

# NOVEL SYNTHESIS OF CHLOROMETHYL-FUNCTIONALIZED WASTE POLYSTYRENE/ AMORPHOUS CARBON THIN FILM COMPOSITE RESIN

# MAHMOUD FATHY<sup>a,\*</sup>, MAHMOUD AHMED MOUSA<sup>b</sup>, TH. ABDEL MOGHNY<sup>a</sup>, ABDEL-HAMEED A-A. EL-BELLIHI<sup>b</sup> and AHMED E. AWADALLAH<sup>c</sup>

 <sup>a</sup>Applications Department, Egyptian Petroleum Research Institute (EPRI), Ahmed El-Zomer, Nasr City, Box. No. 11727, CAIRO, EGYPT
<sup>b</sup>Faculty of Science Banha University, Fred Nada Street, BANHA, CAIRO
<sup>c</sup>Development of Processes Department, Egyptian Petroleum Research Institute (EPRI), Ahmed El-Zomer, Nasr City, Box. No. 11727, CAIRO, EGYPT

# ABSTRACT

This paper aim to synthesise waste polystyrene/amorphous carbon thin film composite resin (WPS/ACTF) beads by grinding and mixing the unused waste polystyrene bottles or others with carbon nanostructure. Such beads were converted into their corresponding Chloromethylated polymer by introducing chloromethyl group. The properties of (WPS/ACTF) composite resin beads and their corresponding chloromethylated polymers were investigated by FTIR and XRD. The surface morphology of ACTF was examined by the high-resolution transmission electron microscope (HR-TEM). It was found from FTIR, the presence of C=C, and C-Cl stretching vibration band of vinyl benzyl chloride monomer. XRD shows a sharp peak at 280 corresponding to (002) plane of graphite and indicated the high crystallinity of ACTF. The HR-TEM of ACTF exhibits amorphous sheets having 2 nm widths and show the vicinity of individual sheets eclipsed over each other to form amorphous carbon thin film. By this technique, we succeed to develop a novel, low-price, but relatively high-performance chlorinated composite resin through the combination of novel amorphous carbon thin film with waste polystyrene using solvent evaporation process.

Key words: Waste polystyrene, Amorphous carbon thin film, Composite resin.

# **INTRODUCTION**

Extended plastics and polystyrene arrive in an assortment of structures. "Polystyrene"

<sup>\*</sup>Author for correspondence; E-mail: fathy8753@yahoo.com; Ph: + (013) 3223769, (202)22747847; Fax: + (013) 3231888, + (202)22747433

is the name given to the sort of plastic, and the chemicals and structures inside of it; however, there are two fundamental sorts of polystyrene being used today-unbending polystyrene, and extended polystyrene (otherwise called styrofoam or polystyrene foam). Rigid polystyrene (PS); for instance, yogurt tubs, is just polystyrene plastic, with no air pockets included. The unused waste polystyrene bottles and others (polystyrene foam and additive-containing TV cabinets) are much less demanding to reuse, and can basically be softened and shaped into new compartments and other products. Expanded polystyrene (EPS) or polystyrene froth, the white "bubbly" plastic edges frequently utilized as a part of bundling for furniture or electronic products is really up to 98% air, and as meager as 2% plastic. Subsequently, it is truly hard to transport and reuse productively and economically<sup>1</sup>.

Amorphous carbon is free, responsive carbon that does not have any crystalline structure (additionally called jewel-like carbon)<sup>2</sup>. Indistinct carbon materials may be balanced out by ending dangling- $\pi$  bonds with hydrogen<sup>3</sup>. These materials are then called hydrogenated undefined carbon. Similarly, as with every formless strong, some short-range request can be watched. Formless carbon is regularly contracted to a- C for general shapeless carbon, a C: H or HAC for hydrogenated indistinct carbon, or to a-C for tetrahedral nebulous carbon<sup>4</sup>.

Amorphous carbon has an extensive variety of properties that are basically controlled by the diverse bond hybridizations conceivable in such materials. This considers the development of a broad scope of slender movies that can be customized for particular applications<sup>5</sup>. Movies can extend from those with high straightforwardness and are hard precious stone like, through to those which are murky, delicate and graphitic-like<sup>6</sup>. Movies with a high level of sp3 holding giving the precious stone like properties are utilized generally by industry for hard coatings. Application regions including field discharge cathodes<sup>7</sup>, electronic gadgets, medicinal and optical coatings are currently near to showcase. Specialists in undefined carbon have been attracted together to deliver this far-reaching critique on the current state and future prospects of this exceedingly utilitarian material<sup>5</sup>.

In this study, the amorphous carbon thin film synthesized on cobalt silicate catalysis was integrated and utilizing to form waste polystyrene/ amorphous carbon thin film (WPS/ACTF) composite resin. Then such composite resin was converted into their corresponding chloromethylated polymer by introducing chloromethyl group. The surface properties of ACTF and prepared composite resin were explored through Fourier Transform Infrared (FTIR) spectroscopy and X- ray diffraction. The surface morphologies of amorphous carbon thin film were examined by the transmission electron microscope (HR-TEM). Whereas, the surface morphology of the produced composite resin was examined using a scanning electron microscope (SEM).

