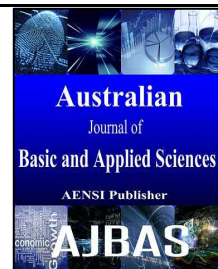




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Enhancement physical properties of (Styrene- Methylacrylate) copolymer with chlorinated Adduct

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ABSTRACT

A composite of Styrene-methylacrylate copolymer (ST co-MA) and new adduct (hexachloro- cyclopentadiene HCP with allyl p-bromo phenylether) was synthesized. The new adduct was added with different ratio (2%, 4%, 8% and 16%) to the copolymer to enhance its physical properties. The structure of the prepared (ST co-MA) and the (ST co-MA) /adduct composites were investigated by Fourier Transform Infrared (FTIR), HNMR and the elemental analysis. The FTIR shows characterized peaks of the prepared composites. Thermal gravimetric analysis (TGA) shows that the composites have higher decomposition temperature in comparison with the pure copolymer. Electrical conductivity measurement shows the electrical conductivity increased by increasing the adduct concentration up to 4 wt%.

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INTRODUCTION

Polymers with defined architectures and well-controlled functionalities are currently of great interest in academic research (Günay *et al.*, 2013; Lirong and Shang, 2015). The creation of new polymeric materials with the required combination of properties is of great practical importance. Because of influence of copolymer structure on its properties the estimation of relationship between composition, chain distribution and bulk properties is of great scientific interest for this purpose. For example, styrene/acrylates copolymers obtained in emulsion polymerization were studied in details (Harold *et al.*, 1995; Djekhaba and Guillot, 1990; Doremaele *et al.*; 1992; Geerts *et al.*, 1992; Rivera *et al.*, 1989; Schlund *et al.*, 1989 and Kalugin *et al.*, 2014). Polystyrene is one of the most important polymers of today. The monomer styrene is a very versatile monomer. It can be polymerized by various mechanism such as free radical-, cationic-, anionic-, and group transfer polymerization. Moreover, styrene has the capability to create radicals, which makes thermal polymerisation possible. Styrene can also be used in all types of production processes for polymerisation. The most common methods are emulsion-, suspension-, bulk- and solution polymerisation. The type of process determines the properties of the polymer produced (Ku,1988a and

Ku 1988b). The copolymers of styrene and alkyl methacrylates represent a widely-used class of copolymers since they exhibit great diversity of properties compared to those of homopolymers (Li *et al.*, 2006). Their high thermal and chemical stability, high transparency, easy formability, good electrical and mechanical properties (Penzel, 1992) has led them to be used for a variety of applications in medicine, paper and paint industry, textiles and automobiles etc. For example, solid polystyrene is used in disposable cutlery, plastic models, CD and DVD cases, and the expanded form of polystyrene is used for packing materials and insulation (Mark *et al.*, 1985; Pasupuleti and Madras, 2010). Methyl acrylate-styrene copolymers of different copolymer compositions were free-radically prepared. The relative intensities of the carbonyl frequencies of the methyl acrylate units at ν 1730 cm^{-1} were correlated with the copolymer composition. The positions and shapes of the carbonyl bands in the infrared absorption spectra of the copolymers-dissolved in chloroform were shown to depend on the composition of the copolymers and upon the presence of different proportions of methyl acrylate centered triads (Kandil and El-Gamal, 1986). In the present work we reported synthesis of Styrene-methyl acrylate copolymer and Styrene-methyl acrylate copolymer /chlorinated adduct by deposition technique to improve polymer properties like thermal

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resistance, electrical conductivity etc. The chemical structures were investigated by FTIR and N.M.R. respectively. The thermal behavior of copolymer and copolymer/adduct composites were studied by thermal gravimetric analysis (TGA). Electrical conductivity of the samples was also measured.

