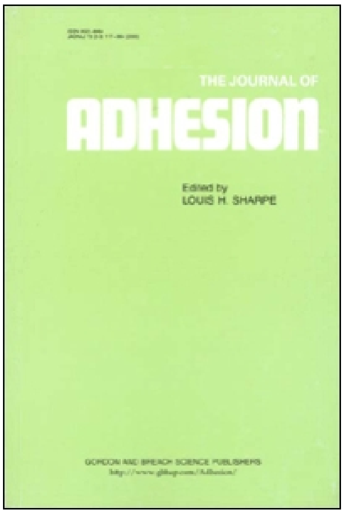

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Characterization of EPDM Vulcanizates Modified with Gamma Irradiation and Trichloroisocyanuric Acid and Their Adhesion Behavior with Natural Rubber

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The adhesion strength between surface-modified vulcanized ethylene propylene diene methylene (EPDM) rubber and unmodified natural rubber (NR) was investigated by a 180° peel test. Surface modification of EPDM vulcanizate was carried out by two different techniques: (a) irradiation of the surface by gamma radiation in the presence and absence of trimethylol propane triacrylate (TMPTA) as a sensitizer and (b) chemical treatment of the surface with trichloroisocyanuric acid (TCICA). The modified EPDM surface was thoroughly characterized by attenuated total reflection infrared spectroscopy (ATR-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), energy dispersive X-ray sulfur mapping (EDX), surface energy measurements, and free sulfur and gel content analysis. The joint between the modified vulcanized EPDM and the unmodified unvulcanized NR was prepared by a co-curing method. The adhesion strength between these two surfaces was found to depend on the nature of oxidation, roughness of the joining surfaces, and extent of blooming of sulfur on the modified surface. Surface modification of EPDM sample with 1 kGy of gamma irradiation in the presence of 10 wt% TMPTA resulted in a good increase in the adhesion strength between EPDM and NR (~76% improvement over the untreated sample). On the other hand, for the trichloroisocyanuric acid modified sample, maximum improvement of adhesion strength was observed at 0.5 wt% of TCICA (~29% improvement in comparison with the untreated sample).

Keywords: 180°-Peel test; Adhesion; Co-curing; EPDM vulcanizate; Gamma irradiation; Trichloroisocyanuric acid

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1. INTRODUCTION

It is rare to get a material whose surface and bulk properties are excellent for a particular application [1]. In specific applications, both properties may be essential and, occasionally, surface properties play the major role in comparison with bulk properties. Ethylene propylene diene methylene rubber (EPDM) is such an elastomeric material having superior bulk properties as compared with its surface. Naturally, EPDM could never be an automatic choice when surface properties are of prime importance. Hence, improvement of surface properties of the EPDM rubber is essential, without affecting its bulk properties, since it has high commercial importance. However, the adhesion between EPDM elastomer and other elastomers is generally poor due to its poor surface properties. Additionally, EPDM rubbers are usually crosslinked in all applications and it is well known that the adhesion of any rubber further deteriorates after vulcanization. This is because during crosslinking, compounding ingredients like stearic acid, sulfur, etc., migrate towards the polymeric surface and create a barrier between adsorbent and adsorbate [2]. Therefore, improving the surface properties of EPDM without altering its bulk properties is essential for its adequate adhesion. In the literature, different techniques have been reported for the surface modification of EPDM rubber: (a) physical blending [3], (b) oxidation [4], (c) chemical reaction [5,6], (d) corona discharge, plasma, and laser beam irradiation [7–9], (e) ozone treatment [10], and (f) incorporation of surface grafting agent [11,12].

Generally, gamma (γ) irradiation is effectively utilized for the modification of different polymer surfaces due to its higher penetrating power as well as negligible heat formation and this technique can be used without incorporating any photosensitizer in the polymer [13]. In addition, it is a slow process that takes more time for modification and, as a result, higher oxygen concentration on the polymeric surface enhances the chances of surface oxidation [14]. Other chemical changes that occur due to gamma exposure include: (a) scission and chain crosslinking, (b) formation of gases and low molecular weight compounds, and (c) formation of unsaturated products and sometimes discoloration of the products, especially for those plastics that undergo sterilization before use [15]. However, it has been reported that by carefully monitoring the experimental conditions (*e.g.*, monomer concentrations, irradiation dose, etc.) used for surface modification of polymer surface by gamma irradiation (γ), the final properties of the materials can be tailored in order to produce new materials for specific applications [16].

On the other hand, modification of rubber surfaces using a halogenation technique is one of the most popular chemical methods used for the past two decades [17–22]. Though halogenation creates a health hazard due to the release of chlorinating agent into atmosphere, this could be minimized by incorporating an aromatic moiety such as trichloroisocyanuric acid (TCICA) in the composition [19]. Literature reports reveal that this reagent not only modifies a surface but also changes its morphology [19]. It has been found that the effectiveness of this chlorinating agent depends upon the concentration of TCICA used, the nature of the rubber, the nature of ingredients compounded with the rubber, modification time, and the nature of the solvent used to prepare the TCICA chlorinating solution [17]. Literature reports also reveal that the effectiveness of halogenation can be enhanced by using low evaporating solvents [22]. But these solvents are generally not capable of removing anti-adhering compounds at the surface as compared with the solvents with a higher evaporation rate.

In the literature, there are several reports that examine the adhesion between "polymer to polymer" [23–29], whereas, relatively very few studies are available to the date on adhesion between "rubber to rubber" [30–35]. Moreover, there is no report in the open literature that examines the adhesion between uncured and cured elastomers. There are only a few reports in the patent literature that discuss this issue [36–38]. Recently, we have studied the adhesion between electron beam-modified vulcanized EPDM and unmodified NR; it has been found that the contribution of mechanical interlocking (increasing roughness of the modified surface), chemical interaction (formation of polar groups), and removal of anti-adherent substances (*e.g.,* stearic acid, blooming sulfur, etc.) from the modified surface are very important [39].

In this present work, we have investigated the adhesion between vulcanized EPDM and unvulcanized NR through a co-curing technique. The adhesion strength between EPDM and NR has been enhanced by modifying the surface of the vulcanized EPDM rubber by two techniques. In the first technique, the surface of the EPDM has been modified by γ-irradiation in the presence and absence of TMPTA. In the second technique, the EPDM has been modified by TCICA, a chemical agent. The irradiation dose has been varied from 0.5–3 kGy with and without using 10 wt% TMPTA. On the other hand, the concentration of TCICA has been varied from 0.01–1 wt% in the chemical method. In addition, for the first time, ethyl acetate, a solvent having a moderate evaporation rate, has been used to prepare the TCICA solution and its effect on adhesion strength has been reported.

2. EXPERIMENTAL

2.1. Materials

Ethylene propylene diene methylene rubber [EPDM with E: P 52/48 mol/mol containing ethylidene norbornene as termonomer (4.8 wt%), $ML_{(1+4)}$ at 100°C = 45, density = 860 kg/m^3] was supplied by Uniroyal Chemicals, Middlebury, Connecticut, USA. Natural Rubber [(NR), ISNR-5, molecular weight, $M_W = 7.8 \times 10^5$] was procured from the Rubber Board, Kottayam, India. Trimethylol propane triacrylate [(TMPTA), Flash point >100°C (Cleveland Open Cup), boiling point >100°C, density = 111 kg/m^3] was obtained from UCB Chemicals, Brussels, Belgium. Methyl ethyl ketone (MEK) of chemically pure grade was provided by E. Merck Ltd., Mumbai, India. Formamide (R.I. 1.446–1.448) was purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. Ethyl acetate (Boiling range 70–78°C, density = 899–902 kg/m^3) was supplied by Nice Chemicals Pvt. Ltd., Cochin, India. Trichloroisocyanuric acid was procured from Sigma-Aldrich, Munich, Germany.

2.2. Sample Preparation

2.2.1. Surface Modification

The NR and EPDM were compounded with the requisite ingredients in a two-roll mixing mill (Schwabenthan, Berlin, Germany), as per the formulation given in Table 1. The mixes were compression molded at a temperature of 150°C and a pressure of 5 MPa for 15 minutes in an

TABLE 1 Formulation for the Unmodified Cured EPDM Rubber Vulcanizate and the Unmodified Uncured NR

EPDM		NR	
Ingredients	*phr	Ingredients	*phr
EPDM	100.0	NR	100.0
Stearic acid	1.5	Stearic acid	2.0
ZnO	5.0	ZnO	5.0
S	1.2	Polymerised 1,2-dihydro-2,2,4-trimethylquinoline (TQ)	1.0
Mercaptobenzothiazole (MBT)	0.5	S	2.5
Tetramethyl thiuram disulphide (TMTD)	1.2	N-Cyclohexylbenzothiazyl sulphenamide (CBS)	1.2
		Dibenzthiazyl disulphide (MBTS)	1.0

*phr—parts per hundred grams of rubber.

electrically heated press (David Bridge, Castleton, England). During molding, rectangular sheets having dimensions 15 cm wide × 15 cm length × 0.15 cm thick were formed. The cure time was calculated from a Monsanto rheometer (Model No. S100, Monsanto, Akron, OH, USA). These were then completely immersed in a solution containing 10 wt% TMPTA in MEK and similarly 0.01 to 1 wt% TCICA in EA. After 12 h, the sheets dipped in either TMPTA or TCICA were taken out from the solution and air dried for 30 min at 25°C and finally washed four to five times with acetone.

