Synthesis and Characterization of Grafted Acrylonitrile on Polystyrene modified with Carbon nanotubes using Gamma-irradiation

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Abstract

Acrylonitrile was successfully grafted on polystyrene modified with carbon nanotubes using gamma-irradiation technique. This process was carried out at various gamma doses (0.2-1.5 Mrad). The new grafted polymer (GP) was characterized and its properties were investigated. In this study, it was found that 2 gm of polystyrene, 90% (w/w) acrylonitrile monomer, 2% (w/w) ferrous ammonium sulfate (FAS) catalyst, 1 mg carbon nanotubes powder and 1.25 Mrad gamma dose are the optimum conditions required for the polymerization of GP. The grafted polymer was proved true by fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy and XRD. A mechanism is presented to explain the formation of GP modified with carbon nanotubes.

Keywords: Carbon nanotubes, polystyrene, acrylonitrile, gamma-irradiation, FAS.

Introduction

Carbon nanotubes have long been recognized as the stiffest and strongest man-made material known to date. In addition, their high electrical conductivity has roused interest in the area of electrical appliances and communication related applications. However, due to their miniscule size, the excellent properties of these nanostructures can only be exploited if they are homogeneously embedded into light-weight matrices[1].

The improvement of interfacial adhesion in polystyrene was materialized by grafting polystyrene chains onto the nanotubes surface[2]. The polystyrene was covalently bonded onto the nanotubes surface with an average molecular weight of about 10^4 g mol^{-1} from which composites with different nanotubes weight fraction were synthesized. It was shown that short chains of grafted polymer, i. Enhanced the dispersion of the nanotubes within the matrix, ii. Increased the Young modulus and iii. Increased the stress breaking of the nanocomposites[3].

The in situ grafting-from approach via atom transfer radical polymerization was successfully applied to polystyrene, poly(styrene-co-acrylonitrile) and polyacrylonitrile grafted onto the convex surfaces of multiwalled carbon nanotubes (MWCNTs) with (2-hydroxyethyl 2-bromoisobutyrate) as an initiator. The polymer-grafted MWCNTs exhibited relatively good dispersibility in organic solvents such as tetrahydrofuran[4].

Crosslinked polystyrene-multiwalled carbon nanotubes (PS-MWCNTs) balls, which act as conductive microfillers, were prepared by the in situ suspension polymerization of styrene with MWCNTs and divinyl benzene (DVB) as a crosslinking agent.The diameters of the synthesized crosslinked PS-MWCNTs balls ranged from 10 to 100 nm and their electrical conductivity was about 7.7×10^{-3} S/cm. In addition, the mechanical properties of the PS/crosslinked PS-MWCNTs ball composites were better than those of the PS/pristine MWCNTs[5].

Single-walled carbon nanotubes (SWNTs) reinforced polymer composite membranes have been fabricated using the electrospinning technique. Nanofibers with a diameter in the range of 50–100 nm were obtained by electrospinning SWNTs-filled polystyrene composites[6].

The polystyrene nanocomposite materials were prepared with functionalized SWCNTs as fillers by solution casting from tetrahydrofuran. The functionalized SWCNTs nanocomposite showed a significant improvement in mechanical properties and electrical properties. The dispersibility of the carbon nanotubes in the composite was investigated by using scanning electron microscopy[7].

In this study, we prepared acrylonitrile grafted in the polystyrene and modified with carbon nanotubes by gamma irradiation induced polymerization. The synthetic procedure and surface property were investigated by using FTIR, UV-Visible spectroscopy and XRD.

Material and Methods

Chemicals and materials: Materials used in the present work are: Polystyrene from Sigma Aldrich, commercial, Acrylonitrile from Merck, Germany. Carbon nanotubes and dimethyl formamide (DMF) from BDH Limited Poole England. Ferrous ammonium sulphate (FAS) a grade from Fluka-Garantic used and. Chloroform and ethanol from Scharlau.

