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Synthesis and characterization of SBR- nanocomposite with Carbon black nanoparticle.

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ABSTRACT

Styrene-butadiene copolymer (SBR) nanocomposite is prepared by emulsion polymerization method. SBR latex and carbon black suspension both are mixed and mixture is coagulated at room temperature and forming a SBR- nanocompound by emulsion polymerization method. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetry analysis (TGA, DTA) these properties of the composites are found to improve as carbon black content increases in the composites. Thermal activation energy (E_a) and the order of reaction (n) these kinetic parameters are calculated by using Freeman- Carroll and Sharp- Wentworth method.

Keywords: Styrene- Butadiene rubber, Nanocomposite, Emulsion polymerization method, Carbon black.

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INTRODUCTION

Recently, rubber clay nanocomposites have considerable attraction due to their unique properties, such as enhanced fire retardance, improved physical properties, and improved heat resistance [1-9]. Styrene-Butadiene rubber is an important and widely used synthetic rubber which has many applications. The high filler loading capacity, abrasion resistance and crack initiation resistance. Blends of NR and SBR have been exhibit improved oxidative stability compared to pure component [10]. Polymer materials could be used in various fields especially as the matrix in reinforced composite materials. One of these fields is composite materials [11]. The commercial importance of polymers has been driving intense applications in the form of composites in various fields. In these materials, based on the size of additives, there are some categories of these composites. If the size of additives to the polymeric based composites is less than 100 nm, this category of composites named nanocomposites. Nanocomposites based on polymeric materials have been attracted in recent years [12]. Carbon black is the most important reinforcing filler used in rubber industries. Carbon black is also used as conductive filler in a binary immiscible polymer blends [13-18]. Reinforcement by fillers, especially carbon black, is one of the most important aspects of rubber technology. For a long time technologists accepted the fact that the addition of carbon black gave improved properties to rubber vulcanisates. Increased reinforcement has been defined as increased modulus, rupture energy, tear strength, tensile strength and abrasion resistance. A practical definition of reinforcement is the improvement of the service life of a rubber article [19, 20].

Concentration and type of carbon black affect dispersion of carbon black in the rubber matrix [21]. Carbon black agglomerates and resulting interactions can control the properties and viscoelastic parameters of the compound [22]. In order to have a good adhesion between filler and polymer, surface treatments are therefore needed to improve the wettability of carbon surfaces by promoting the formation of hydrophilic groups, which increase the surface energetic [23]. carbon black is to incorporate polymer matrices with it to act as an electrically conductive filler to improve the conductivity. An electromagnetic shielding material is a material that weakens radiated electromagnetic energy. Although the use of polymers for housing the electronic device is popular due to their light weight, flexible and less expensive characteristics when compared to metal, polymers are electrically insulating and transparent to electromagnetic radiation [24]. In this work, we prepared SBR- nanocomposites copolymer with the use of carbon black as a filler by emulsion polymerization method. Fourier transform infrared (FTIR), Scanning electron microscopy (SEM) and thermal properties (TGA, DTA) were studied. Studies were further extended to thermogravimetric analysis in order to predict its kinetic parameters by implementing Freeman- Carroll and Sharp-Wentworth method.