2.2.2. Irradiation of Samples

The compression molded EPDM rubber sheets, as designated in Table 2, were irradiated by gamma irradiation at the Board of Research in Nuclear Sciences (BRNS), Mumbai, India. Irradiation doses of 0.5 to 3 kGy were used. The irradiation was carried out in a ^{60}Co gamma chamber, GC- 5000 (BRIT, Navi Mumbai, India) at a dose rate of 320 kGy h^{-1}. The dose rate was determined using a Fricke dosimeter.

2.2.3. Sample Preparation for Peel Strength Measurement

The preshaped uncured NR (15 cm wide × 15 cm length × 0.15 cm thick) was prepared by pressing them at 100°C for 2 min between

TABLE 2 Designation of the Samples Used for the Study

Sample designation	Irradiation dose (kGy)	TMPTA concentration (wt%)
$^{*}\mathbf{EP}_{0kGy}$	Without irradiation	
$\mathbf{EP}_{xkGy/0}$	X = 0, 0.5, 1, 1.5, 2, 3	–
$\mathbf{EP}_{xkGy/10TM}$	X = 0, 0.5, 1, 1.5, 2, 3	10
$^{@}\mathbf{EP}_{\mathbf{xkGy/0\ (c)}}\text{-}\mathbf{NR}_{\mathbf{(UC)}}$ and $^{@}\mathbf{EP}_{\mathbf{xkGy/10TM\ (c)}}\text{-}\mathbf{NR}_{\mathbf{(UC)}}$		
Sample designation	**TCICA concentration (wt %)**	
$^{*}\mathbf{EP}_{0TCICA}$	Without TCICA	
$\mathbf{EP}_{zTCICA}$	Z = 0, 0.01, 0.1, 0.5, 1	
$^{\$}\mathbf{EP}_{\mathbf{zTCICA(c)}}\text{-}\mathbf{NR}_{\mathbf{(UC)}}$		

$^{*}\mathbf{EP} =$ EPDM rubber, $\mathbf{EP}_{0kGy} = \mathbf{EP}_{0TCICA}$ means untreated vulcanized EPDM rubber surface.

$^{@}\mathbf{EP}_{\mathbf{xkGy/0\ (c)}}\text{-}\mathbf{NR}_{\mathbf{(UC)}}$, Here $\mathbf{EP}_{\mathbf{xkGy/0(c)}}$ means cured modified EPDM rubber vulcanizate with varying irradiation dose (0 to 3 kGy) and $\mathbf{EP}_{\mathbf{xkGy/10TM\ (c)}}$ implies cured modified EPDM rubber vulcanizate with varying irradiation dose (0 to 3 kGy) in presence of 10 wt.% TMPTA.

Similarly $EP_{\mathbf{z(c)}}$ in $^{\$}\mathbf{EP}_{\mathbf{z(c)}}\text{-}\mathbf{NR}_{\mathbf{(UC)}}$ means vulcanized surface modified with TCICA (trichloroisocyanuric acid). Here, Z stands for concentration of TCICA and C means cured EPDM rubber.

$\mathbf{NR}_{\mathbf{(UC)}}$=designation of uncured rubber.

smooth aluminium foils at 5 MPa pressure in an electrically heated press. The surface-modified EPDM vulcanized rubber sample (15 cm wide × 15 cm length × 0.15 cm thick) was kept in the 3-mm mold cavity having an aluminium foil of 2-cm width on its upper portion. The Al foil is inserted to provide arms for the 180° peel test. The preshaped unvulcanized and unmodified NR was placed over the modified samples. The EPDM-NR assembly was co-cured in the hot molding press at a temperature of 150°C and a pressure of 5 MPa until curing of the uncured NR was completed. A 10-min cure time was provided, which was calculated using a Monsanto rheometer (Model No. S100).

3. CHARACTERIZATION OF THE SAMPLES

3.1. Fourier Transform Infrared (FTIR) Spectroscopic Analysis

Unmodified and modified rubber samples were subjected to attenuated total reflection (ATR)-FTIR spectra in the range of 4000 to 650 cm^{-1} using an infrared spectrophotometer (Nicolet Nexus, Madison, WI, USA). The spectra were obtained at a resolution of 4 cm^{-1} using a zinc selenide crystal. An average of 120 scans was reported for each spectrum.

3.2. Gel Fraction Measurements

Previously weighed samples were immersed in n-heptane at 35°C for 12 h to reach equilibrium. The test specimens were taken out thereafter and dried in open atmosphere to a constant weight. The percent gel fraction was calculated using Eq. (1):

$$\text{Gel content} = (\text{W}_2/\text{W}_1) \times 100, \tag{1}$$

where W_1 = initial weight of the polymer and W_2 = weight of the insoluble portion of the polymer after immersion in solvent.

3.3. Calculation of Surface Energy

Surface energy of the modified rubber vulcanizates was calculated through contact angle (θ) measurements using the Owens and Wendt equation (Eq. (2)) [40]:

$$\cos\theta = -1 + \frac{2(\gamma_s^d \gamma_l^d)^{1/2}}{\gamma_l} + \frac{2(\gamma_s^p \gamma_l^p)^{1/2}}{\gamma_l}, \tag{2}$$

where γ^d and γ^p are the dispersion and the polar components of the free surface energy of liquid and solid, respectively (s = solid and l = liquid).

Bidistilled water and formamide were selected as the probe liquids. The surface parameters of these liquids were taken from the literature for calculating contact angle (θ) [41].

3.4. Free Sulfur Estimation

Free sulfur was estimated in the unmodified and few modified EPDM vulcanizates according to the standard ASTM test method D297-72A.

3.5. Scanning Electron Microscopy (SEM)

The surface topography of the neat, gamma, and TCICA modified samples were examined by using a JEOL JSM-800 scanning electron microscope (JEOL JSM-800, Tokyo, Japan) operating at an accelerating voltage of 20 kV. The samples were sputter coated with gold before analysis.

3.6. Energy Dispersive X-Ray Sulfur Mapping (EDX)

EDX of the surfaces of the unmodified and the modified EPDM vulcanizates was also concurrently carried out in an Oxford EDX system attached to the scanning electron microscope (JEOL JSM-800, Tokyo, Japan).

3.7. Atomic Force Microscopy (AFM)

The morphology of the unmodified EPDM, γ-, and TCICA-modified EPDM vulcanizates was investigated by atomic force microscopy (AFM). The experiments were carried out in air at 25°C and 60% RH, utilizing a multimode AFM instrument from Veeco Digital Instruments, Santa Barbara, CA, USA. Topographic phase images were recorded in the tapping mode (TMAFM) with a set point ratio of 0.9 with the help of a rotated tapping etched silicon probe (RTESP) tip having a spring constant of 40 N/m. The cantilever was oscillated at a resonance frequency of ~280 kHz. The changes in surface topography were determined quantitatively by the root mean square (RMS) roughness (Rq) and mean roughness (Ra) calculation, respectively.

3.8. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra of the samples were taken in a KRATOS-AXIS165 instrument (Kratos Analytical, Manchester, UK) equipped with dual aluminium–magnesium anodes using MgKα

radiation. The X-ray power supply was run at 15 kV and 5 mA. The working pressure in the instrument was 10^{-9} Torr. The peak positions were based on calibration with respect to the C_{1s} peak at 284.6 eV. The XPS spectra were fitted by nonlinear squares method with the convolution of Lorentzian and Gaussian functions after the polynomial background subtraction from the raw data.

3.9. Adhesion Measurements

Peel testing at 180° was done for all the samples on a Zwick UTM, Model Z010 (Zwick GmbH and Co., Ulm, Germany) using a strain rate of 50 mm/min at 25°C. All the joints were tested within 4 h after preparation of the samples. The peel strength (G_c) was calculated by using the following equation (Eq. (3)):

$$G_c = 2F/w, \tag{3}$$

where F is the average peel force and w is the width of the specimen. Peel tests were conducted over a range of peel rates from 50 to 150 mm/min. One side of the EPDM and NR rubber sheets were backed by a fabric having ~1 mm thickness in order to prevent the material from stretching.

4. RESULTS AND DISCUSSION

4.1. Characterization of Unmodified EPDM Vulcanizate Surface

In the current investigation, the standard formulation used for the EPDM vulcanizate is given in Table 1. The ratio of sulfur to accelerator used was 1.2:1.7. The unmodified vulcanizate surface was characterized by using ATR-IR, XPS, and SEM techniques.

