Chapter 7
Study of Morphology and Environmental Properties of Styrene-Butadiene Rubber-Carbon Black Nanocomposites

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Abstract Rubber-nanocomposite (SBR-carbon black) was incorporated by the emulsion method. Rubber-nanocomposite pieces have been resolved based on their elemental examination. FTIR and Raman spectra were concentrated to clarify the structure. The exterior morphology of the copolymer gum was examined by checking SEM and it sets up the transition state among crystalline and shapeless nature. Ozone resistance was concentrated to clarify intermittent perceptions of the outside of the examples were made for break commencement. Tests were uncovered for longer moment in time. Fire resistance was concentrated to measures the simplicity of annihilation of a fire and four evaluations are conceivable, contingent on the consuming point and the nearness of burning drips. The current examination involving the emulsion method where environmental performance of rubber-nanocomposite is found to be good.

7.1 Introduction

As of late, incredible considerations have been paid to nanoparticles because of its uncommon highlights, for example, surface impacts, little size impacts, limit reactions and the naturally visible quantum impacts [1–3]. Polymer degradation includes the difference in at least one physical property, bringing about defeat of the appropriateness of the objects for the expected functions [4]. Be that as it may, the total of nanoparticles inferable from the high surface vitality and surface extremity debilitates their exceptional nature [5]. Trans-polyoctylene elastic (TOR) has been presented as a compatibilizer for inconsistent elastic mixes including polar elastics, for example, acrylonitrile butadiene elastic and non-polar elastic styrene butadiene elastic (SBR), and as a preparing helps for a very firm elastic compound, for

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example, profoundly filled elastic mixes for skim-covering of steel wires for tires [6]. Trans-polyoctylene elastic (TOR) is a low atomic weight polymer, produced using cyclo-octene by metathesis polymerization, it is an elite polymer that exhibits a double character: during preparing, it has the capacity of a plasticizer, and after vulcanization, it carries on as an elastic and has been known as a compatibilizer for inconsistent mixes. Styrene elastic (SBR) is a broadly useful manufactured elastic having high filler stacking limit; great flex obstruction, split commencement opposition and scraped spot safe, which make it helpful for a few designing and modern application. By and by, as other unsaturated rubbers, it's profoundly helpless against debasement because of essence of twofold securities in the fundamental chain [7]. When alluding to enduring presentation there are a kind of corruption that ought to be viewed as, for example, bright light debasement which is the elastic influenced by UV beam and photo degradation and furthermore the ozone debasement. In spite of the fact that ozone is available in the climate at fixations regularly in the scope of 0–7 sections for each pphm, it can seriously assault on non safe elastics. The cooperation of elastic with ozone is great recorded when the elastic is focused or extended being used. Progression of splits creates, after some time, which is opposite to the applied pressure. Further presentation of these split surfaces to ozone cause the break to end up more extensive and more profound until the elastic falls flat [8, 9].

In this work, we prepared SBR- nanocomposites copolymer with the use of nano carbon black as filler by emulsion polymerization method. The impact of nano carbon black on the elemental, spectral, SEM and environmental properties has been studied. Elemental analysis, fourier transform infrared (FTIR), raman spectroscopy, morphology and environmental properties are carried out for all five composites (Fig. 7.1).

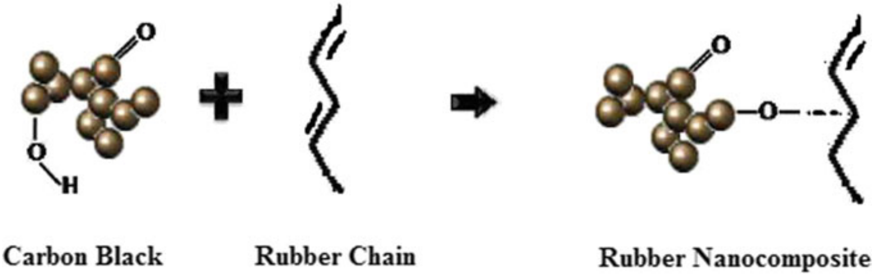

Fig. 7.1 Graphical diagram of SBR-carbon black nanocomposites

7.2 Experimental

7.2.1 Materials

Nanocomposites were acquired from Centre Scientific Company Nagpur, India. Tetramethyl Thiuram Disulfide, 2, 2′- Dithiobis, Stearic Acid and *N, N*′- Diphenyl *P*-Phenylene Diamine were purchased from Centre Scientific Company Nagpur, India. Zinc oxide and sulphur (Post Graduate Department of chemistry Kamla Nehru Mahavidyalaya, Nagpur, India). Styrene butadiene rubber latex obtained from Shree Radha Polymer Company, Nagpur, India.