Experimental:

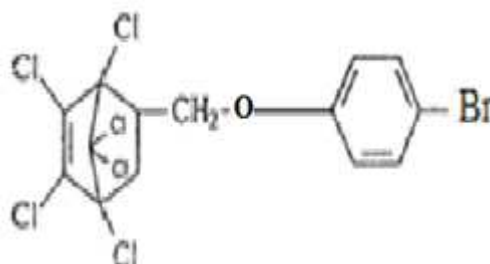
Materials:

Styrene monomer (C_8H_8), Methyl acrylate monomer ($C_4H_6O_2$), Benzoyl peroxide (C_6H_5COO)₂ as an initiator, $CHCl_3$ as a solvent were obtained from Aldrich.

Method:

Preparation of adduct:

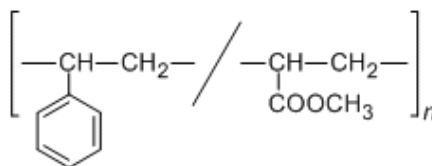
The chlorinated cyclo-adduct was carried out as mentioned in (Youssif, 1983; Youssif *et al*, 2011). The structure of adduct was:



Preparation of (Styrene- Methyl acrylate) copolymer:

The reaction was carried out in a flask connected with a condenser system. 1/1 molar ratio between (St) and (MA) was placed in 100 ml $CHCl_3$ and 0.1% of benzoyl peroxide as an initiator. The reaction was carried out at 86 °C for 2 hours. The resultant

solution was poured in a petri dish to make film. The precipitated polymer was vacuum-filtered and washed several times with methanol and water then dried at 65 °C for 10 hours till constant weight (Abdul-Jaleel and W. Younis, 2012).



Preparation of (Styrene- Methyl acrylate) copolymer with Adduct:

The chlorinated cycloadduct was added to the (Styrene- Methyl acrylate) copolymer in situ polymerization with different weight % as shown in Table 1 in the presence of 0.1 gm benzoyl peroxide as

an initiator in 100 ml $CHCl_3$ as a solvent at 86°C at 2.30 hour. The precipitate was characterized. The elemental analysis of the prepared (ST co-MA) and the (ST co-MA) /adduct composites is given in (Table 2)

Table 1: Identification of the samples

Adduct wt%	Styrene-co- Methyl acrylate %
0	100
2	98
4	96
8	92
16	84

Table 2: Elemental analysis of the samples

Adduct wt%	C,%	H,%	Cl,%	Br,%
0	77.69	7.36	-	-
16	46.07	7.64	33.23	10.93

Characterizations:

Molecular weight:

Molecular weight determination was done by gel permeation chromatography (GPC), the weight average molecular weight was determined by using CRYETTEA instrument- Automatic cryoscopy. The method was based on Avogadro-Gerhardt law. The

weight average molecular weight, M_w , was found to be 18763 for copolymer.

Fourier-transform infra-red (FTIR):

The IR analysis was carried out using a FTIR spectrometer at wavelengths from 500 - 4000 cm^{-1} and transmittance % from 30 - 100.

Nuclear Magnetic Resonance (NMR):

Proton NMR spectra in deuterated CHCl_3 containing tetra methyl silane as an internal standard were recorded in an A Varian instrument division EM-390 90M HZ NMR spectrometer.

Thermo-gravimetric analysis (TGA):

TGA was performed using a Shimadzu TGA-50H instrument. The rate of heating was $10^\circ\text{C}/\text{min}$ up to 600°C under a nitrogen atmosphere.

Electrical conductivity:

The samples prepared were pressed into pellets of 1.33 cm diameter and 1 mm thickness in a hydraulic press (Kimaya Engineers, India, and Model WT-324) at five metric ton pressure. The conductivity measurements were carried out by a Kiethley electrometer model 6517A. The pellet used in this measurement was placed between two copper electrodes, which were connected to the two terminal of the Keithley electrometer.