#### **EXPERIMENTAL**

#### Material and experiment

Waste polystyrene, acetone, toluene, SDS, distilled water, amorphous carbon. All the chemical were of Sigma-Aldrich.

# Preparation of waste polystyrene hybrid nanocomposites/self-assembled amorphous carbon film (WPS/ACTF)

10 g of waste polystyrenes was solubilized in 5ml toluene, then 1% from total carbon nanotubes was added and mixing for 30 minutes using ultrasonic apparatus for 20 minutes at 30°C and 1000 Watt electric capacity. Black carbon nanotube suspensions folded by long and short polystyrene chain were obtained by the strong non-covalent bond. After that, 0.5 wt/wt of sodium dodecyl sulfate was completely dissolved in 500 mL distilled water and mix well with 0.1 wt/wt hydroxyl propyl cellulose for 20 min. Organic solution slowly adds to an aqueous solution with stirring at 900 rpm for 4 hours and at 80°C, a solid polystyrene with carbon deposit resins (WPS/ACTF) was obtained. Such solid was subjected to washing well with hot water and dried for 24 hrs at 40°C.

#### Chloromethylation of copolymer resins

2.0176 g of resins (WPS/ACTF), 2.5 mL of chloromethyl methyl ether 1.1530 g of ZnCl<sub>2</sub> and 10 mL of nitrobenzene was added to a 50 mL flask equipped with a refluxing condenser and anhydrous CaCl<sub>2</sub> tube. After stirring at room temperature for 5-10 min, the chloromethylation reaction was carried out at 45°C for 4 hrs. Then, 0.5770 g of ZnCl<sub>2</sub> was added to the system, the polymerization was carried out at 80°C for 12 hrs. The resulting polymer washed with hot deionized water and extracted with acetone in a Soxhlet apparatus. The product was dried under vacuum to give 2.3907 g of resin.

### **RESULTS AND DISCUSSION**

#### **FTIR** analysis

The IR ingestion diminishes emphatically when the  $\pi$  holding gets to be limited, as in tetrahedral amorphous carbon thin film. The infrared ACTF spectrum is given in Figure 1. such spectrum exhibit a band around 1384 cm<sup>-1</sup> demonstrated hydroxyl and carboxylic groups<sup>10</sup>. The spectrum also exhibits a peak at 1620 cm<sup>-1</sup> that can be characteristic assigned to C=C bond in amorphous carbon thin film. The band at about 1160 cm<sup>-1</sup> is assigned to C–C bonds. Also, the spectrum shows the carbonyl characteristic peak at 1650 cm<sup>-1</sup>, which is assigned to the carbonyl group from quinine or ring structure. More characteristic peak to the carboxylic group is the peak at  $1720 \text{ cm}^{-1}$ .<sup>10</sup>



Fig. 1: FTIR of amorphous carbon thin film

FTIR of waste polystyrene resin in Figure 2 show C-H broad band at 3442 cm<sup>-1</sup> - 3024 cm<sup>-1</sup>, and aliphatic CH bonds at 2922 cm<sup>-1</sup> and 2851,40 cm<sup>-1</sup>, and aromatic C=C stretching vibration band at 1820 cm<sup>-1.11</sup>



Fig. 2: FTIR of waste polystyrene resin

The FT-IR spectra of chlorinated waste polystyrene/amorphous carbon thin film resin were given in Figure (3). In the base polymer, the assimilation group's like C=C, C-C

were seen to an extent from 1440 to 1695 cm<sup>-1</sup>. The range has an assimilation band at 827 cm<sup>-1</sup> that can be ascribed to the C-Cl stretch of the  $CH_2Cl$  gotten from the vinyl benzyl chloride monomer<sup>12</sup>. These outcomes demonstrate that the amine group was effectively acquainted with the base polymer through the functionalization process.



Fig. 3: FTIR of chlorinated waste polystyrene/amorphous carbon thin film resin

#### X-ray analysis

It's clear from X-ray analysis of waste polystyrene resin (shown in Fig. 4), that the waste polystyrene resin can't be allowed to crystalline where it have an amorphous broad band at  $20^{\circ}$  at 20. Whereas, the X-ray diffraction investigation of waste polystyrene/ amorphous carbon film resin demonstrates that both are defined in Fig. 5. XRD was performed on waste polystyrene/amorphous carbon film that shows that there is a sharp break at  $28^{\circ}$  that corresponding to (002) plane of graphite and indicated the high crystallinity of ACTF<sup>13</sup>. The sharpness of the tops recommends the vicinity of crystalline carbon stage inside of the carbon spheres<sup>7</sup>.

## HRTEM of amorphous carbon film

HR- TEM pictures in Figure (6) demonstrated that the amorphous carbon thin film consists of collected amorphous slight sheets folded together and connected with each other and forming a confused strongly network semicrystalline sheets. The amorphous sheets have normal widths of 2 nm, which shows the vicinity of individual sheets eclipsed over each other to form amorphous carbon thin film<sup>13</sup>.