7.2.2 Styrene Butadiene Rubber Nanocomposites Preparation

In the first place, carbon black was scattered in toluene with lively stirring and carbon black mixture was acquired at room temperature. At that point styrene butadiene rubber matrix was included into the carbon black mixture and mixed up to consistent blending of SBR into the carbon black. The blend was coagulated at room temperature. At that point rinsed with water a few times and afterward dried at 70 °C for 12 h. At that point SBR-nanocomposite was obtained.

7.2.3 Rubber Compounding

SBR matrix was blended with different fixings appeared in Table 7.1. The SBR-nanocompound then was vulcanized at 150 °C. The blend of SBR-nanocomposites

Table 7.1 Rubber formulation

Fixings	Parts per hundred ratio of rubber				
Sample code	1	2	3	4	5
Styrene Butadiene Rubber	100	100	100	100	100
Carbon black	0	2	6	10	12
Stearic Acid	2	2	2	2	2
Zinc Oxide	5	5	5	5	5
2, 2′-Dithiobis	0.5	0.5	0.5	0.5	0.5
Tetramethyl Thiuram Disulfide	0.2	0.2	0.2	0.2	0.2
N, N′- Diphenyl *P*-Phenylene Diamine	1	1	1	1	1
Sulphur	2	2	2	2	2

were straightforwardly operate on two-roll mill and blending for 15 min., at that point including every single fundamental fixings which are recorded in Table 7.1 and blending for 10 min. The final complex was vulcanized at 150 °C.

7.3 Characterizations

7.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of SBR-nanocomposites were obtained by using a shimadzu IR-Affinity spectrophotometer (Kamla Nehru Mahavidyalaya, Nagpur, India).

7.3.2 Raman Spectra

The Raman distribution analyses were carried out by employing a Jobin-Yvon T64000 spectrometer. In order to restrict the fluorescence sway, Styrene Butadiene Rubber, SBR with nanocompound were lit up with an argon-krypton molecule laser (Coherent model Innova 70C) working at the 647.1 nm (red line). The laser bar was locked in by a × 100 enhancement focuses of a confocal intensifying focal point (Olympus BX40) (from National Chemical Laboratory Pune, India). Each range was accumulated in the repeat run 400–3500 cm^{-1} in excess of 60 s and with 10 collections to avoid electronic apexes and ordinary establishment.

7.3.3 Morphology

Exterior morphology of the nanocomposites was investigated by using Scanning electron microscope JEOL (JSM-6390, STIC Cochin) at a speeding up voltage of 3 kV. Because of the extremely restricted electron shaft, SEM images have a huge profundity of field yielding a trademark 3-dimensional form helpful for identifying the exterior structure of tests.

7.3.4 Ozone Obstruction

The cavity gave an air a restricted grouping of ozone and temperature. Ozone focus chose was 50 pph, which is created by UV light. The examination was completed according to ASTM D1149-99 particulars at 38.50 C (from Shree Radha Polymer Rubber Industry Nagpur, India).

7.3.5 *Flame Resistance*

Fire resistance of vulcanizates of SBR elastic nanocomposites were assessed according to UL 94 diagram examination for combustibility of rubber samples for parts in gadgets and apparatuses (from Shree Radha Polymer Rubber Industry Nagpur, India). Strategy V 94, utilized for perpendiculars consume examination was applied. The experimental examples were (portions of 12 × 100 and width 2.0 mm slice from formed vulcanizates) seized toward one side in the perpendicular place.