Techniques: Gamma irradiation technique: Irradiation procedure was carried out by introducing polystyrene in a Pyrex tubes with acrylonitrile as a monomer and activated carbon as modifying agent using chloroform as a solvent and FAS as a catalyst. The irradiation was accomplished under ambient air. The resulted grafted polymer was dissolved in DMF solvent and precipitated by ethanol then filtered by a funnel. Precipitated process was repeated three times and the yield was kept under reduced pressure in order to ensure complete removal of the solvent. The gamma-irradiation was achieved at a rate of 1. 1 Mrad h^{-1} using gamma cell 220 of Co^{60} Canadian type[8].

FTIR Measurement: The FTIR spectra were obtained from the IRAFFINITY-1 (8400) Fourier Transform spectrophotometer SHIMAZAU, Japan, at room temperature using KBr disc method for characterizing the polymer. In the disc method, the sample was dried and grounded with the KBr powder until they were in a well mixed, powdered form. The powder was then pressed at 8 tons for 1 min to produce the disc. The sample was scanned at wave number range of 4000-400 cm^{-1}.

UV - Visible Measurement: The UV – Visible spectrophotometer METERTECH-SP8001, China, was used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. The sample was dissolve in chloroform and placed in the cuvex and then put into the machine by using 600 nm wavelengths.

X-ray Diffraction Measurement: The powder X-ray diffraction patterns of the grafted polystyrene with acrylonitrile modified with carbon nanotubes films were performed by a wide angle X-Ray scattering using Siemens D5005 X-Ray Diffractometer.

Results and Discussion

FTIR Analysis: Table-1 and figure-1 show the FTIR assignment and spectra of acrylonitrile, polystyrene and grafted polymer (polystyrene grafted with acrylonitrile modified with carbon nanotubes), respectively. In pure acrylonitrile, there are peaks in the region 3076 – 2857 cm^{-1} which correspond to the CH stretch in alkene. The CN peak is detected at 2229 cm^{-1} which is the main functional group in acrylonitrile. Moreover, the band of C=N appeared at 1614 cm^{-1}is corresponding to the resonance of the nitrile group when it was in the acrylonitrile form. Very strong broad band appear in the spectrum of acrylonitrile at 965 cm^{-1} which indicate the C=C, CH$_2$. The peaks within the range of 685 – 1412 cm^{-1} correspond to the C=C stretch, C-C stretch, and C-H stretch in alkene structure. For FTIR in polystyrene, there are peaks detected between the region 3059 – 2850 cm^{-1} which correspond to the CH alkene and aromatic ring. Then the peaks within the range 1942– 537 cm^{-1} correspond to the C=C stretch, C-C stretch, and C-H stretch in alkene and aromatic structure of polystyrene. For the grafted polymer (polystyrene grafted with acrylonitrile modified with activated carbon), the CN can still be observed at 2242 cm^{-1}. The peaks in 3060 – 538 cm^{-1} range correspond to the

present of C-H, C=C, C-C functional groups that appeared in the structure of both acrylonitrile and polystyrene. However the spectrum of polystyrene alone has no indication of (-CN) absorption band; this band (2229 cm^{-1}) appears in the grafted polymer at 2242 cm^{-1} for CN. Moreover ,the band of C=N appeared at 1614 cm^{-1} is corresponding to the resonance of the nitrile group when it was in the acrylonitrile form. The peaks of grafted polymer for both C=N and C=CH$_2$ are detected in 1600 cm^{-1} and 967 cm^{-1} [9].

Table-1
FTIR assignment of acrylonitrile, polystyrene and grafted polymer (polystyrene grafted with acrylonitrile modified with activated carbon)

Assignment	Acrylonitrile	Polystyrene	Grafted Polymer
NH stretch	---	---	3497
CH	3076	3059	3060
CH	----	3025	3025
CH	2925	2918	2921
CH	2857	2850	2851
CN	2229	---	2242
C=C	1943	1942	1946
C=C	---	1871	1873
C=C	1736	1742	1743
C=N	1614	---	1600
C-C stretch	---	1598	---
CH ring	1412	1491	1492
C=C ring	---	1448	1449
CH ring	---	1367	1363
CH	---	---	1216
CH	---	1154	---
CH	1091	1066	1068
C=C ring		1024	1026
C=CH$_2$	965	---	967
C=CH	---	905	907
CH	870	841	843
CH ring	---	752	752
CH	685	693	695
CH ring	---	537	538