4.1.1. ATR-IR Spectroscopy

Figure 1 shows the ATR-IR spectrum of the untreated vulcanized EPDM rubber surface. Some significant absorption peaks are depicted in Table 3. The characteristic peaks of EPDM are observed at 2926 and 2856 cm^{-1} (saturated hydrocarbon backbone), 1460 cm^{-1} (CH_2 scissoring), 1376 cm^{-1} (CH_3 stretching), and 722 cm^{-1} (CH_2 rocking for long ethylene sequence). Compounding ingredients utilized for this study display their corresponding absorption peaks as well. For example, the peak appearing at 1538 cm^{-1} is attributed to the asymmetric –C=O band of Zn-stearate present in the system. Likewise, the

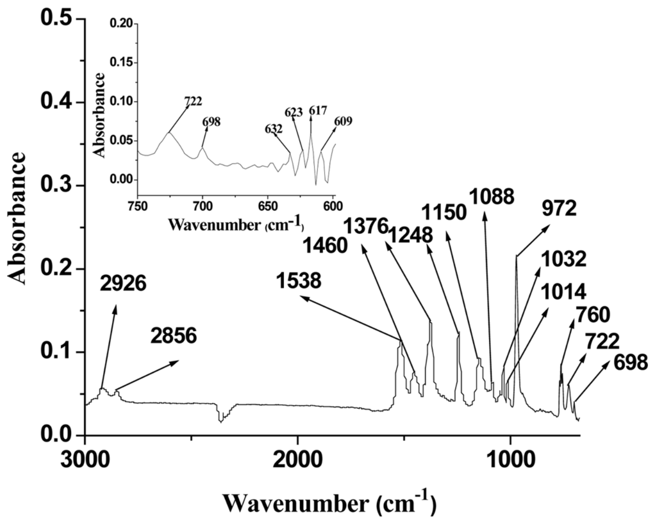


FIGURE 1 ATR-IR spectra of untreated vulcanized EPDM rubber surface.

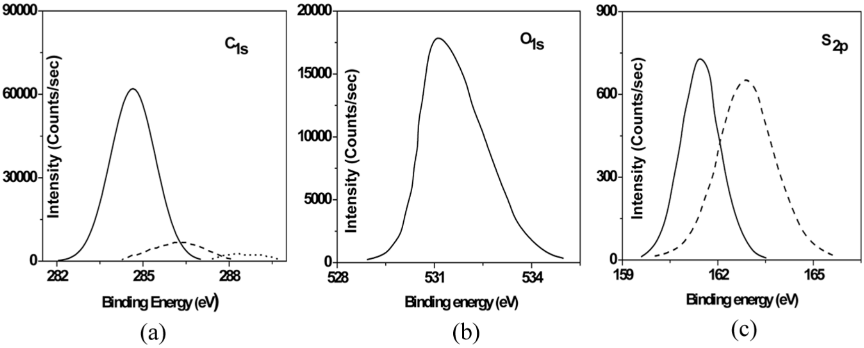
TABLE 3 Characteristic Infrared Peaks of EPDM Rubber Vulcanizate

Observed region (cm^{-1})	Peak assignment
	Unmodified and modified samples
2926 and 2856	Saturated HC backbone of aliphatic alkyl asymmetric/symmetric stretching vibration
1538	Asymmetric “C–O bond stretching vibration for Zn-stearate
1460	$>CH_2$ scissor vibration
1376	$-CH_3$ stretching vibration
1248	C–C stretching vibration for residual MBT
1150	CH in plane stretching vibration for residual MBT
1032	–CN stretching vibration for MBT
1032	Symmetric C–O–C stretching vibration
1088	Symmetric C–O–C stretching vibration
1014	C–C–C bending for residual MBT
972	>N–CS=S stretching vibration for residual TMTD
722	(CH2)n where $n \geq 5$, for –CH2 rocking vibration of sequence ethylene presence in EPDM
698	C–S–C stretching vibration
698–609	C–S and S–S stretching vibration
	Additional peaks for TCICA modified samples
1110 and 1053	Asymmetric C–O stretching vibration of C–O–C group
1420	CH_2-halogen bending deformation
1630	ketone group of $-CO-C=CH_2$
1710	–CO stretching vibration

characteristic absorption peaks at 1248, 1150, 1032, and 1014 cm^{-1} correspond to residual MBT present as an accelerator. Similarly, peaks at 1032 cm^{-1} (merged with that of MBT) and 1088 cm^{-1} indicate the presence of an oxygenated group such as ether (C-O-C) on the vulcanizate surface and the peak at 972 cm^{-1} is ascribed to N-C-S=S stretching vibration for the residual TMTD molecules. Also, many small and congested peaks appear in the range of 700–600 cm^{-1}. These are probably due to the presence of different sulfur linkages such as C-S-C, C-S, and S-S characterizing the crosslinked EPDM structure along with different accelerator systems on the vulcanizate surface.

4.1.2. XPS Analysis

Figure 2 exhibits the high resolution XPS spectra for the untreated EPDM vulcanizate in the C_{1s}, O_{1s}, and S_{2p} regions. The data on individual peak position, O/C ratio, and their relative peak area are incorporated in Table 4. In Fig. 2a, the C_{1s} peak appears at 284.6 eV binding energy. In addition, two peaks are also observed on curve fitting of the C_{1s} spectrum at 286.1 eV (a shift of 1.5 eV) and 288.5 eV (a shift of 3.9 eV), respectively, indicating the presence of C-O and C=O groups on the surface. The O_{1s} peak appears at 531.9 eV binding energy (Fig. 2b). This indicates the presence of different oxygenated groups on the vulcanizate surface. Two peaks for S_{2p} are observed at 161.7 and 163.1 eV binding energies (Fig. 2c). The low binding energy peak probably denotes the presence of bonded sulfur on the surface. The peak at 163.1 eV (a shift of 1.4 eV) is exclusively ascribed to free sulfur present on the EPDM vulcanizate surface [42].



(a) (b) (c)

FIGURE 2 a) C_{1s}, b) O_{1s}, and c) S_{2p} spectra of untreated vulcanized EPDM rubber surface.

TABLE 4 XPS Details of C_{1s}, O_{1s}, and S_{2p} Spectra from the Unmodified and the Modified Samples

	C_{1s}		O_{1s}		S_{2p}			
Sample designation	Peak position (eV)	Relative area (%)	Peak position (eV)	Relative area (%)	Peak position (eV)	Relative area (%)	O/C	Free sulfur (mg)
EP_{0kGy}	284.6	59.1	531.9	28.1	161.7	0.9	0.010	0.224
	286.2	7.6			163.1	1.1		
	288.5	2.3			-			
$EP_{1kGy/0}$	284.6	30.8	532.2	29.6	161.9	10.5	0.132	0.736
	286.2	14.2			163.3	6.8		
	288.6	2.7						
$EP_{1kGy/10TM}$	284.6	46.1	532.2	30.9	162.0	4.6	0.141	0.256
	286.2	10.1			163.4	4.0		
	288.8	3.5						
$EP_{0.03TCICA}$	284.7	45.1	532.2	32.4	162.0	2.9	0.132	0.128
	286.3	12.5			163.3	2.8		
	287.6	3.2			168.9	0.60		
					169.9	0.26		
EP_{1TCICA}	284.6	33.1	532.6	38.8	162.8	0.77	0.141	0.096
	286.0	18.3			164.5	0.63		
	287.2	7.6			169.1	0.33		
					170.1	0.31		

N.B.—Free sulfur of EPDM $_{3kGy}$ is 2.016 mg.