7.4 Results and Discussion

7.4.1 *Elemental Measurements*

All five rubber nanocomposites were analyzed at Sophisticated Analytical Instrumentation Facility, Cochin for C, H, N and S. The empirical formula for all the five SBR, SBR-carbon black (2 phr), SBR-carbon black (6 phr), SBR-carbon black (10 phr) and SBR-carbon black (12 phr) were determined on the basis of C, H, N and S by messenger method. The watched outcomes are seen as in great concurrence with the determined qualities. From the empirical formula, the observational load of a single repeating unit was determined. Analytical data for all the five SBR-carbon black nanocomposites are presented in Table 7.2.

Table 7.2 Microanalysis information of Styrene-Butadiene rubber-carbon black composites

Rubber samples	% of C observed (Cal.)	% of H observed (Cal.)	% of N observed (Cal.)	% of O observed (Cal.)	% of S observed (Cal.)	Empirical formula	Empirical weight
Styrene butadiene rubber	83.44	8.11	2.56	5.85	2.34	$C_{38}H_{44}N_1O_2S$	546.993
	(81.44)	(8.05)	(2.31)	(5.08)	(1.39)		
SBR-CB (2 phr)	85.12	8.16	2.10	5.40	1.07	$C_{42}H_{48}NO_2S$	592.657
	(84.87)	(8.10)	(2.21)	(5.04)	(1.00)		
SBR-CB (6 phr)	84.26	9.09	2.24	5.34	1.07	$C_{42}H_{54}N_1O_2S$	598.705
	(83.20)	(8.99)	(2.20)	(5.01)	(1.02)		
SBR-CB (10 phr)	80.40	9.65	2.23	5.66	2.99	$C_{42}H_{60}N_1O_1S_1$	627.008
	(81.22)	(8.89)	(2.10)	(4.60)	(2.05)		
SBR-CB (12 phr)	82.89	10.27	2.29	5.26	1.58	$C_{42}H_{62}N_1O_2S$	612.963
	(80.67)	(9.12)	(2.12)	(4.20)	(1.02)		

7.4.2 Fourier Transform Infrared Spectroscopy

FTIR spectra of various loadings levels of carbon black shows in Fig. 7.2. In every spectrum, the expansive top at 3400 cm^{-1} is appointed to extending vibration of –OH group stretching vibrations alongside adsorbed water. The tops at 950 and 860 cm^{-1} are because of C–H bending of aromatic ring in carbon black. The peak at 1100 and 470 cm^{-1} are because of antisymmetric and symmetric extending. The presence of two sharp peaks at 2930 and 2840 cm^{-1} and one top around 1450 cm^{-1} for all the spectra of SBR-filler also of the assimilation groups comparing to the vibration of explicit useful gathering. These little pinnacles of around 2930 and 2840 cm^{-1} are main groups of symmetric and antisymmetric extending vibrations of $–CH_2$ bunch individually. 1450 cm^{-1} corresponding to bending vibrations of $–CH_2$ group. Every one of these pinnacles is seen in spectra of SBR-nanocomposites in