RESULTS AND DISCUSSION**Fourier-transform infra-red (FTIR):**

FTIR analysis is the most extensively method used for the investigation of polymer structure and analysis of the functional groups. The FTIR spectra of the 4 wt% of St co-MA/ adduct composite made

in the present study (Fig.1.) show the asymmetric stretching vibrations of $-\text{CH}_3$ groups in the region 2922 cm^{-1} . The symmetric stretching vibrations of the $-\text{CH}_3$ group seem to overlap with the stretching vibrations of the $-\text{CH}_2$ group in the region 2851 cm^{-1} . The absorption band show the characteristic absorption bands of a phenyl ring in the styrene. The $-\text{C}-\text{C}-$ stretching vibrations of a phenyl ring appear at 1601 cm^{-1} , and the $-\text{C}-\text{H}$ deformation vibrations of ring hydrogens in the 1732 cm^{-1} region is characteristic of the ester carbonyl $-\text{C}=\text{O}$ stretching vibrations, and its overtone was observed near 3450 cm^{-1} . The absorption band in the region 1451 cm^{-1} results from the bending vibrations of $-\text{CH}_3$ group, and the bending vibrations of $-\text{CH}_2$ group was found in a slightly higher region in the IR absorption spectra. The rocking vibrations of $-\text{CH}_2$ can be observed in the region 759 cm^{-1} . The skeletal vibrations of polymer backbone and the $-\text{C}-\text{O}-\text{C}-$ stretching resonances appear in the regions 1161 and 1111 cm^{-1} respectively. The IR spectra also are found by noticing a signal at 759 cm^{-1} . The 3059 and 3026 cm^{-1} peaks are assigned to $-\text{C}-\text{H}$ stretching vibrations of ring's hydrogen, and its overtone (Reddy *et al.*, 2000; Vijayaraghavan *et al.*, 2003; Siddiqui *et al.*, 2013) . As well as the absorbance band assigned for C-Br appears at 539 cm^{-1} and a sharp peak appears at 697 cm^{-1} could be due to C-Cl (Youssif *et al.*, 2011).

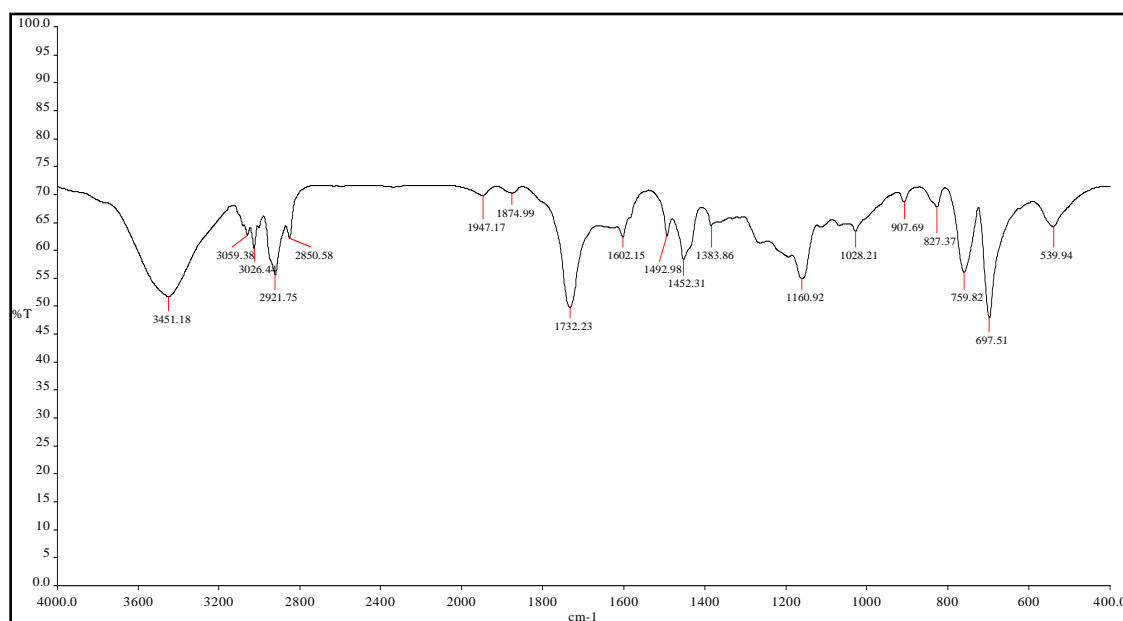


Fig. 1: FTIR of the St co-MA/ adduct composite

Composition by ^1H NMR (Kalugin *et al.*, 2014):