UV – Visible analysis: The UV-Visible analysis was accomplished by using chloroform as a solvent at different concentrations. Figure-2 c shows two absorbance peaks of grafted polymer (modified with carbon nanotubes) ; 0.5500 and 0.2880 at wavelengths 350 and 400 nm respectively. For the acrylonitrile, the absorbance peaks with shoulder are 0.2545 and 0.1464 at wavelengths 293 and 262 nm respectively, as shown in figure-2 a. For pure polystyrene, the absorbance peak is 2.3276 at a wavelength of 260 nm and is shown in Figure 3.2 b. There are two peaks for the spectrum of grafted polymer (modified with carbon nanotube) observed in transition metals in the composition. The absorbance peaks 0.5500 and 0.2880 for grafted polymer (modified with carbon nanotube) and 2.3276 for pure polystyrene occurred at wavelengths 350, 400 and 260.0 illustrate that there are aromatic ring in the both compounds. In acrylonitrile, the absorbance 0.2545 and 0.1464 at wavelengths 293 and 262 nm refer to the C=C and C≡N groups and listed in table-2.
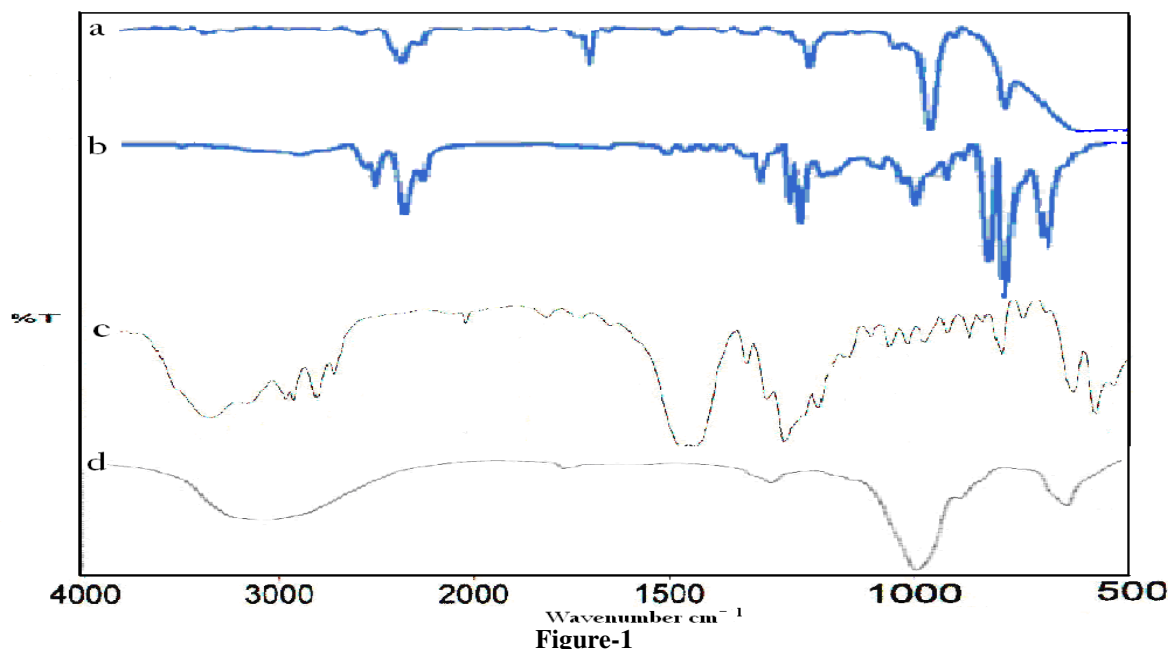
Figure-1
FTIR spectra of (a) Acrylonitrile (b) Polystyrene and (c) Grafted acrylonitrile on polystyrene modified with carbon nanotubes and (d) carbon nanotubes
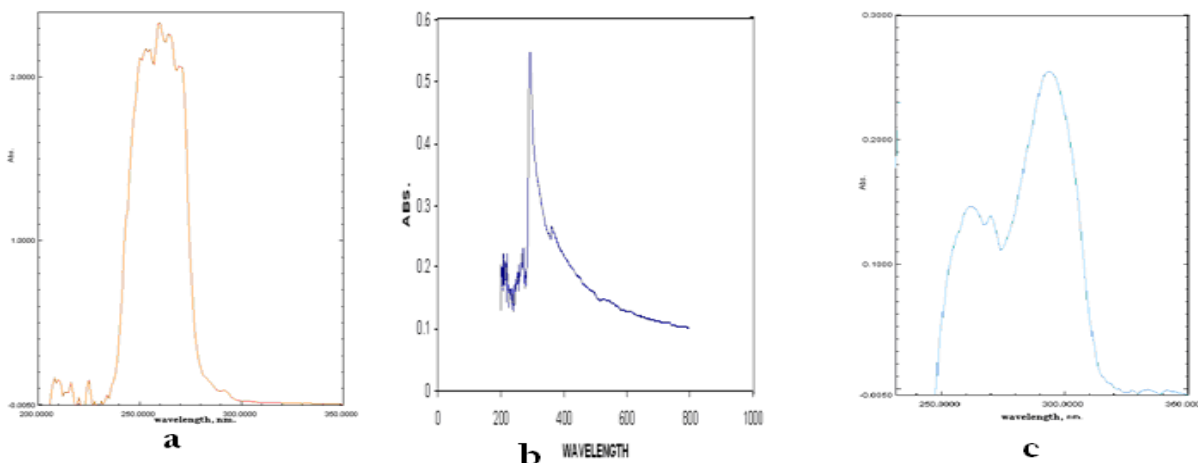