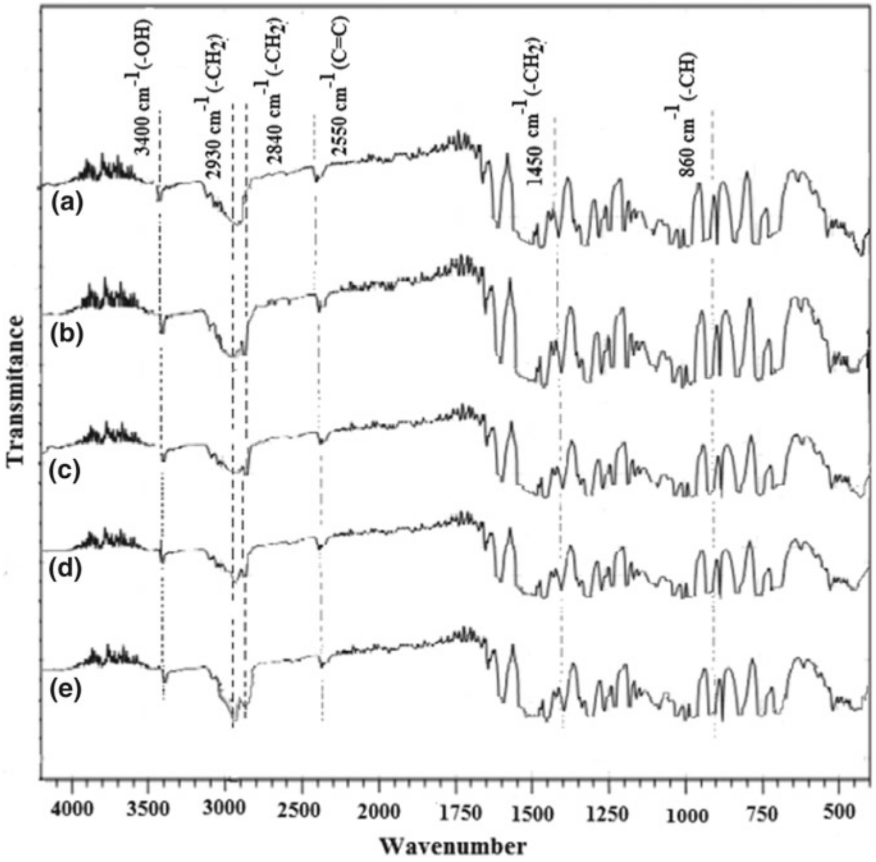

Fig. 7.2 FTIR spectra of SBR-nanocomposite **a** unfilled rubber composites, **b** 2 phr carbon black, **c** 6 phr carbon black, **d** 10 phr carbon black, **e** 12 phr carbon black

Table 7.3 FTIR spectral data of SBR-carbon black nanocomposites

Assignment	Expected wavenumber (cm^{-1})	Observed wavenumber (cm^{-1})
OH (phenolic)	3100–3500	3400 (b)
Functional group(C=O)	1700–1730	1750 (st)
Aromatic ring (C–H)	960–990	950 and 860 (sh)
[(CH_2) methylene bridges]	2500–3100	2930 and 2840 (sh)
Alkene group	990–1000	1080 (w)
Aromatic ring (C=C)	2100–2550	2550 (b)
[(CH_2) methylene bridge]	1250–1360	1450 (sh)

Sh sharp, *b* broad, *st* strong, *w* weak

Fig. 7.2. This is furthermore bolstered by the nearness of group at 1080 cm^{-1} which is characteristic band of alkene gathering. The top at 1750 cm^{-1} of carbon black when CO initiation which shows the nearness of C=O functional gatherings portrayed by aldehydes, ketones, carboxylic acids and esters. The nearness of band at 2550 cm^{-1}, which is trademark band of C=C fragrant gathering. On account of carbon black, the filler-rubber collaboration is mostly of objective character [10] (Table 7.3).

7.4.3 Raman Spectra

The closeness of contaminating impact and development of crosslinking operators, fillers and other elastic fixings into versatile are the essential reasons of fluorescence parasite flag in Raman dispersing range, principally with the laser excitation lines in the noticeable locale [11]. The yield of the fluorescence procedure is a lot greater than that of the Raman procedure, and in this way the primary raman data is covered. So as to unmistakably distinguish the trademark groups of SBR and SBR-nanocomposites, the coagulated elastic without carbon black was initially chosen to carry out Raman spectroscopy. The spectrum of SBR and SBR-carbon black composites are analyzed in Fig. 7.3 and band assignments are done dependent on correlation with writing spectra. The Raman pinnacles of SBR are just halfway doled out in the writing [12]. This work gives a complete credit for which Raman investigation of styrene and butadiene elastic is great direction. Both symmetric and unbalanced $–CH_2$ and $–CH_3$ extending sensations ordinarily show up in the 2800–3000 cm^{-1} district. Clearly, C=C extending atmosphere of SBR are seen at 1666 and 1668 cm^{-1}, individually. Likewise, there are a couple of secured indication of SBR and SBR-carbon black