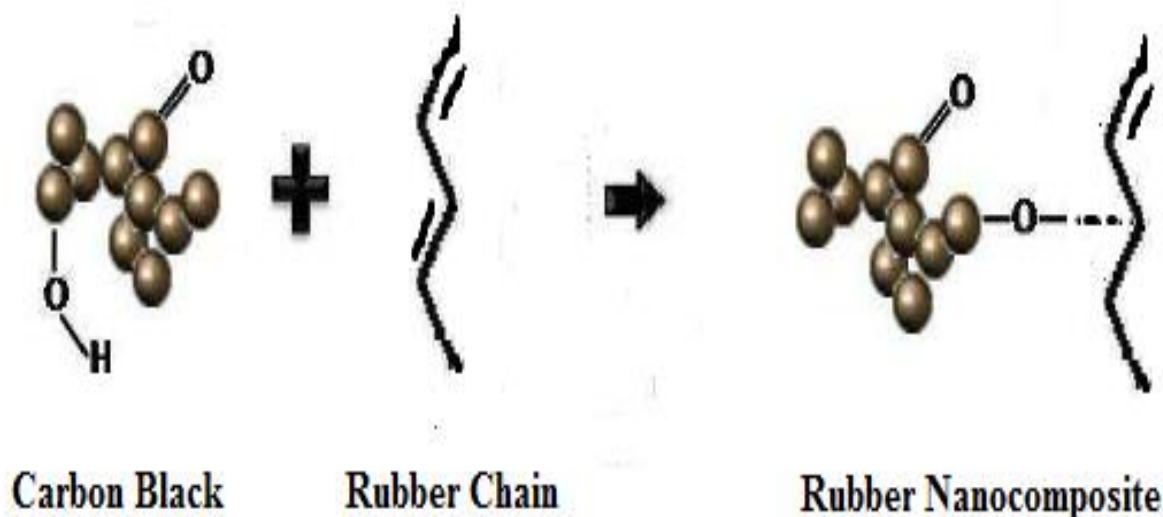


Fig 1: Schematic diagram of SBR- carbon black nanocomposites

EXPERIMENTAL

Materials

Nanocomposites were purchased 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 (from Post Graduate Department of chemistry Kamla Nehru Mahavidyalaya, Nagpur, India). Styrene butadiene rubber purchased from shree Radha Polymer Company, Nagpur, India.

Preparation of SBR- nanocomposite

Carbon black was dispersed in toluene with vigorous stirring and carbon black suspension was obtained at room temperature. Then SBR latex were added into the carbon black suspension and stirred up to uniform mixing of carbon SBR into the carbon black. The mixture was coagulated at room temperature. Then washed with water several times and then dried at 70°C for 12h. Then SBR- nanocompound was formed.

Compounding of rubber

SBR- nanocompound was mixed with various ingredients shown in the table 1. The SBR- nanocompound then were vulcanized at 150°C. The mixture of SBR- nanocompound were directly used on two- roll mill and mixing for 15 min., then adding all necessary ingredients which are listed in table 1 and mixing for 10 min. After that the resultant compound were vulcanized at 150°C.

Table 1: Formulation of rubber compound

Ingredients	Phr				
	1	2	3	4	5
SBR	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 (TMTD)	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

CHARACTERIZATION

Fourier- transform infrared spectroscopy (FTIR)

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

Scanning electron microscopy (SEM)

The surface morphology of SBR- nanocomposites were investigated by using scanning electron microscope JEOL (JSM- 6390) at an acceleration voltage of 3 kV (from sophisticated Analytical Instruments Facility, SAIF, Cochin).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the vulcanizates was carried out by a Perkin Elmer Thermal Analyser. Thermal stability and filler content of the rubber composites were determined by thermogravimetric analysis and differential thermal analysis. The sample was placed on pan and heated in temperature range of RT to

700°C under air and heating rate was 10°C/min (from sophisticated Analytical Instruments Facility, SAIF, Cochin).

RESULTS AND DISCUSSION

FTIR Spectroscopy

FTIR (Fourier- transform infrared spectroscopy) spectra of different loadings levels of carbon black shows in (fig 2). In all these spectra, the broad peak at 3400 cm^{-1} is assigned to stretching vibration of -OH group stretching vibrations along with adsorbed water. The peaks at 950 cm^{-1} and 860 cm^{-1} are due to C-H bending of aromatic ring in carbon black. The peak at 1100 cm^{-1} and 470 cm^{-1} are due to asymmetric and symmetric stretching. The presence of two sharp peaks at 2930 cm^{-1} and 2840 cm^{-1} and one peak around 1450 cm^{-1} for all the spectra of SBR-filler in addition of the absorption bands corresponding to the vibration of specific functional group. These small peaks of around 2930 cm^{-1} and 2840 cm^{-1} are characteristic bands of symmetric and antisymmetric stretching vibrations of -CH_2 group respectively. 1450 cm^{-1} corresponding to bending vibrations of -CH_2 group. All these peaks are observed in spectra of SBR-nanocomposites in (fig 2). This is also supported by the presence of band at $1,080\text{ cm}^{-1}$ which is characteristic band of alkene group. The peak at $1,750\text{ cm}^{-1}$ of carbon black before and after CO activation which indicates the presence of C = O functional groups characterized by aldehydes, ketones, carboxylic acids and esters. The presence of band at $2,550\text{ cm}^{-1}$, which is characteristic band of C=C aromatic group [25]. In the case of carbon black, the filler-polymer interaction is mainly of physical nature [26].