Fig. 4: X-ray analysis of waste polystyrene resin



Fig. 5: X-ray analyses of waste polystyrene resin/amorphous carbon film resin



Fig. 6: HRTEM analysis of amorphous carbon film

#### SEM analyses of waste polystyrene resin/amorphous carbon film resin

SEM micrograph of the combined polystyrene resins prepared by solvent evaporation is given in Figure (7), and exhibit the presence of superball due to adding solvent evaporation that affected the measurement of self-gathering of polystyrene microspheres with ACTF by  $\sim 150$  mm.<sup>14</sup> The solvent evaporation procedure includes evaporating adequately extensive toluene drops scattered in water during the preparation process, with every drop containing numerous a large numbers of polystyrene microspheres. Therefore, we find that the ACTF nanoparticles impeded inside the resin, where the resin make a sandwich-like shape with ACTF as seen on the top left the side of Figure (7).



Fig. 7: SEM analyses of waste polystyrene resin/amorphous carbon film resin

## **CONCLUSION**

In solvent evaporation method the waste polystyrene amorphous carbon film resin was treated with chlorodimethylether to obtain a chloropolystyrene amorphous carbon film resin. Thereby, we succeed to develop a novel, low-price, but relatively high-performance chlorinated composite resin.

## REFERENCES

- 1. Y. Chen and K. Liu, Preparation and Characterization of Nitrogen-Doped TiO<sub>2</sub>/Diatomite Integrated Photocatalytic Pellet for the Adsorption-Degradation of Tetracycline Hydrochloride using Visible Light, Chem. Engg. J., **302**, 682-696 (2016).
- 2. M. Daud et al., Graphene/Layered Double Hydroxides Nanocomposites: A Review of Recent Progress in Synthesis and Applications. Carbon, **104**, 241-252 (2016).
- 3. M. Enterría and J. L. Figueiredo, Nanostructured Mesoporous Carbons: Tuning Texture and Surface Chemistry. Carbon, **108**, 79-102 (2016.).

- 4. X. Li et al., Graphitized Hollow Carbon Spheres and Yolk-Structured Carbon Spheres Fabricated by Metal-Catalyst-Free Chemical Vapor Deposition. Carbon, **101**, 57-61 (2016).
- 5. G. Mamba and A. K. Mishra, Graphitic Carbon Nitride (g-C3N4) Nanocomposites: A New and Exciting Generation of Visible Light Driven Photocatalysts for Environmental Pollution Remediation, Appl. Catal. B: Environ., **198**, 347-377 (2016).
- 6. M. El-Sayed, M.R., R. Hosny, M. Fathy and Th. Abdel Moghny, Breakthrough Curves of Oil Adsorption on Novel Amorphous Carbon Thin Film, Water Sci. Technol., **73(10)** (2016).
- T. A. M. Mahmoud Fathy, Mahmoud Ahmed Mousa, Abdel-Hameed A-A. El-Bellihi and Ahmed E. Awadallah, Synthesis of Transparent Amorphous Carbon Thin Films from Cellulose Powder in Rice Straw, Arabian J. Sci. Engg. DOI: 10.1007/s13369-016-2273-5 (2016).
- 8. M. Fathy et al., Incorporation of Multi-Walled Carbon Nanotubes in Microspheres used as Anion Exchange Resin Via Suspension Polymerization, Appl. Nanosci., **4**(5), 543-549 (2014).
- 9. T. A. M. Mahmoud Fathy, Ahmed Elsayed Awad Allah and A.-H. A.-A. El-Bellihi, Preparation of Anion-Exchange Resin from Styrene-Divinylbenzene Copolymer with High Cross-Linking Structure, Elixir Int. J. (2014).
- E. F. Abdrashitov et al., Synthesis and Properties of Stretched Polytetrafluoroethylene -Sulfonated Polystyrene Nanocomposite Membranes, Solid State Ionics, 286, 135-140 (2016).
- L. Gonsalvesh et al., Preparation, Characterization and Application of Polystyrene Based Activated Carbons for Ni(II) Removal from Aqueous Solution, Fuel Processing Technol., 149, 75-85 (2016).
- 12. L.-C. Chen et al., Fabrication of Macroporous Polystyrene/Graphene Oxide Composite Monolith and its Adsorption Property for Tetracycline, Chinese Chem. Lett., **27(4)**, 511-517 (2016).
- 13. M. Fathy et al., Study the Adsorption of Sulfates by High Cross-Linked Polystyrene Divinylbenzene Anion-Exchange Resin, Appl. Water Sci., 1-5 (2014).
- D. J. Kim et al., Characterization of the Sulfonated PEEK/Sulfonated Nanoparticles Composite Membrane for the Fuel Cell Application, Int. J. Hydrogen Energy, 41, 5793-5802 (2016).

Revised : 23.04.2016

Accepted : 26.04.2016