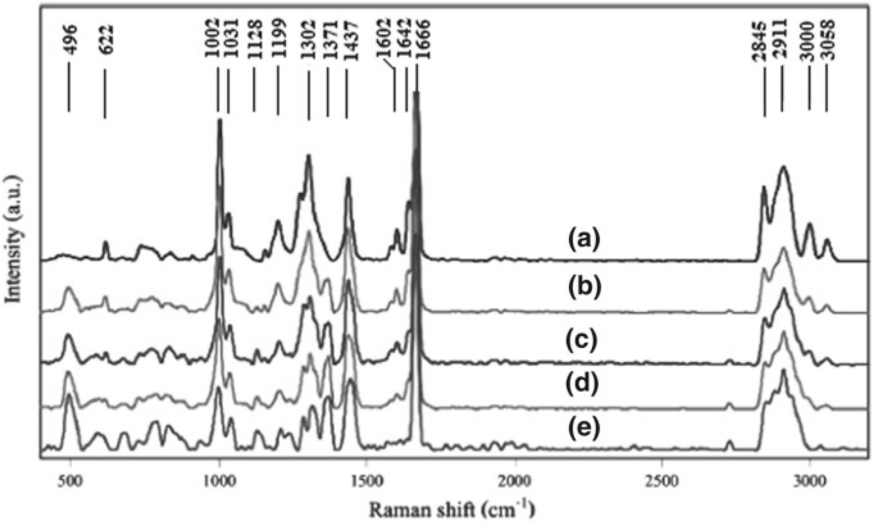

Fig. 7.3 Raman spectra of SBR-nanocomposite **a** unfilled rubber composites, **b** 2 phr carbon black, **c** 6 phr carbon black, **d** 10 phr carbon black, **e** 12 phr carbon black

matrix which can't be utilized to perceive their responsibilities, in this way just the characteristic pinnacles allowing partition will be based on. Raman spectra of unfilled SBR tests at various blend extents are appeared in Fig. 7.3. The outcomes show that force of Raman pinnacles relies upon the mix piece. As can be seen, the powers of characteristic signals at 1002, 1302, 1602 and 3058 cm^{-1} will in general increment with expanding carbon dark substance in the SBR elastic, though the forces of the confined trademark groups of SBR at 1371, 1128 and 496 cm^{-1} lessening. The top at 1666 cm^{-1} isn't subject to SBR proportion and is utilized as an interior standard. From this relationship, it is conceivable to affirm synthesis in the mixes by plotting the power proportion of trademark sign of each elastic versus mix proportion. It could be noted here that the characteristic signals at 1371 and 1302 cm^{-1} of –CH_3 antisymmetric deformation and =C–H in-plane deformation for SBR, individually, were picked for construct an modification bend. This is on the grounds that these selected tops have the best aims and the characteristic top at 1371 cm^{-1} isn't covered. Raman trademark sign of SBR are not fundamentally changed after expansion of carbon black. This perception is presumably because of the combination of low quantum effectiveness in this recurrence run (647.1 nm) and the frail Raman force of carbon black particles which have an indistinct character. Tragically, pinnacles of SBR appointed to =CC_2 shaking and C–CH_2 extending are situated in a similar recurrence district at 496 and 1000 cm^{-1}, separately, [13]. In this manner, it is hard to recognize the Raman sign of carbon black from those of SBR.

7.4.4 Morphology

Figure 7.4 shows SEM pictures for SBR-carbon black nanocomposites. The estimations were performed legitimately on the break surface (cross area) of the examples utilizing amplification level of multiple times [14, 15]. Morphology of the elastic complex at a variety of filler load up viz. at 2, 6, 10 and 12 phr was researched by scanning electron microscopy (SEM) and micrographs are appeared in Fig. 7.4. Figure 7.4 demonstrates the filler elements are homogenously spread all through the elastic lattice with few totals at 2 phr filler content in rubber composites (Fig. 7.4a)