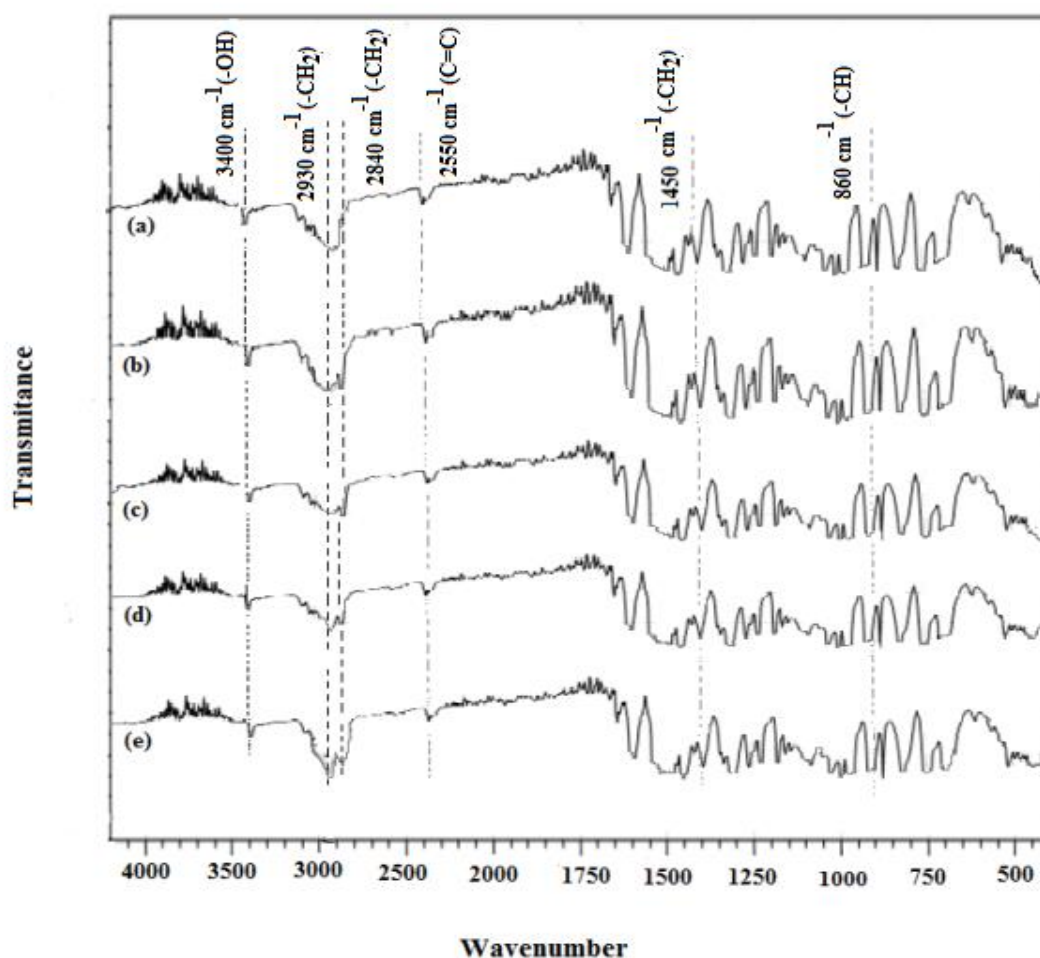


Fig 2: FTIR (Fourier- transform infrared spectroscopy) spectra of SBR- nanocomposite (a) unfilled composites (b) 2 phr carbon black in SBR (c) 6 phr carbon black in SBR (d) 10 phr carbon black in SBR (e) 12 phr carbon black in SBR