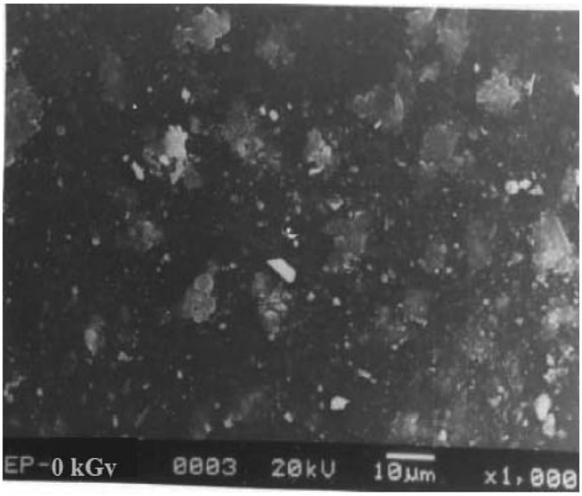


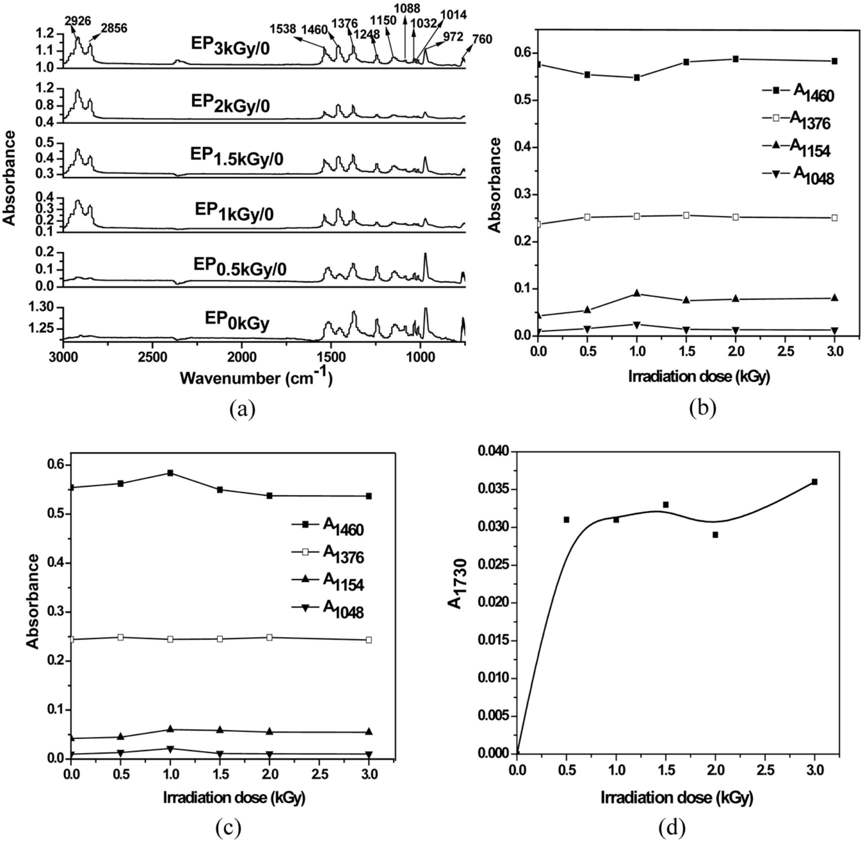
FIGURE 3 SEM micrograph of untreated vulcanized EPDM rubber surface ($\times$ 1000).

4.1.3. Surface Morphology and Energy Characteristics

The SEM picture shows the migration of different compounding ingredients on the surface, marked as white deposits (Fig. 3). Surface energy of the untreated EPDM rubber vulcanizate was calculated from the contact angle data and is found to be 64.2 mJ/m^2. The surface energy of pristine EPDM rubber is only 33 mJ/m^2. The higher surface energy is ascribed to high temperature oxidation (during molding) and addition of polar compounding ingredients to the neat EPDM.

4.2. Characterization of γ- and TCICA Modified EPDM Rubber Vulcanizate Surface Using ATR-IR Analysis

Figure 4a shows the representative IR spectra of γ-modified samples. Exposure of the rubber surface to γ-irradiation changes the intensity of $-CH_2$ bands and increases the intensity of C-O-C bands (1048 and 1154 cm^{-1}) by oxidation of the $-CH_2$ groups. These are clearly elucidated in Fig. 4b, where the absorbances at both 1154 and 1048 cm^{-1} due to asymmetric and symmetric stretching vibration of C$-$O$-$C are shown against various irradiation doses. The peak at 1154 cm^{-1} registers a slight upward trend up to 1 kGy and, thereafter, attains an almost constant value, while the peak at 1048 cm^{-1} exhibits negligible change with irradiation dose. The γ- irradiation generates a large number of highly reactive carbon radicals on the EPDM, which after

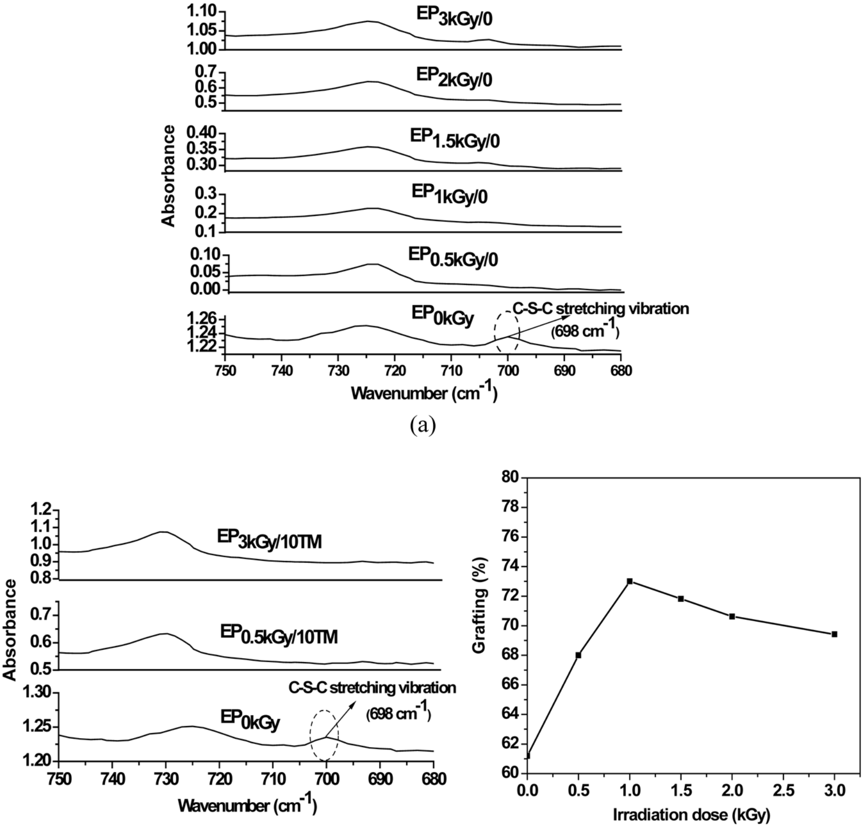


(a) (b)

(c) (d)

FIGURE 4 Characteristic IR-peaks of a) $EP_{xkGy/0}$, and plots of change of absorbance at A_{1460}, A_{1376}, A_{1154}, and A_{1048} for b) $EP_{xkGy/0}$ and c) $EP_{xkGy/10TM}$, and d) plot of change of absorbance at A_{1730} cm^{-1} for $EP_{xkGy/10TM}$.

reaction with atmospheric oxygen form C–O–C linkages. The ether group intensity increases with increasing irradiation doses up to 1 kGy, as the concentration of the radical increases. However, beyond a 1 kGy irradiation dose, chain scission, self crosslinking, and disproportion action reactions probably predominate over oxidation [40]. Furthermore, the peak at 1460 cm^{-1} due to $>CH_2$ scissor vibration slightly decreases up to 1 kGy irradiation dose, beyond which it remains constant. The peak at 1376 cm^{-1} does not show any significant change with irradiation dose. This is due to formation of free radicals on active $-CH_2$ groups in comparison with $-CH_3$ groups. Figure 5a reveals the ATR-IR spectra of the vulcanized surfaces



(a)

(b) (c)

FIGURE 5 ATR-IR spectra of a) $EP_{xkGy/0}$, b) $EP_{xkGy/10TM}$ in the region of 750 to 680 cm^{-1}, and c) plot of percent grafting *vs.* irradiation dose of the 10 wt% TMPTA modified system.

modified with 0–3 kGy irradiation dosage in the range of 750 to 680 cm^{-1}. The absorption at 698 cm^{-1} due to the C$-$S$-$C stretching vibration vanishes on irradiation, which is probably due to breakdown of the weak C$-$S$-$C bond upon exposure to γ- irradiation. This observation is further substantiated from the increases in the blooming sulfur of the γ- irradiated samples shown in Figs. 6a–6b and Table 4.

In the case of the sample irradiated in the presence of TMPTA, the peak absorbances at both 1460 and 1376 cm^{-1} due to $>CH_2$ scissor vibration and $-CH_3$ stretching vibration, when plotted against different irradiation doses, show that these increase up to 1 kGy (Fig. 4c).This is probably due to enhancement of grafting by the

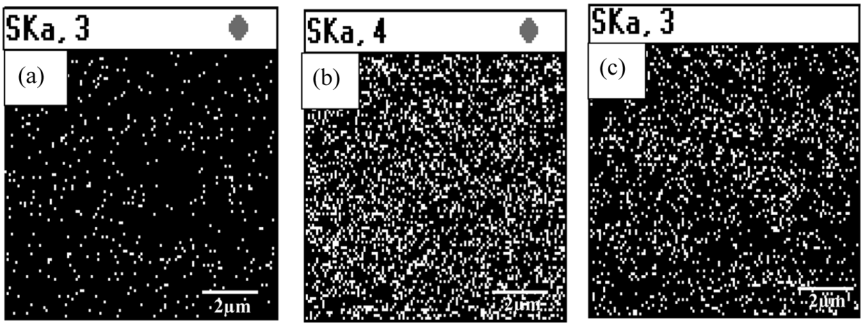


FIGURE 6 EDX study of sulfur for the unmodified and the modified EPDM rubber vulcanizates a) EP_{0kGy}, b) $EP_{1kGy/0}$, and c) $EP_{1kGy/10TM}$.