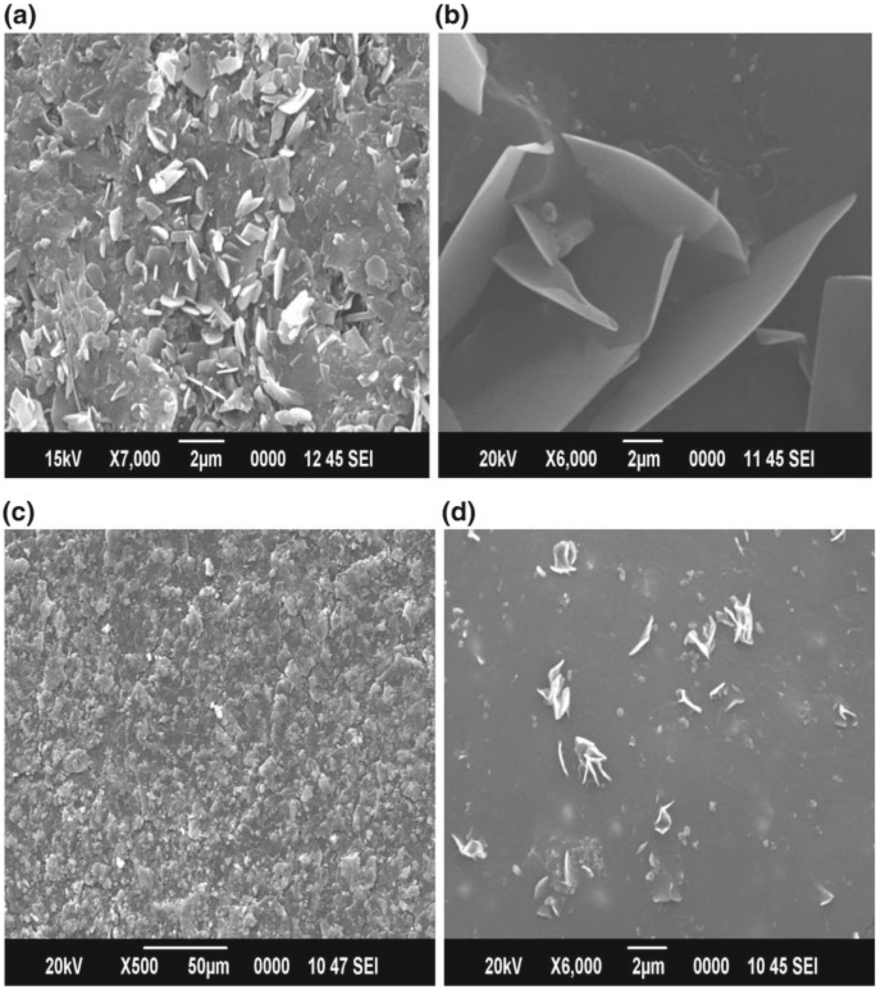

Fig. 7.4 SEM images of SBR-nanocomposite: **a** 2 phr filler, **b** 6 phr, **c** 10 phr, **d** 12 phr

with growth in filler loading (10 and 12 phr), the collection tendency of filler particles growth and it is a lot of overwhelming for elastic grid loaded up with 12 phr (Fig. 7.4d). In Fig. 7.4d, demonstrates the molecule size dispersion is in the scope of 100–150 nm for littler elements while size of larger filler elements totals deception in the scope of 300–450 nm. Homogeneous dispersion of filler into rubber structure is apparent in all plane arranged filler compounds a–d (Fig. 7.4).

7.4.5 Ozone Resistance

SBR elastic nanocomposites vulcanisates show great defense from ozone for the reason that of its polar character. Figures 7.5 and 7.6 reveals the visual photos of the ozone lighted planes of SBR elastic nanocomposites in an ozone compartment at 50 pphm ozone fixations at 380 °C. Inside the principal 4 h itself breaks were formed on the exterior of SBR gum analysis. In any case, it is considered that to be the filler load up is expanded up to 12 wt% the time taken for the initiation of split is extended. For SBR-nanocomposites at 2, 6, 10 and 12 weight percent of carbon black fillings, the breaks were grown after 5, 6, 7 and 8 h separately. It is comprehended that SBR-Carbon black nanocomposites (12 phr) up to specific carbon black substance are fewer disposed to ozone light which shows that the best probable spreading of carbon black in the elastic network is up to that level. The spreading out in carbon black filling verified a more slow improvement and proliferation of breaks.

Elastomers, principally those including energetic twofold bonds in the principle series, are genuinely ambushed by ozone realizing significant parts toward a way inverse to the applied weight. Insurance against ozone assault can be cultivated by the use of antiozonants. A couple of assessments have been represented on the affirmation of versatile against ozone ambush [16]. The pro pack tests shows favored ozone restriction over the basic techniques on account of increasingly unmistakable obstacle to the headway of break front experienced on account of the identical transport of carbon black in the versatile cross section and the superior flexible filler collaboration.