Composition of St/MA copolymers was estimated with ^1H NMR analysis Fig. 2. Signals at 6.5-7.5 ppm correspond to protons of aromatic ring (a) in styrene, methylene group $-\text{CH}_2-$ (b) has signals at 1-2 ppm and signals at 3-4 ppm are related to

protons of methoxy $-\text{OCH}_3$ -group (c) in methyl acrylate. The NMR spectra of the copolymers / adduct were not additive with those of copolymer, but it was found that the multiplicity of the signals shifted at 6-8 ppm which belongs to proton of aromatic ring due to the extra aromatic group of the

adduct (Fig.3.) .Also the signals at 1-3 ppm was appears due to the activated methylene group $-CH_2-$.

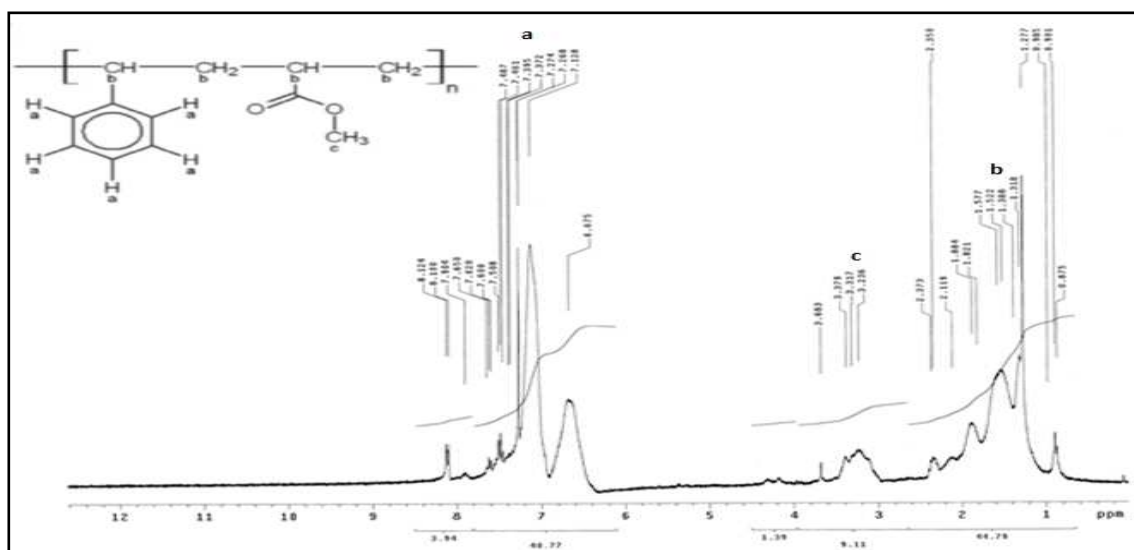


Fig. 2: Typical 1H NMR spectra of St co-MA

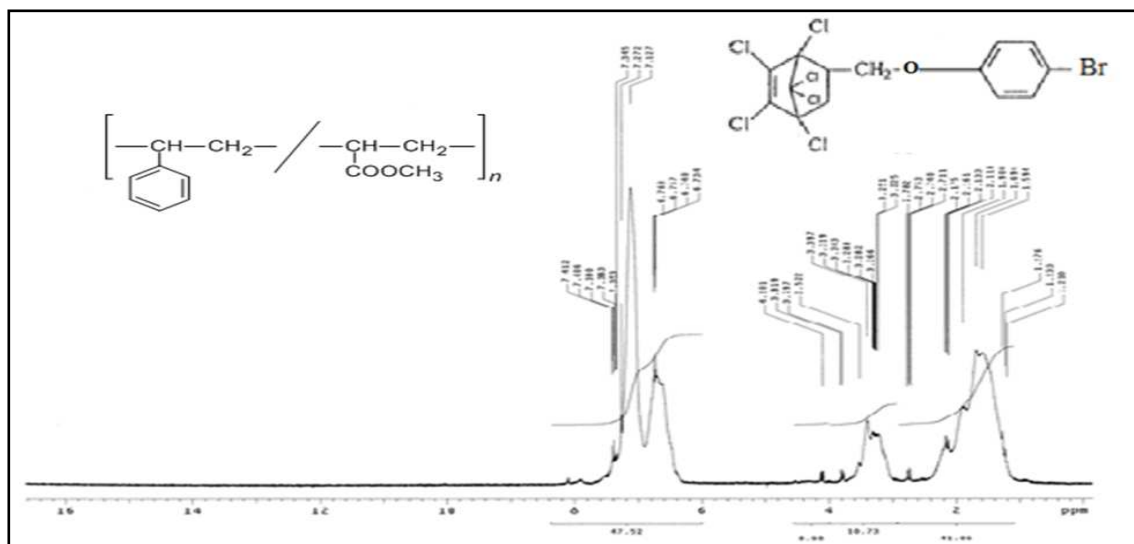


Fig. 3: Typical 1H NMR spectra of St co-MA /adduct

Thermo-gravimetric analysis TGA:

Thermo-gravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. When heating occurs under an inert gas flow, a non-oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties.

The TGA thermograms of the pure copolymer and the PS co-MA/adduct composites are shown in (Fig.4). The onset degradation temperatures of all samples at 5% loss of the weight $T_{5\%}$ were determined. Also T_{max} °C and char residue at 500 °C weight loss data evaluated by TGA for the PS co-MA and the PS co-MA /adduct composites and illustrated in Table 3. We could see from (Table 3), $T_{5\%}$ increased by about 76, 26 and 