Figure-2
UV spectra for (a) acrylonitrile (b) polystyrene and (c) grafted polymer modified with carbon nanotubes

Table-2
UV–Visible analysis of grafted polymer (modified with carbon nanotubes), acrylonitrile and polystyrene

Compound	Wavelength (nm)	Absorbance
Grafted Polymer (modified with carbon nanotubes)	350	0.5500
	400	0.2880
Acrylonitrile	293	0.2545
	262	0.1464
Polystyrene	260	2.3276

X-ray diffraction (XRD) analysis: Figure-3a, b and c show the XRD patterns of grafted polymer modified with carbon nanotube (polystyrene-acrylonitrile-CNT), grafted polymer (polystyrene-acrylonitrile) and for CNT only, respectively.

From these spectra show that the XRD patterns of CNT at the angular (2θ) of 42°, 62° and 76° are shown at figure 3.3a of polystyrene-acrylonitrile-CNT in the same angular (2θ) and not appear at figure-3b of polystyrene-acrylonitrile. These peaks are well characterized in grafted polymer and correspond to specific crystallographic planes[10]. The intensity of the crystalline peaks of grafted polymer is high and sharp. These features are indicative of the grafting that occurs in the crystallinity of the grafted polymer modified with carbon nanotubes. The XRD peaks of CNT are slightly shifted at grafted polymer, indicating the modification of carbon nanotube in the polystyrene matrix. These results suggested that the inherent crystallinity of the polymer is not from the grafted polymerization of polystyrene and that the grafting occurs only in the amorphous regions[11,12].
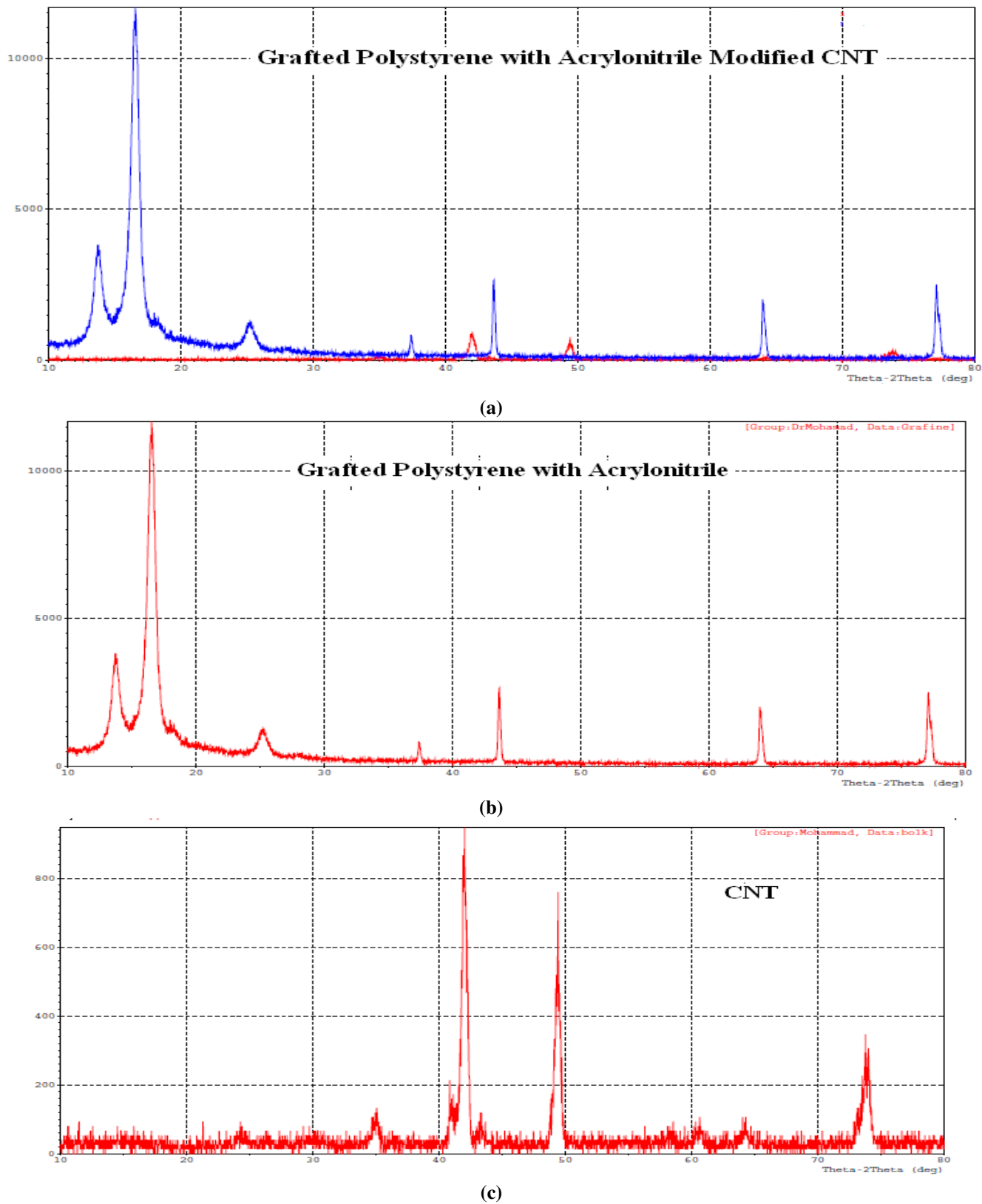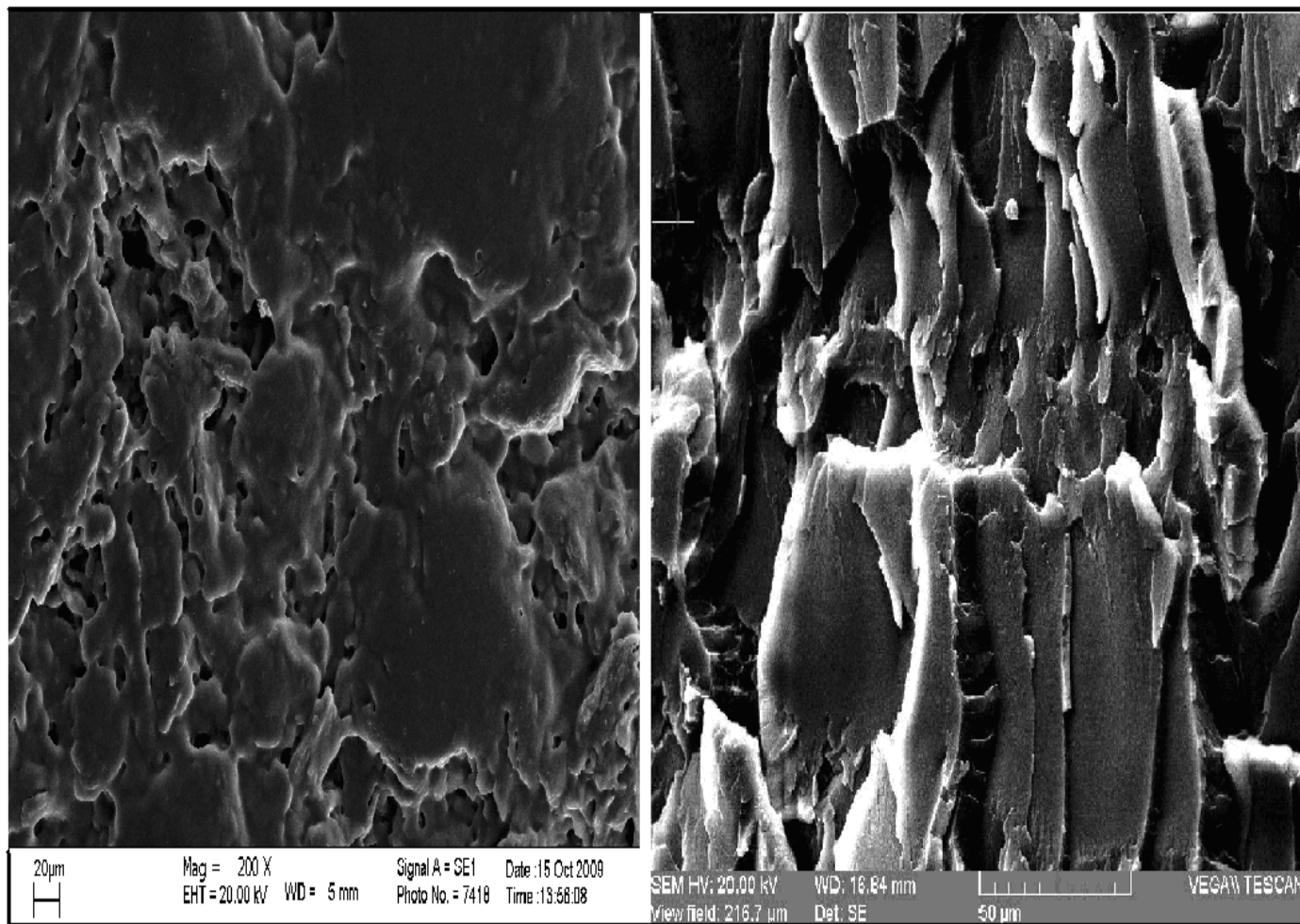
(a)