Fig. 7.5 Ozone images of SBR rubber after exposure of 4 h

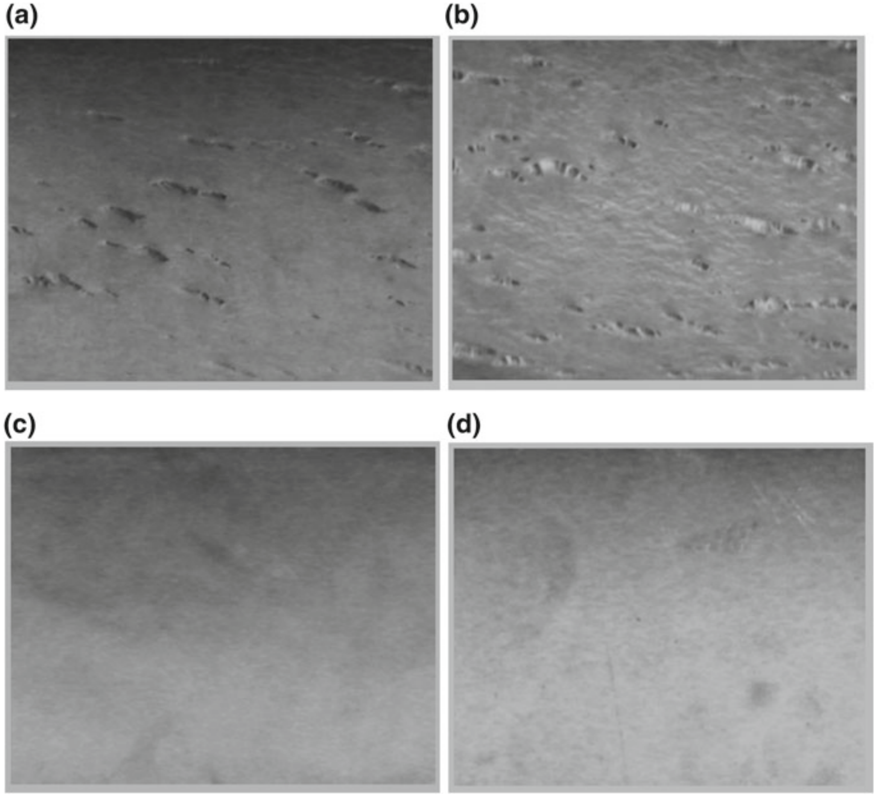

Fig. 7.6 Ozone images of SBR-nanocomposites **a** 2 phr carbon black, **b** 6 phr carbon black, **c** 10 phr carbon black, **d** 12 phr carbon black after exposure of 8 h

7.4.6 Flame Resistance

Fire resistance of vulcanisates of SBR elastic carbon dark nanocomposites were surveyed by UL 94 outline test for instability Vulcanizates of shifting carbon black substance in Styrene Butadiene Rubber were tried according to UL 94 by vertical consume test. SBR-carbon black nanocomposites kept consuming after the burner fire application and flaring dribbles touched off the cotton set beneath the example, yet set aside more effort to finish consuming than unadulterated SBR, showing improvement in fire opposition [17, 18]. In the event that we need to use a framework as a fire retardant, it must qualify under the UL-94 convention. This is just a test that estimates the simplicity of annihilation of a fire and four evaluations are conceivable, contingent on the consuming time and the nearness of blazing dribbles. On the off chance that a material stifles quickly, without trickling, it's managed the ranking V-0; a substance that consumes to some degree longer, yet doesn't dribble, is delegated V-1; a material that doesn't self-smother in a brief timeframe yet dribbles is specified

Table 7.4 Dripping and consuming attributes, just as the UL-94 arrangement for the frameworks

Nanocomposites	Dripping	Consuming	UL-94
Styrene butadiene rubber	Slow	Yes	NC
SBR-carbon black (2 phr)	Slow	Yes	NC
SBR-carbon black (6 phr)	Yes	Little	V-2
SBR-carbon black (10 phr)	Yes	Little	V-2
SBR-carbon black (12 phr)	Yes	Little	V-2

the ranking V-2; if a substance consumes longer than the convention determines, it's said to be not grouped, NC. SBR-carbon black nanocomposites at 2, 6, 10 and 12 phr weight percentage of carbon black stacking indicates fairly improved combustibility property than its gum as given in Table 7.4. This improvement in property is a direct result of the fireproof property of carbon black.