Morphology

Morphology of the rubber composites at different filler loading viz. at 2 phr, 6 phr, 10 phr and 12 phr was investigated by scanning electron microscopy (SEM) and micrographs are shown in (fig 3). (fig 3) shows the filler particles are homogenously dispersed throughout the rubber matrix with few aggregates at 2 phr filler content in rubber composites (fig 3) (a) with increase in filler loading (10 and 12 phr), the aggregation tendency of filler particles increases and it is much dominant for rubber matrix filled with 12 phr (fig 3) (d). In (fig 3) (d), shows the particle size distribution is in the range of 100 to 150 nm for smaller particles while size of larger filler particles aggregates lies in the range of 300 to 450 nm. Uniform dispersion of filler into rubber matrix is evident in all surface modified filler composites (a) to (d) (fig 3).

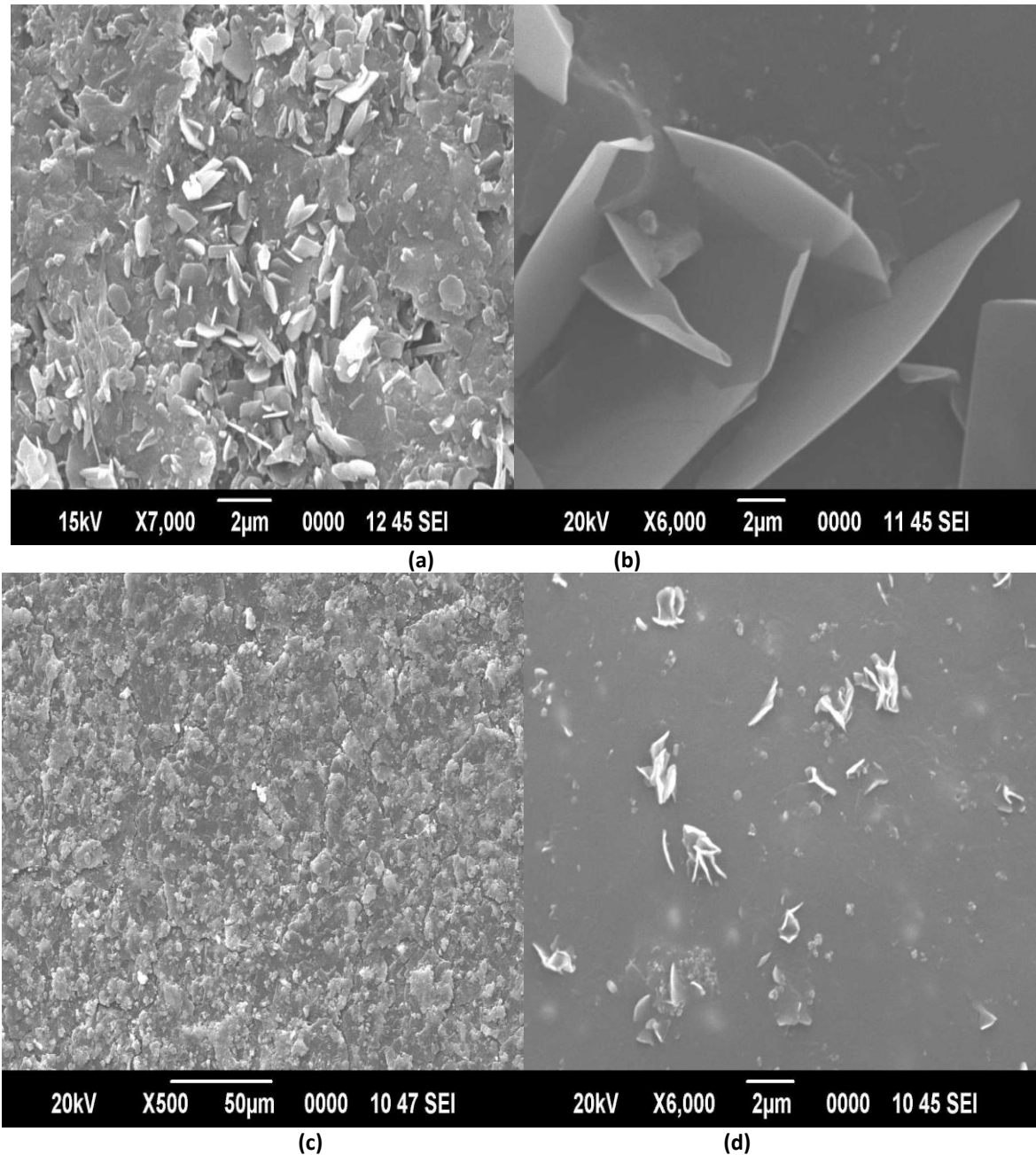


Fig 3: Scanning electron microscopy (SEM) images of SBR-nanocomposite: (a) 2 phr filler, (b) 6 phr, (c) 10 phr, (d) 12 phr.

Thermogravimetric analysis

Thermogravimetric analysis was performed to evaluate the thermal stability of the composites in (fig 4). The amount of carbon black content in the rubber composites are determined from residual weight percentage of a particular composites. Thermogravimetric curves are similar for all the rubber composites (1-5). First weight loss observed at the temperature range 350°C to 480°C is due to degradation of rubber component. The next weight loss appear at the temperature range 550°C to 640°C is due to carbonaceous residue [27]. Temperature at maximum weight loss (T_{max}) is given from the peak of DTG curve. All the composites show similar thermal stability and T_{max} is found to be 260°C and 445°C, respectively, for all composites. With the help of thermogravimetric data the thermal activation energies (E_a) and order of reaction (n) calculated reported in the table 2.

