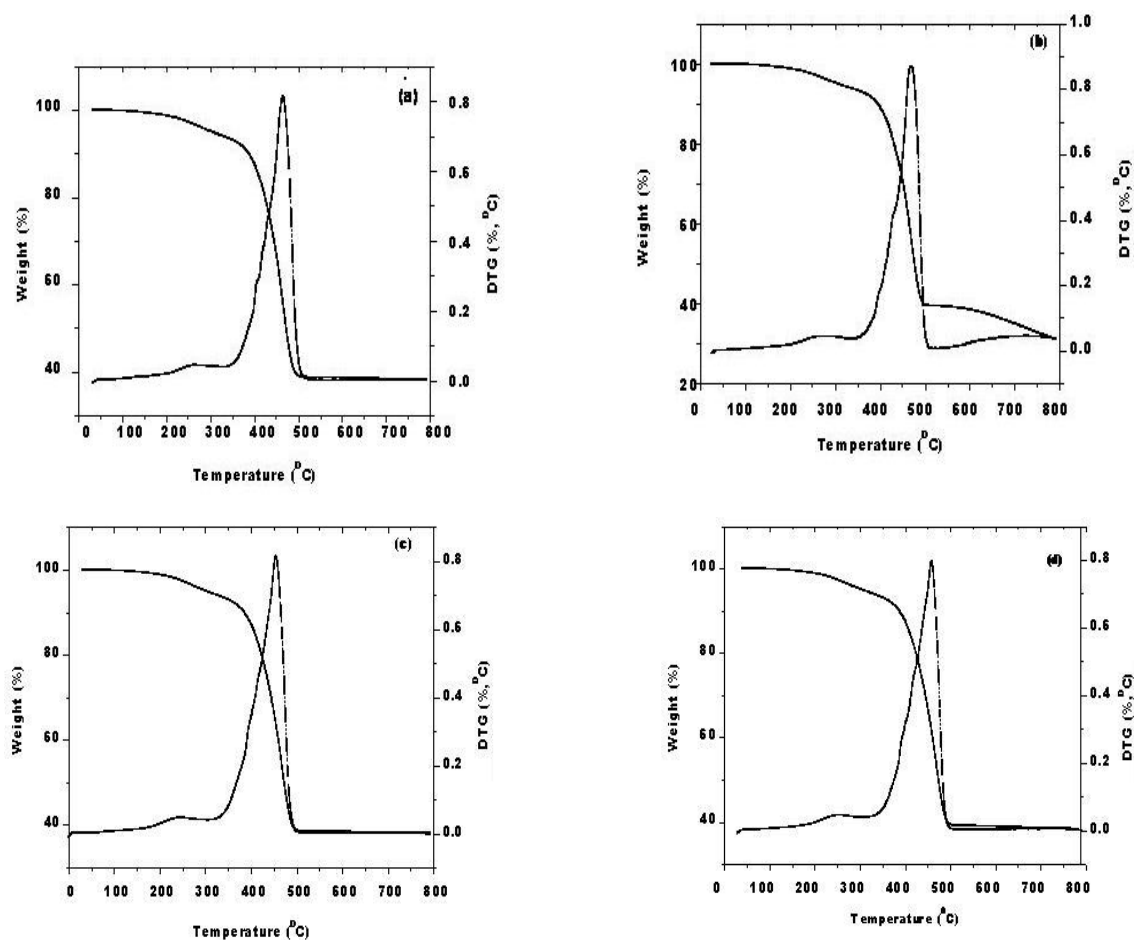
The thermal stability of the composites with varying amount of FA contents was determined using TGA thermograms under nitrogen atmosphere. The TGA thermograms of SBR/FA composites are shown in Figures 1 (a) & (e). From the

thermograms, it was observed that the thermal degradation pattern is almost identical for all SBR/FA composites. The different stages of thermal degradation were analyzed from the TGA thermograms and are given in Table 7.

The TGA curves for all composites indicate that there are three stages of thermal degradation. The weight loss which occurred in the first stage is ranging from 4.0 to 6.5 % in the temperature range 210–341 °C. The main pyrolysis product could be carbon dioxide [16-18]. The weight loss in this step is due to processing oil and low volatile content/moisture. The major weight loss occurred in the second step of thermal degradation process. The second step of weight loss occurred in the temperature range 337–525 °C with a weight loss ranging from 54.8 to 56.8 %. The major weight loss occurred in the second step which could be due to de-cross linking/degradation of rubber phase.

The weight loss in this step is almost identical for all formulations, because rubber content is similar for all formulations.