(b)

(c)

Figure-3
XRD patterns for (a)grafted polystyrene with acrylonitrile modified CNT
(b) grafted polystyrene with acrylonitrile and (c) CNT only

<div align="center">(a)</div>

<div align="center">(b)</div>

<div align="center">

Figure-4
Scanning electron micrographs SEM of Grafted Polymer evaporation attached to a basal plane pyrolitic graphite electrode (a) Grafted polystyrene with acrylonitrile (b) Grafted polystyrene acrylonitrile modified with CNT

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Scanning electron microscopy (SEM): Scanning Electron Microscopy (SEM) of the grafted polymer (GP) was studied using a JEOL attached to an Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20 to 30 kV. The scanning electron micrographs were recorded at a magnification of 100 kX times depending on the nature of the sample.

Samples were dehydrated for 45 min before being coated with gold particles using a Baltec SC030 Sputter Coater. SEM was used to examine the morphology of the grafted polymer by solution evaporation method on a graphite electrode surface. Figure-4a is the SEM of the GP without modified with CNT. Figure-4b is the SEM of the GP modified with CNT. Figure-4b appears that CNT forms on the matrix of GP.

Polymerization Methods: Free radicals, used to initiate polymerization, can be generated in irradiation curing. The gamma irradiation is more economical on a larger scale. Based on the outline of steps proposed, the detailed mechanism of grafted polystyrene with acrylonitrile modified AC is shown in scheme 1^{13}. The suggested structure of grafted polymer in presence of carbon nanotubes can be made crosslinking as shown in scheme $2^{14\text{-}16}$.

where:
i. A free radical catalyst or gamma-irradiated polymer generates the free radicals (R• + R.•). Polystyrene• + Polystyrene•
ii. Initiation step: R• + M (monomer) →R-M•Polystyrene• + Acrylonitrile → Polystyrene+Acrylonitrile•
iii. Propagation step: $R\text{-}(M)_n\text{-}M\bullet + M \rightarrow R\text{-}(M)_{n-1}\text{-}M\bullet$ Polystyrene-(Acrylonitrile)$_n$- Acrylonitrile• + Acrylonitrile→ Polystyrene-(Acrylonitrile)$_{n-1}$ - Acrylonitrile•
iv. Termination step (coupling mechanism): $R\text{-}(M)_n\text{-}M\bullet + R\text{-}(M)_n\text{-}M\bullet \rightarrow R\text{-}(M)_n\text{-}M\text{-}M\text{-}(M)_n\text{-}R$Polystyrene-(Acrylonitrile)$_n$ - Acrylonitrile• + Polystyrene - (Acrylonitrile)$_n$ - Acrylonitrile• → Polystyrene-(Acrylonitrile)$_n$ – Acrylonitrile- (Acrylonitrile)$_n$ – Polystyrene.

(a)

(b)