TMPTA molecule on irradiation. The above phenomena are well supported by gel content data (Table 5). Similarly, the absorbances at both 1154 and 1048 cm^{-1} due to asymmetric and symmetric stretching vibrations also marginally increase with irradiation dose up to 1 kGy, beyond which not much change in the peak intensities is observed (Fig. 4c). Figure 4d shows the variation of peak intensity of the carbonyl group at 1730 cm^{-1} with change in irradiation dose. Here, the peak intensity significantly increases up to 1 kGy. All these results indicate that by incorporating polyfunctional monomer, the oxidation of the EPDM surface increases due to grafting of the polyfunctional monomer. After 1 kGy irradiation dose, self-crosslinking and

TABLE 5 Gel Fraction Study of Unmodified and Modified EPDM Vulcanizates

Designation	Gel fraction (%)	Designation	Gel fraction (%)
EP_{0kGy}	95.0	EP_{0kGy}	95.0
$EP_{0.5kGy/0}$	95.3	$EP_{0.5kGy/10TM}$	96.3
$EP_{1kGy/0}$	95.4	$EP_{1kGy/10TM}$	96.9
$EP_{1.5kGy/0}$	95.3	$EP_{1.5kGy/10TM}$	96.3
$EP_{2kGy/0}$	95.3	$EP_{2kGy/10TM}$	96.4
$EP_{3kGy/0}$	95.3	$EP_{3kGy/10TM}$	96.3
$^{*}EP_{0TCICA}$	95.0		
$^{*}EP_{0.01TCICA}$	95.0		
$^{*}EP_{0.03TCICA}$	95.1		
$^{*}EP_{0.1TCICA}$	95.1		
$^{*}EP_{0.5TCICA}$	95.1		
$^{*}EP_{1TCICA}$	95.2		

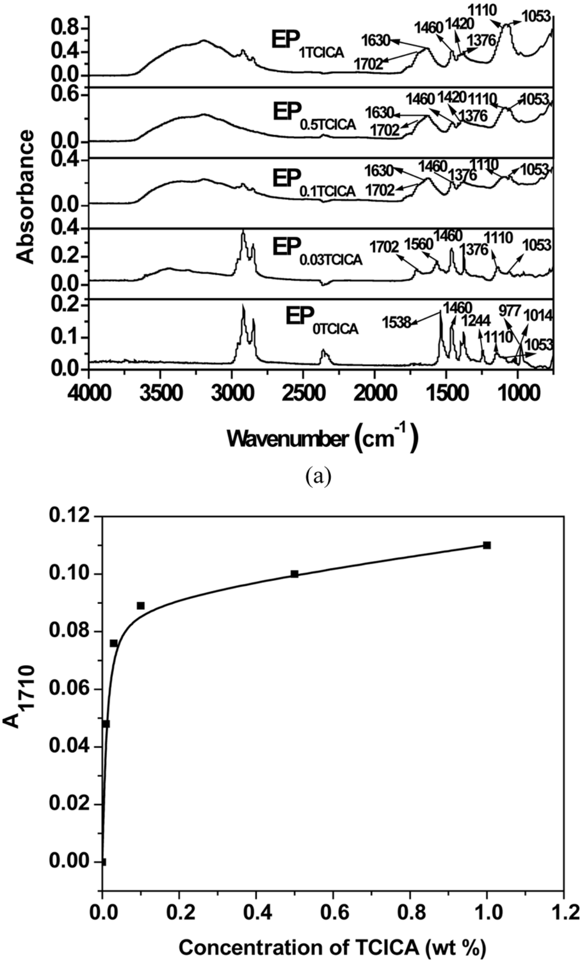
*TCICA modified sample.

cyclization among TMPTA molecules take place that reduce further extent of grafting. The % grafting, as calculated from the ATR-IR analysis, strongly supports this as well (Fig. 5c). In addition, Fig. 5b shows that the absorption at 698 cm^{-1} due to the C–S–C stretching vibration disappears on irradiation in the presence of 10 wt% TMPTA. This is due to a reason similar to that described in the preceding paragraph and is well supported by the results in Table 4 and images shown in Figs. 6a and 6c. It is also observed that the percentage of free sulfur is less for the TMPTA-treated samples in comparison with irradiated samples without TMPTA. This might be due to the removal of free sulfur from the rubber surfaces during dipping in TMPTA solution.

Figure 7a demonstrates a representative ATR-IR spectrum of TCICA-modified samples. Interestingly, it is noticed that with increasing concentration of TCICA, most of the residual ingredients, including stearic acid, are wiped out from the surface (compare the 1538 cm^{-1} peak in the IR spectra of the unmodified and the modified surfaces). In addition, it has also been seen that above 0.03% concentration of TCICA, a broad peak in the region of 3600–3000 cm^{-1} appears which is due to absorption of moisture from the atmosphere. A prominent peak at 1630 cm^{-1} appears as a consequence of oxidation of the 0.1 wt% TCICA-modified vulcanizate due to the presence of the ketone group of $-CO-C{=}CH_2$[43]. It increases with increasing concentration of TCICA. In addition, the CH_2-halogen bending deformation (1420 cm^{-1}) appears at higher concentration of TCICA due to the presence of excess chlorinating agent. Some significant and relevant peaks are given in Table 3. Figure 7b shows that the absorbance at 1710 cm^{-1}, corresponding to –CO stretches, increases with increasing concentration of TCICA. This implies that during TCICA treatment, oxidation of the EPDM vulcanizate surface has taken place and as a result the –CO group is formed on the EPDM surface. Figure 8 shows the EDX picture of TCICA-modified rubber vulcanizates. It is observed that the concentration of sulfur on the TCICA-modified surfaces is less compared with γ- modified surfaces due to wiping out of bloomed sulfur in the presence of TCICA; these results are in line with the values obtained from free sulfur analysis (Table 4). Gel content values depicted in Table 5 show that these do not change appreciably for the TCICA-modified samples.

4.3. XPS Analysis

The XPS results of two representative samples are shown in Fig. 9: EPDM vulcanizate after a 1 kGy irradiation dose ($EP_{1kGy/0}$) and



(a)

(b)

FIGURE 7 Characteristic IR-peaks of a) EP_{zTCICA} and b) plot of change of absorbance at A_{1710} for EP_{zTCICA}.

surface-grafted EPDM irradiated at 1 kGy after soaking in 10 wt% TMPTA solution ($EP_{1kGy/10TM}$). The individual peak positions, relative peak areas, concentrations of carbon, oxygen, and sulfur, and the corresponding O/C ratio are depicted in Table 4. For untreated EPDM vulcanizate, the C_{1s} peak appears at 284.6, 286.2, and 288.5 eV binding energies (Fig. 2a), as already described. Upon irradiation, the peaks corresponding to C-O and C=O marginally

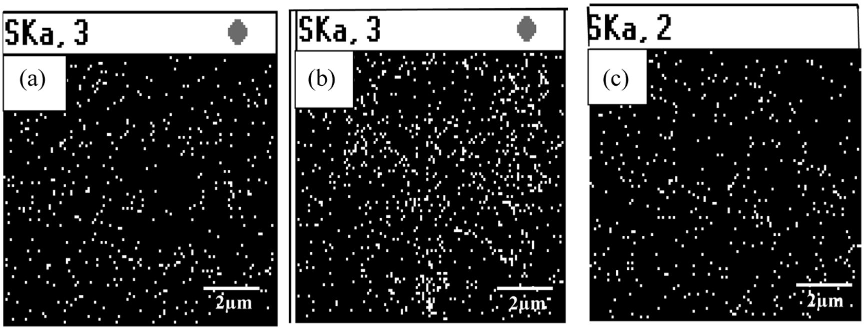


FIGURE 8 EDX study of sulfur for the unmodified and the modified EPDM rubber vulcanizates a) EP_{0TCICA}, b) $EP_{0.03TCICA}$, and c) $EP_{0.5TCICA}$.

shift towards higher binding energy. This indicates oxidative modification of the carbon at the EPDM vulcanizate surface. When the rubber vulcanizate is modified further in the presence of TMPTA ($EP_{1kGy/10TM}$), the relative peak area at 288.8 eV is increased. Concentration of oxygen is higher for $EP_{1kGy/10TM}$ in comparison with $EP_{1kGy/0}$. This means that the presence of TMPTA brings about formation of oxidized groups on the surface. For instance, the oxygen concentration increases from 28.1 to 29.6% when the EPDM surface is modified at 1 kGy irradiation dose, and from 28.1 to 30.9% when a 1 kGy irradiation dose in the presence of TMPTA (10 wt%) is used (Figs. 9b and 9e, Table 4). Another significant observation is that on exposure to gamma irradiation, the concentration of free sulfur is enhanced in both of these modified samples (Figs. 9c and 9f, Table 4). This is probably due to breakage of some polysulfidic crosslinks under high-energy irradiation offering free sulfur to bloom at the surface. But the concentration of sulfur on the TMPTA-modified samples is less as compared with the irradiated sample without TMPTA. This may be due to wiping out of some residual sulfur during soaking with TMPTA solution and modification of TMPTA first by γ- irradiation (Figs. 6b and 6c).