Table 2: Result of Kinetic parameters of SBR- carbon black nanocomposites

Composite	Order of reaction (n)	Activation energy (KJ/mol) (E_a)	
		F.C	S.W
SBR- carbon black	0.40	3.76	2.97

To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth and Freeman-Carroll. The ‘average E_a ’ calculated by Freeman-Carroll (3.76 KJ/mole) and ‘average E_a ’ by Sharp- Wentworth (2.97 KJ/mole) is nearly same.

Sharp -Wentworth method:

Using the equation derived by Sharp and Wentworth (1),

$$\log [(dc/dT)/(1-c)] = \log (A/\beta) - [E_a/2.303R]. 1/T \dots\dots\dots(1)$$

Where,
 dc/dT = rate of change of fraction of weight with change in temperature
 β = linear heating rate dT/dt .

By plotting the graph between $(\log dc/dt)/(1-c)$ vs $1/T$ we obtained the straight line which give energy of activation (E_a) from its slope. Where β is the conversion at time t , R is the gas constant (8.314 Jmol⁻¹K⁻¹) and T is the absolute temperature. The plots (fig 5) give the activation energies at different stages of degradation reaction take place.

Freeman-Carroll method:

The straight-line equation derived by Freeman and Carroll, which is in the form of n

$$[\Delta \log (dw/dt)] / \Delta \log W_r = (-E / 2.303R). \Delta (1/ T) / \Delta \log W_r + n \dots\dots\dots(1)$$

Where,
 dw/dt = rate of change of weight with time.
 $W_r = W_c - W$
 W_c = weight loss at completion of reaction.
 W = fraction of weight loss at time t .
 E_a = energy of activation.
 n = order of reaction.

The plot between the terms $[\Delta \log (dw/dt)] / \Delta \log W_r$ Vs $\Delta (1/T) / \Delta \log W_r$ gives a straight line from which slope we obtained energy of activation (E_a) and intercept on Y-axis as order of reaction (n) (fig 6) and (fig 7).