(c)
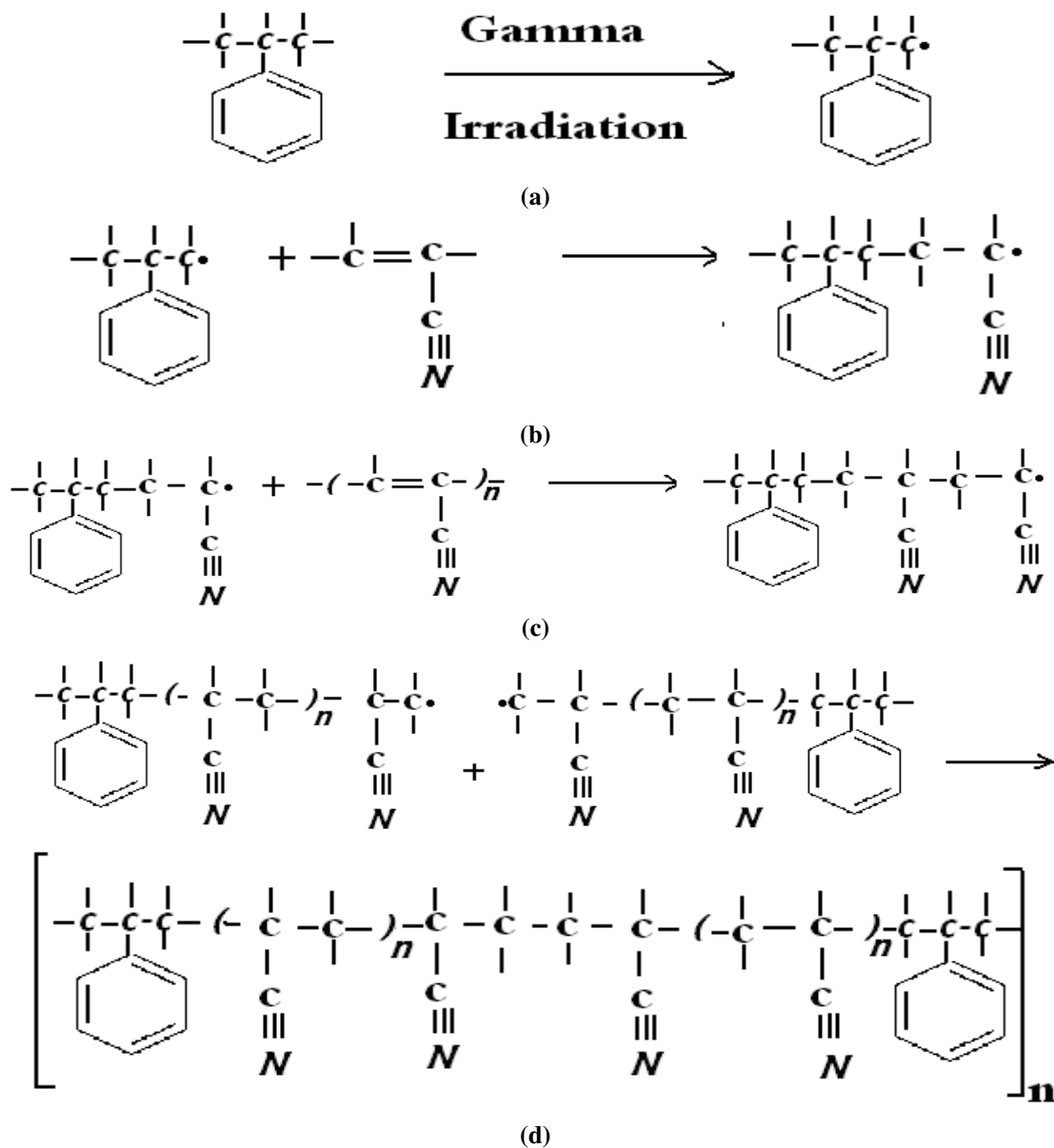
(d)
Scheme-1
The proposal mechanism of polystyrene with acrylonitrile
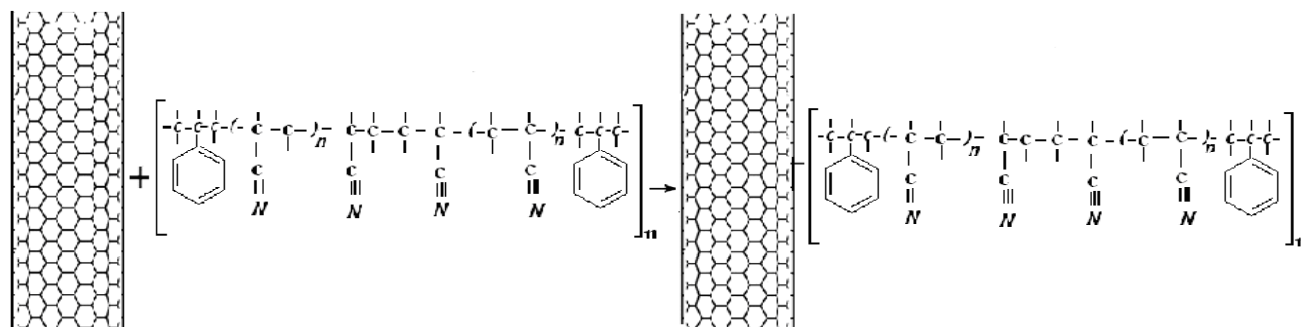
Scheme-2
Grafting of grafted polymer with carbon nanotubes

Conclusion

It was possible to graft a monomer onto polystyrene by a free radical process such as acrylonitrile and be modified with carbon nanotubes using gamma irradiation. The extent of grafted polymer (GP) formation or efficiency of polymerization is dependent on the amount of monomer, ferrous ammonium sulfate (FAS) catalyst and gamma irradiation dosage. In this study, it was found that for 2 gm of polystyrene (polymer), 90% (w/w) acrylonitrile (monomer), 2% FAS (catalyst), 1% carbon nanotubes and 1.25 Mrad gamma dose were the optimized conditions required for the polymerization of GP. The formation of a GP was successfully carried out using carbon nanotubes to improve mechanical and chemical properties of the new GP. Latter was characterized by using FTIR, UV-Visible spectroscopy and XRD analysis.

Acknowledgement

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