Figure 10 depicts the XPS results of $EP_{0.03TCICA}$ and EP_{1TCICA} as representative samples. The individual peak positions, relative peak areas, concentrations of carbon, oxygen, and sulfur, and the corresponding O/C ratio are included in Table 4. The percent relative area for oxygen is increased from 28.1 to 32.4% for the 0.03 wt% TCICA-modified sample and 28.1 to 38.8% for the 1 wt% TCICA-modified sample (Table 4). In the same table, it has been further noticed that the concentration of sulfur on the EPDM surface decreases with increasing concentration

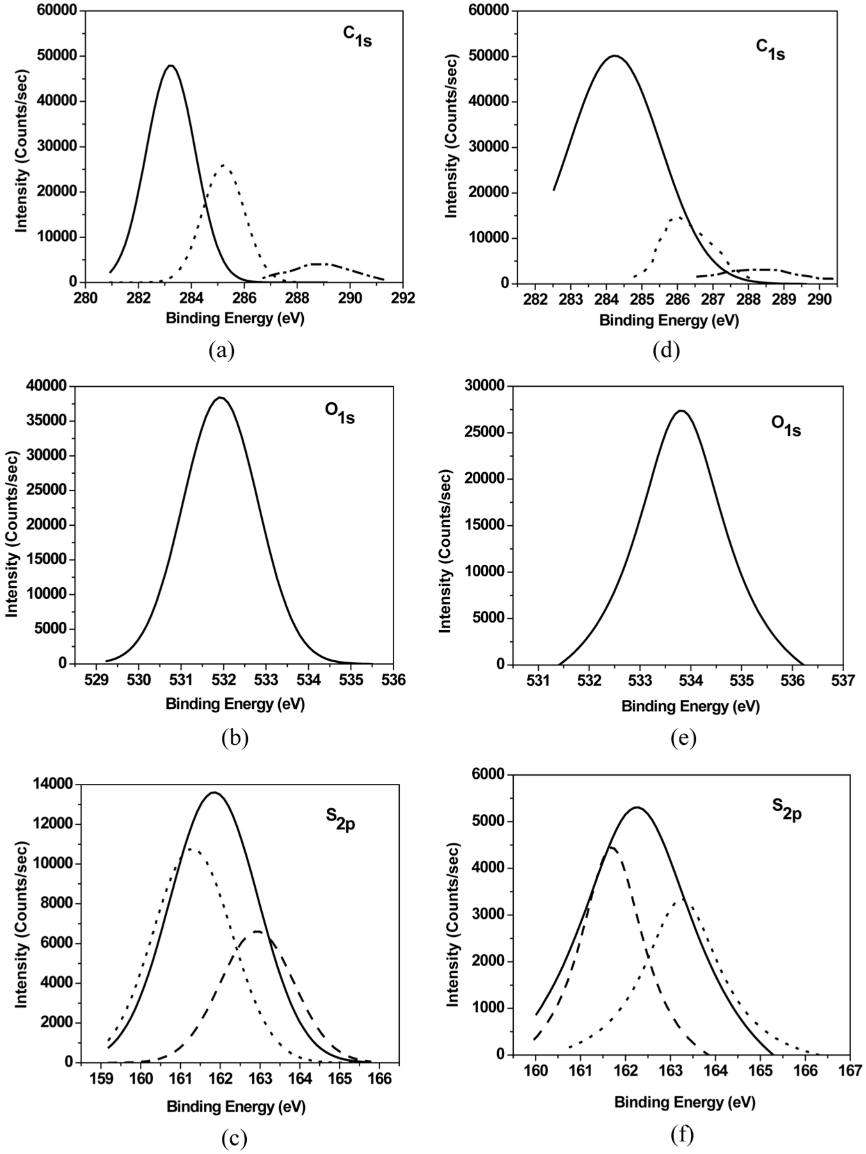


FIGURE 9 XPS spectra for different modified systems a) C_{1s}, b) O_{1s}, and c) S_{2p} spectra for $EP_{1kGy/0}$ and d) C_{1s}, e) O_{1s}, and f) S_{2p} spectra for $EP_{1kGy/10TM}$.

of TCICA. This may be due to the wiping out of bloomed sulfur in the presence of TCICA. This result is in line with the sulfur determined qualitatively from EDX analysis (Fig. 8).

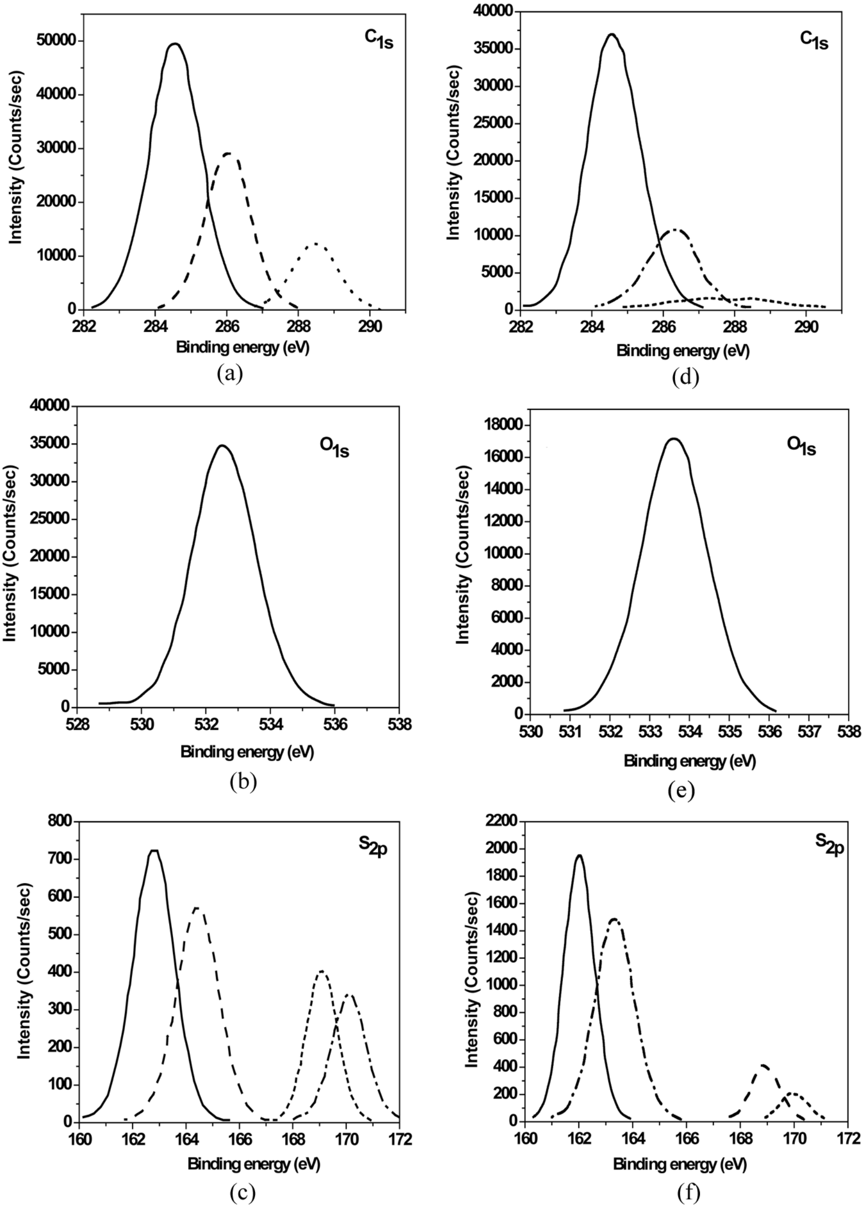


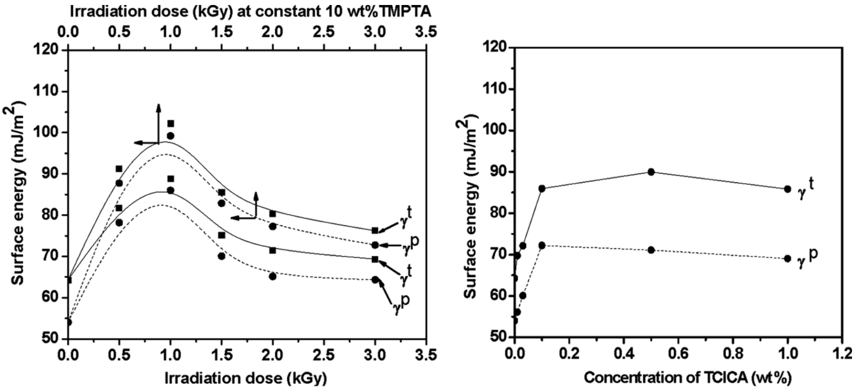
FIGURE 10 XPS spectra for different modified systems a) C_{1s}, b) O_{1s}, and c) S_{2p} spectra for $EP_{0.03TCICA}$ and d) C_{1s}, e) O_{1s}, and f) S_{2p} spectra for EP_{1TCICA}.