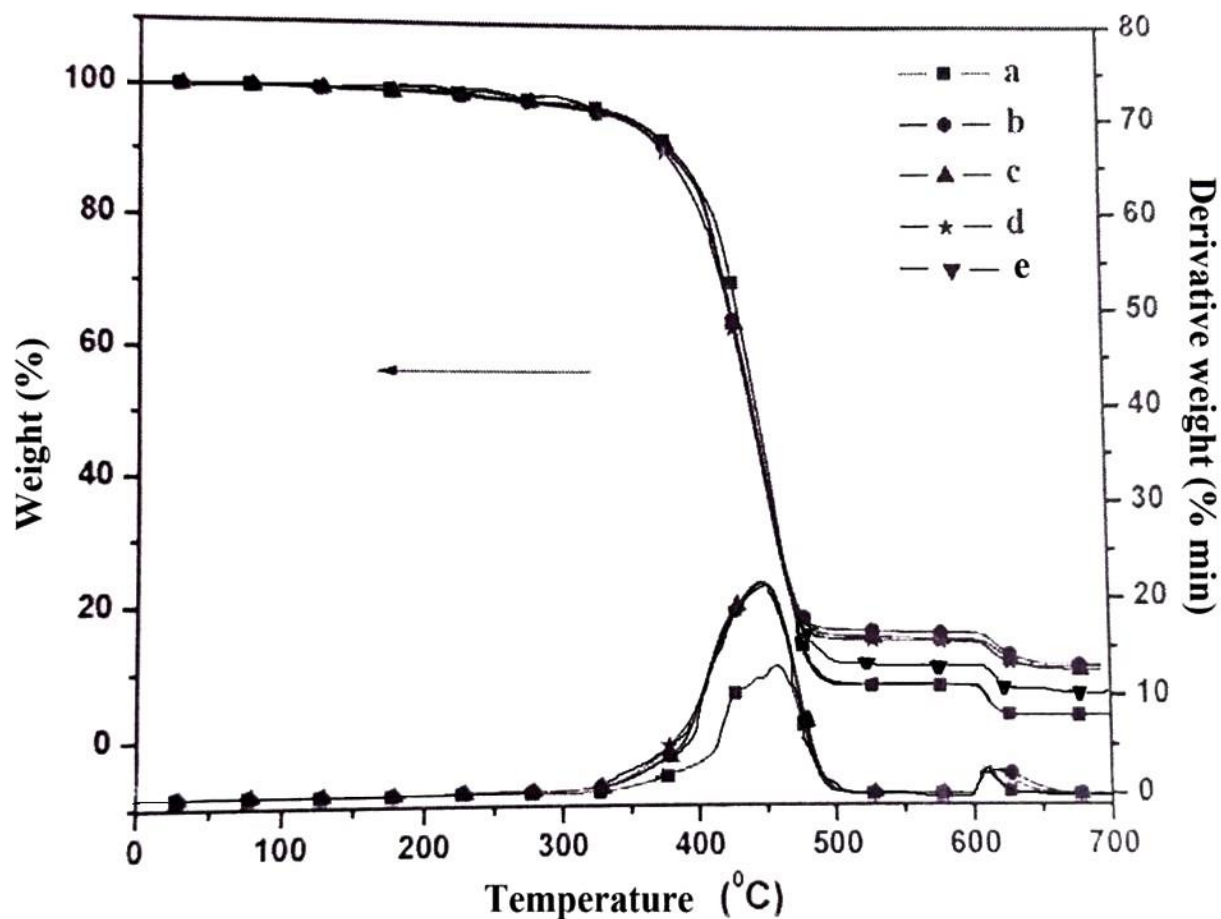


Fig 4: Thermogravimetric curves of SBR- nanocomposite (a) unfilled composites (1) (b) 2 phr carbon black in SBR (2) (c) 6 phr carbon black in SBR (3) (d) 10 phr carbon black in SBR (4) (e) 12 phr carbon black in SBR (5)