In the third and final step, the major weight loss occurred above 525 °C and weight loss in this step may be due to filler. But, in this investigation, TGA scans were taken in inert (nitrogen) atmosphere, hence partial or no degradation of filler was noticed. This conclusion was drawn on the basis of ash content, which lies in the range 38.7-39.4 %. This result clearly indicates that there are no significant changes in ash content of the composites according to the fact that both CB and FA fillers are not degraded in inert atmosphere.



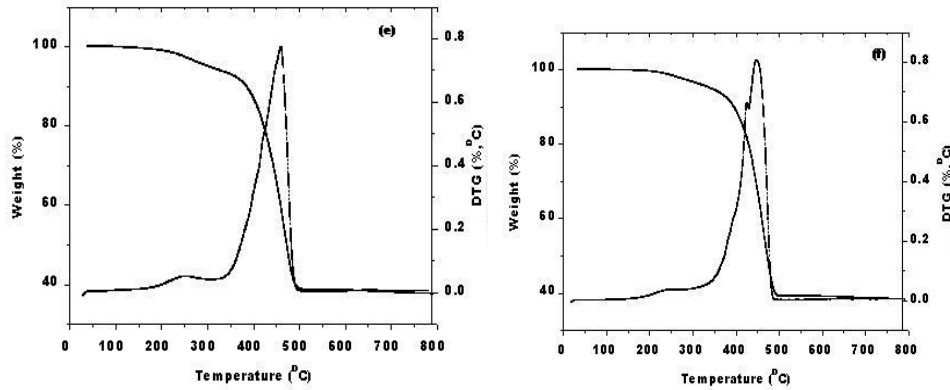


Figure 1. TGA and its derivative thermograms of (a) 0, (b) 5, (c) 10, (d) 15, (e) 20 and (f) 40 phr of FA filled SBR Composites

Table 7. Thermal data obtained from TGA thermograms for SBR/FA composites

Fly ash content (phr)	Degradation stages	Temperature (°C) ± 2			Weight loss (%)
		T _i	T _{max}	T _f	
0	1	210	260	340	6.5
	2	342	465	518	54.8
	Ash	-	-	-	38.7
5	1	212	265	341	6.4
	2	343	470	519	54.2
	Ash	-	-	-	39.4
10	1	213	263	335	6.4
	2	337	468	525	55.0
	Ash	-	-	-	38.6
15	1	210	270	329	6.0
	2	330	470	521	54.8
	Ash	-	-	-	39.2
20	1	213	262	330	6.3
	2	332	471	518	55.0
	Ash	-	-	-	38.7
40	1	213	270	317	4.0
	2	318	463	509	56.8
	Ash	-	-	-	39.2

Some of the degradation transition temperatures such as onset (T₀), 10% (T₁₀), 20% (T₂₀), 50% (T₅₀) weight loss and complete degradation (T_c) obtained from TGA curves are tabulated in Table 8. It was found that 10% weight loss of the SBR/FA composites with 0, 5, 10, 15, 20 and 40 phr FA contents were obtained at

387, 395, 385, 386, 385 and 395 °C respectively and that of 50 % weight losses of SBR/FA composites occurred at 472, 477, 472, 473, 473 and 473 °C. This result reveals that, the effect of FA filler on thermal stability of the composites is insignificant.

Table 8. Transition temperature data obtained from TGA curves for SBR/FA composites

Fly ash content (phr)	Temperature at different weight loss (°C) ± 2				
	T _i	T ₁₀	T ₂₀	T ₅₀	T _c
0	210	387	425	472	547
5	212	395	431	477	529
10	213	385	423	472	506
15	210	386	424	473	537
20	213	385	423	473	530
40	212	395	430	473	497

Conclusion

From the aforesaid study, a significant reduction in mechanical properties such as tensile strength, tensile modulus and tear strength after replacing CB with FA filler into SBR matrix was noticed. This is due to the poor interaction between rubber and FA in which FA acts as non-reinforcing filler in SBR matrix. However, up to 10 % of FA loading was retained or a slight reduction in tensile strength and surface hardness was noticed. A significant improvement in percentage elongation at break for SBR/FA systems was observed. But, there is no systematic variation in percentage elongation as a function of filler content. After heat ageing a marked improvement in surface hardness and tensile modulus of the composites were noticed. The swelling behavior data of SBR/FA compounds in brake fluid indicates that the swelling behaviour is sensitive to temperature. From TGA thermograms, it was noticed that all SBR/FA composites are stable up to 210 °C and undergo three steps of thermal degradation in the temperature ranges 210–341°C, 337–525 °C and above 525°C for first, second and third steps, respectively. The weight loss in the third step is very insignificant and higher ash content was noticed for all

formulation due to the fact that TGA scans were recorded in inert atmosphere. TGA data reveal that there is no significant improvement in thermal stability after incorporation of FA filler.

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