4.4. Surface Energy

The contact angle value gives an idea of wettability. The values of dispersion and polar components of surface energy (γ^t) calculated by the Owens and Wendt equation provide clues about the nature of the surface. From Fig. 11a, it is found that in the presence or absence of the TMPTA molecule, the surface energy increases considerably with increasing irradiation dose up to 1 kGy, beyond which it decreases. On the other hand, for the TCICA-modified samples, the surface energy increases with increasing concentration of TCICA (Fig. 11b). In both the cases, no significant difference between the dispersion component (γ^d) of the surface energy of the untreated and the treated sample is observed, which implies that the improvement of surface energy is due to an increment of the polar component (γ^p). These results are in line with those obtained from the ATR-IR spectroscopy. The increase in surface energy upon irradiation may result in improvement of wettability and consequently enhancement of adhesion of the EPDM vulcanizates.

4.5. Surface Topography

The bondability of a substance is characterized, in part, by its surface texture. It can influence bondability in two ways: microroughness which leads to an increased effective contact area and mechanical interlocking which increases with increasing roughness [44].



(a) (b)

FIGURE 11 a) Plots of surface energy against irradiation dose of $EP_{1kGy/0}$ and $EP_{1kGy/10TM}$; b) plot of surface energy against concentration of TCICA of EP_{zTCICA}.

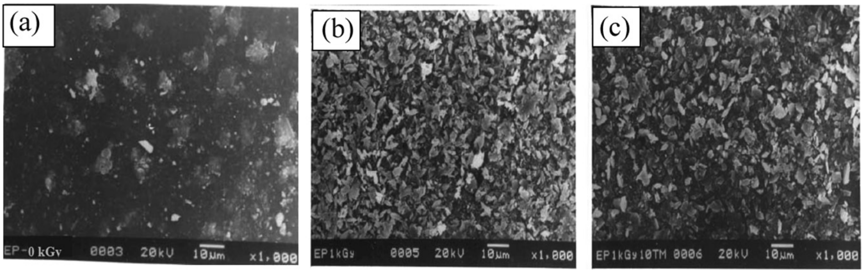


FIGURE 12 SEM picture of a) EP$_{0kGy}$, b) EP$_{1kGy/0}$, and c) EP$_{1kGy/10TM}$ samples.

Figure 12 shows the SEM microphotographs of the unmodified and the modified EPDM rubber vulcanizates. The unmodified EPDM rubber represents a smooth surface with some unevenness which may be due to the presence on the surface of migrating additives used in the compounding process. After irradiation, the surface irregularity increases irrespective of the presence or absence of TMPTA. In the case of TCICA-modified samples (Fig. 13), more whitish flakes appear on the EP$_{0.03TCICA}$ surface as compared with the unmodified EPDM vulcanizate. The whitish flakes are reduced at higher concentration, *e.g.*,, EP$_{0.5TCICA}$, and a relatively lower, uneven texture is generated on the surface. The whitish flakes indicate the presence of residual ingredients on the surface and the change in texture may be due to the etching tendency of TCICA at higher concentration.

The three-dimensional texture of γ-modified (EP$_{0/0}$, EP$_{1kGy/0}$, and EP1$_{kGy/10TM}$) and TCICA-modified (EP$_{0TCICA}$, EP$_{0.03TCICA}$, and EP$_{0.5TCICA}$) representative samples is shown in Figs. 14–15,

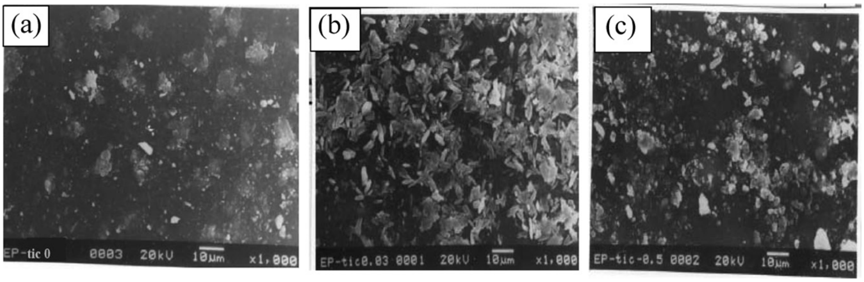
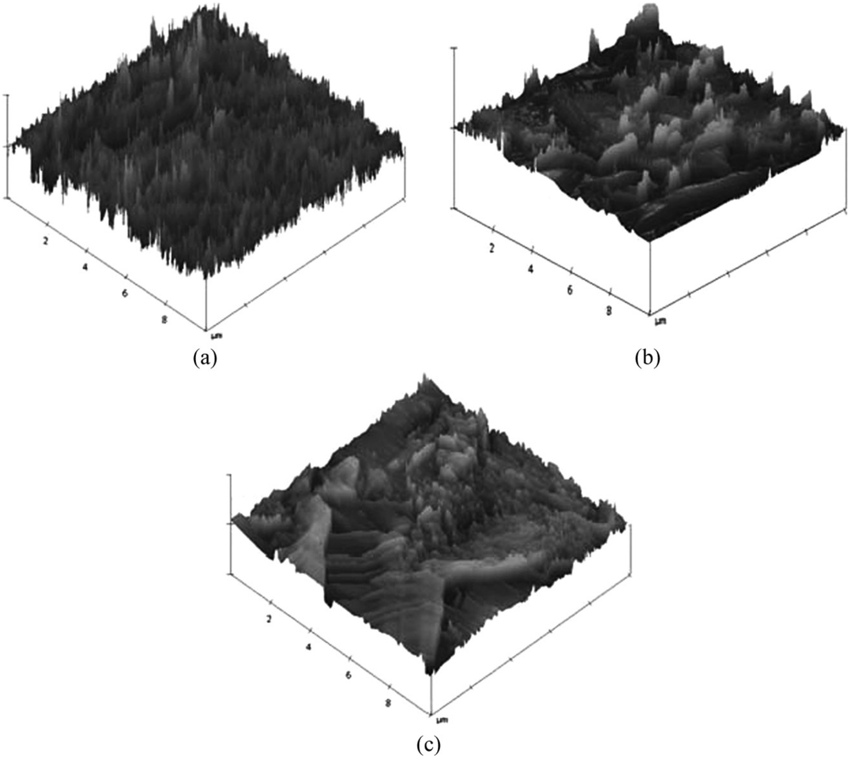


FIGURE 13 SEM picture of a) EP$_{0TCICA}$, b) EP$_{0.03TCICA}$, and c) EP$_{0.5TCICA}$ samples.



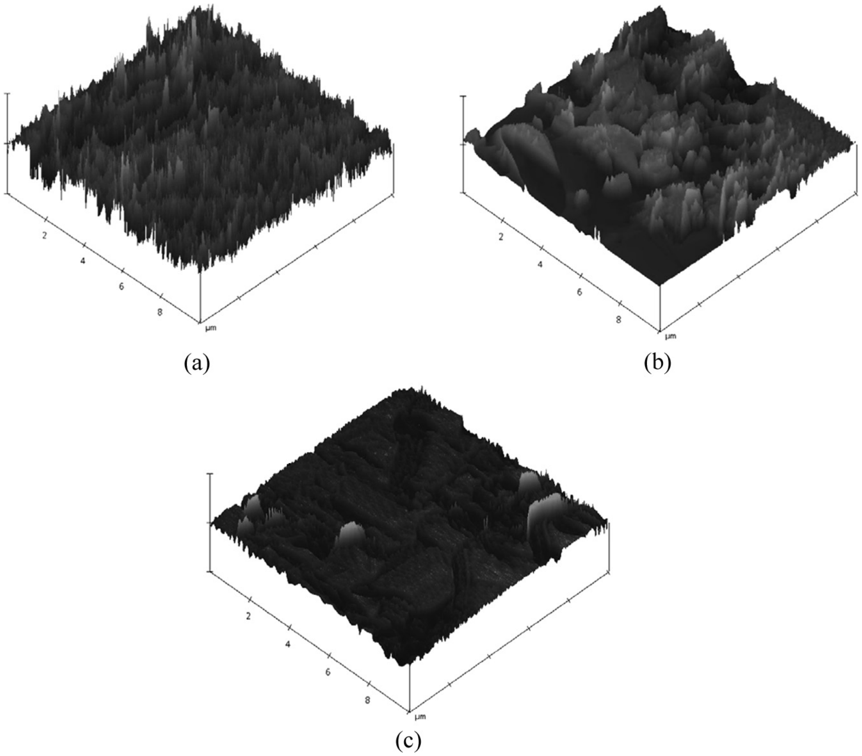
(a) (b) (c)

FIGURE 14 Three-dimensional tapping mode phase morphology of a) $EP_{0/0}$, b) $EP_{1kGy/0,}$ and c) $EP_{1kGy/10TM}$ samples.

respectively, and their corresponding roughness values (Rq and Ra) calculated from the phase images are depicted in Table 6. The surface roughness increases with γ- irradiation and also with TCICA modification in the initial stage. The AFM studies strongly support the conclusions drawn from the SEM photomicrographs.