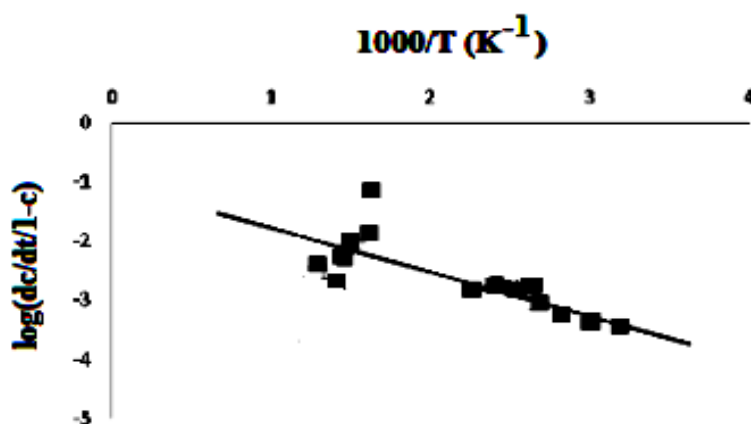


Fig 5: Sharp- Wentworth plot of SBR- carbon black nanocomposites

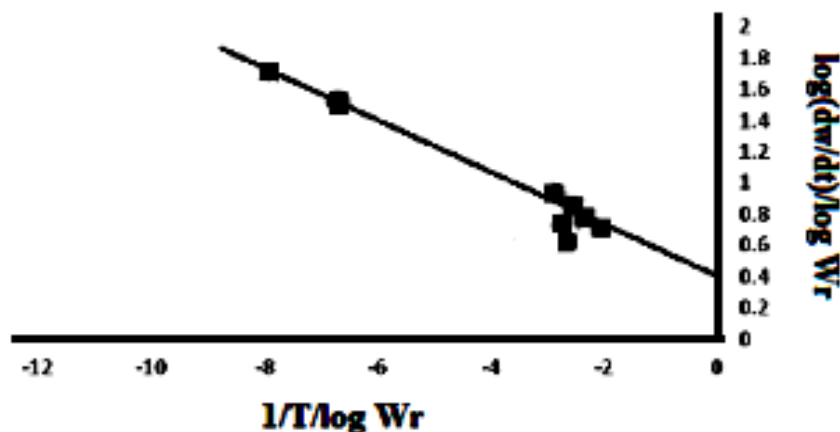


Fig 6: Thermal activation energy plot of SBR- carbon black nanocomposites

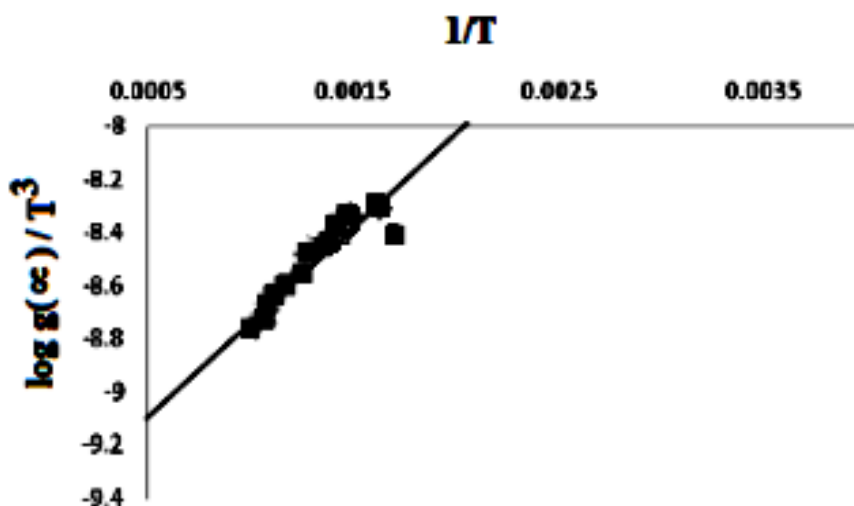


Fig 7: Freeman- Carroll plot of SBR- carbon black nanocomposites

CONCLUSIONS

SBR- nanocomposite is prepared by coagulation of SBR latex and carbon black suspension. Addition of carbon black in SBR rubber are improved the FTIR properties by using the emulsion polymerization method. SBR- CB nanocomposites are expected to be good candidates for inner materials. Emulsion polymerization method causes to much more improvement in the properties. Morphology study shows uniform carbon black dispersion in rubber matrix as evidenced by SEM images. Improvement in thermal stability of rubber nanocomposite is also observed in thermogravimetric analysis. The activation energy values are calculated by using Freeman- Carroll method and Sharp- Wentworth method. Hence, better improvement in rubber matrix.

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