7.5 Conclusions

Rubber-nanocomposite was prepared by the process of emulsion polymerization of SBR with carbon black and other ingredients i.e. accelerators and antioxidants. Morphology of rubber-nanocomposite demonstrates the filler particles are homogenously dissipated all through the flexible cross section. The ace group tests shows preferable ozone resistance over the normal methods because of more noteworthy deterrent to the advancement of break front experienced because of the uniform dissemination of carbon dark in the elastic grid and the improved elastic filler cooperation. Fire obstruction use a framework as a fire retardant, it must qualify under the UL-94 convention. This is essentially a test that estimates the simplicity of elimination of a fire and four evaluations are conceivable, contingent on the consuming time and the presence of flaming drips. SBR-carbon black nanocomposites at 2, 6, 10 and 12 phr weight percentage of carbon black stacking demonstrates to some degree enhanced combustibility property than its gum. This upgrade in property is because of the flame resistant property of carbon black.

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References

1. A. Hoffman, A. Lafosse, Sh Michaelson, M. Bertin, R. Azria, Surf. Sci. **602**, 3026 (2008)
2. H. Du, S.W. Lee, J. Gong, C. Sun, L.S. Wen, Mater. Lett. **58**, 1117 (2004)
3. D.G. Peng, J.S. Zhang, Q.L. Liu, E.W. Taylor, J. Inorg. Biochem. **101**, 1457 (2007)
4. T. Sahin, T. Sınmazcelik, S. Sahin, The effect of natural weathering on the mechanical, morphological and thermal properties of high impact polystyrene (HIPS). Mater. Des. **28**, 2303–2309 (2007)
5. J. Viguie, J. Sukmanowski, B. Nölting, F. Royer, Colloids Surf. A **302**, 269 (2007)
6. C. Nah, Effects of trans-polyoctylene rubber on rheological and green tensile properties of natual rubber/acrylonitrile-butadiene rubber blends. Polym. Int. **51**, 245–252 (2002)
7. C.K. Radhakrishan, A. Rosamma, G. Unnikrishnan, Thermal, ozone and gamma ageing of styrene butadiene rubber and poly (ethylene-co-vinyl acetate) blends. Polym. Degrad. Stab. **91**, 902–910 (2006)
8. P.B. Sulekhaa, R. Josepha, K.N. Madhusoodanan, K.T. Thomas, New oligomer-bound antioxidants for improved flex crack resistance and ozone resistance. Polym. Degrad. Stab. **77**, 403–416 (2002)
9. F. Findik, R. Yilmaz, T. Koksal, Investigation of mechanical and physical properties of several industrial rubbers. Mater. Des. **25**, 269–276 (2004)
10. J. Frohlich, W. Niedermeier, H.D. Luginsland, Compos.: Part A. **36**, 449 (2005)
11. T. Jawhari, A. Roid, J. Casado, Raman spectroscopic characterization of some commercially available carbon black materials. Carbon N. Y. **33**, 1561–1565 (1995)
12. S.W. Cornell, J.L. Koenig, The Raman spectra of polybutadiene rubbers. Macromolecules **2**, 540–545 (1969)
13. P.J. Hendra, K.D.O. Jackson, Applications of Raman spectroscopy to the analysis of natural rubber. Spectrochim. Acta A Mol. Spectrosc. **50**, 1987–1997 (1994)
14. T.A. Vilgis, Polymer **46**, 4223 (2005)
15. C.A. Rezende et al., Natural rubber-clay nanocomposites: mechanical and structural properties. Polymer **51**, 3644–3652 (2010)
16. N. Celette, I. Stevenson, L. Devenas, G. David, Vigier, IRAP Nucl. Instr. Meth. B. **185**(2001), 305, (2000)
17. D. Wang, K. Echols, A.W. Charls, Fire Mater. **29**, 283 (2005)
18. J.C. Wang, W.L. Hao, Effect of organic modification on structure and properties of room-temperature vulcanized silicone rubber/montmorillonite nanocomposites. J. Appl. Polym. Sci. **129**, 1852–1860 (2013)