4.6. Peel Strength

The γ-modified sample in the presence and absence of TMPTA shows greater strength at a particular irradiation dose as compared with the unmodified sample. Figure 16a illustrates that the peel strength is a function of irradiation dose as well as sensitizer concentration. However, it is noted that the sample in the presence of TMPTA at 1 kGy γ- irradiation dose shows maximum peel strength in comparison



(a) (b)

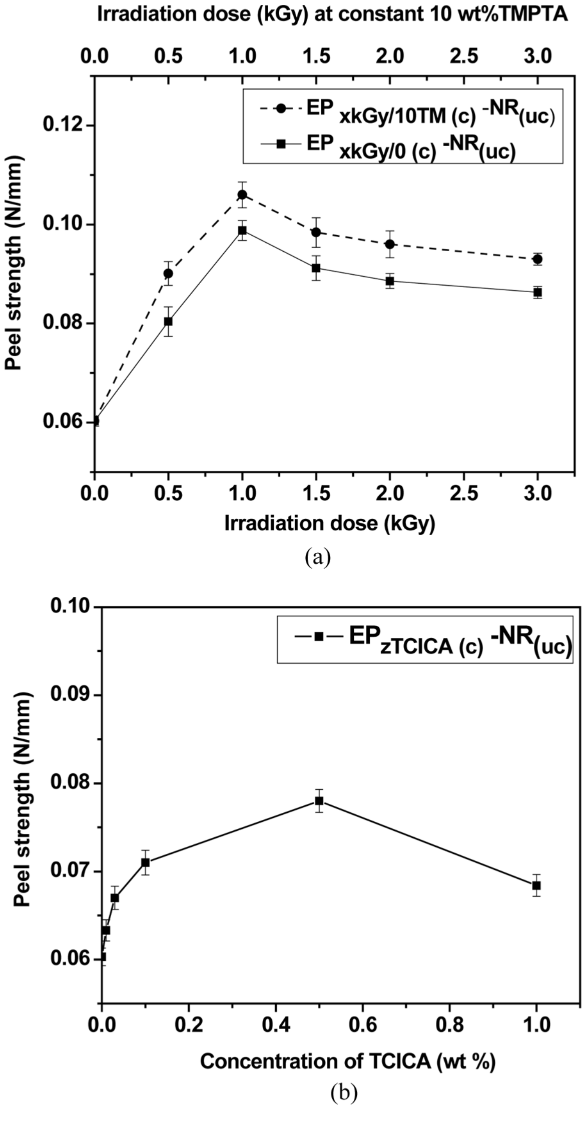
(c)

FIGURE 15 Three-dimensional tapping mode phase morphology of a) EP_{0TCICA}, b) $EP_{0.03TCICA}$, and c) $EP_{0.5TCICA}$ samples.

with the other modified samples. The average peel strength value of $EP_{1kGy/10TM}$ is 7% higher as compared with $EP_{1kGy/0}$. The above results are in line with the surface energy data and are strongly supported by the ATR-IR analysis. From the SEM photographs (Fig. 12), it is observed that surface texture increases marginally upon exposure to irradiation in the presence or absence of TMPTA and the increment is not prominent after a certain dose. On the contrary, the

TABLE 6 Quantitative Roughness Parameters from the Modified and the Unmodified EPDM Vulcanizates

Parameters	$EP_{0/0}$	$EP_{1kGy/0}$	$EP_{1kGy/10TM}$	$EP_{0.03TCICA}$	$EP_{0.5TCICA}$
RMS (Rq), nm	13.62	18.50	21.72	17.93	8.89
Ra, nm	10.85	15.26	17.01	14.74	7.57



(a)

(b)

FIGURE 16 a) Peel strength of $\mathrm{EP}_{\mathrm{xkGy/0}}$ and $\mathrm{EP}_{\mathrm{xkGy/10TM}}$ and b) peel strength of $\mathrm{EP}_{\mathrm{zTCICA}}$ samples.

concentration of free sulfur on the modified surface is also increased with increasing irradiation dose (Table 5). Sulfur plays a role as an anti-adherent material on the surface. Therefore, it is suggested that a 1 kGy dose in the presence and absence of 10 wt% TMPTA is

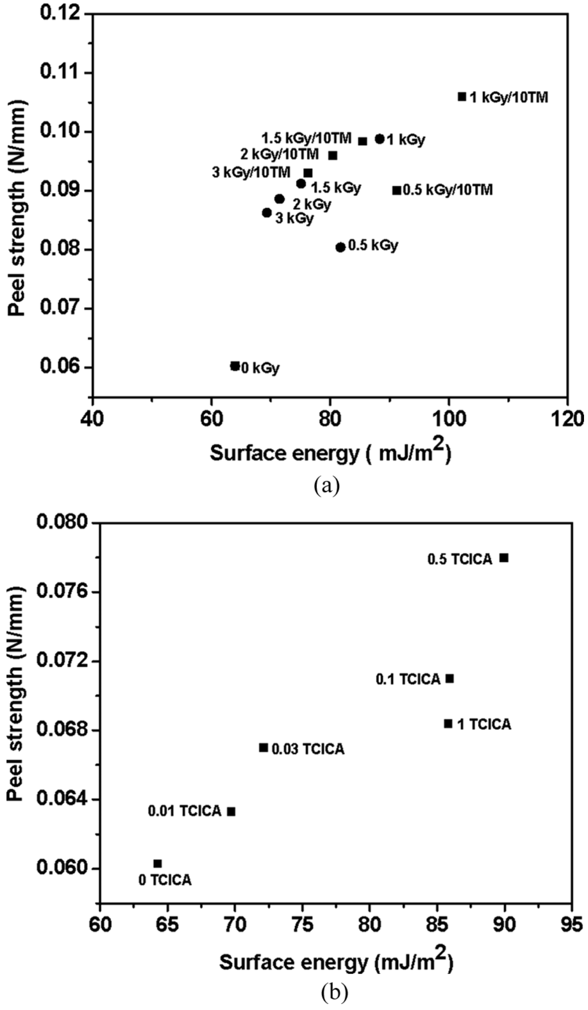


FIGURE 17 Correlation between peel strength and surface energy of a) $EP_{xkGy/0}$ and $EP_{xkGy/10TM}$ and b) EP_{zTCICA} samples.

optimum in this study. Similarly, for the TCICA-modified samples, the peel strength increases, because the surface energy increases with increasing concentration of TCICA due to an increasing polar component on the surface (demonstrated from ATR-IR analysis and surface energy values) (Fig. 16b). But the peel strength value increases up to 0.5 wt% concentration of TCICA, beyond which no significant improvement takes place. At higher concentration of TCICA (>0.5 wt%), it penetrates more deeply into the rubber and, as a result, a thicker chlorinated layer is produced. This acts an anti-adherent material, which tends to migrate to the rubber surface and prevents EPDM adhesion to natural rubber. Consequently, the peel strength value decreases above 0.5 wt% concentration of TCICA. In all cases, the nature of failure appears to be interfacial.

In order to discover a correlation between peel strength and surface energy, peel strength values are plotted against surface energy in Figs. 17a and 17b. It has been observed that peel strength increases linearly with surface energy up to a certain modification level. The correlation is poor after that. This infers that surface energy plays a considerable role up to a particular modification level.

Ansarifar and Lake studied a much wider range of peel rates (10^{-6} to 10^{0}) in comparison with our study and obtained a modest increase in peel strength with rate [45]. The effect was insignificant over the rates used in our investigation (not shown here). It can be concluded that the rate-sensitivity of adhesion between modified EPDM with NR is small under the test conditions used.

5. CONCLUSIONS

In this present research work, EPDM vulcanizate surface was modified by γ-irradiation (0.5–3 kGy irradiation dose) in the presence and absence of 10 wt% TMPTA as a sensitizer and TCICA (0.01–1 wt% concentration). Subsequently, the modified EPDM vulcanizate surfaces were characterized and adhered with the unmodified NR surface through a co-curing procedure.

It was concluded that better results could be obtained using the sensitized system. This is obviously due to grafting of the TMPTA molecule onto EPDM vulcanizate surface for the γ-modified sample, which enhances surface polarity as well as texture. The detrimental effect on peel strength after a specific radiation dose might be explained on the basis of lower surface energy and the anti-adherent nature of blooming sulfur. A maximum of $\sim$76% improvement was obtained for the gamma-modified system in the presence of TMPTA at 1 kGy γ-irradiation dose. On the other hand, for the TCICA modified samples, the peel strength increased with increasing concentration of TCICA up to 0.5 wt%, beyond which it decreased. The reduction in peel strength value might be due to formation of anti-adherent layers with poor cohesive strength. A maximum of 29% improvement was observed for the treated sample versus the untreated one.

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