3 °C respectively compared with the pure PS co-MA, which indicated that the thermal stability of the composites was enhanced (Shengpei, 2003). However it was found that the T_{max} is slightly improved for the composites by about 6 °C compared to pure copolymer. The improvement of the thermal stability of the composites is due to higher thermal stability of the chlorinated bicyclic adduct.

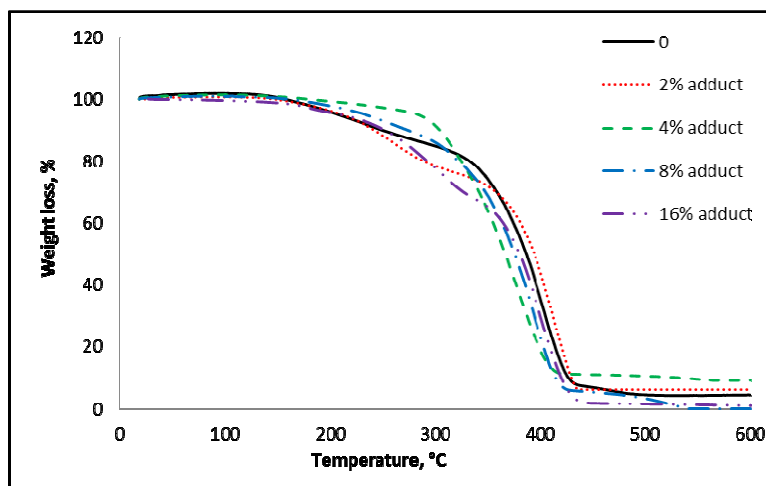


Fig. 4: TGA of the pure PS co-MA and the PS co-MA /adduct composites

Table 3: Thermal parameters of the samples

Adduct %	T _{5%} °C	T _{max} °C	char residue
			(wt% at 500 °C)
0%	207	395.7	4.4
2%	211	398.4	6.0
4%	283	401.1	10.4
8%	233	381.7	3.2
16%	210	384	1.5

Electrical conductivity of the composites:

The temperature dependence of the electrical conductivity of the PS co-MA/adduct composites with different wt. %, over the temperature range 293 to 400 K, is shown in Fig. 5. It clear from the figure that the conductivity is slightly increases with increasing temperature for all the composites and the neat copolymer. In general, the electrical conductivity is slightly thermally activated according

to the well-known Arrhenius law in a way typical of semiconductors (Motawie *et al.*, 2014):

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right)$$

σ_0 is pre-exponential factor and inversely proportional to the temperature T, K is Boltzman constant = $1.38 \times 10^{-23} \text{ J K}^{-1}$ and E_a is the activation energy.

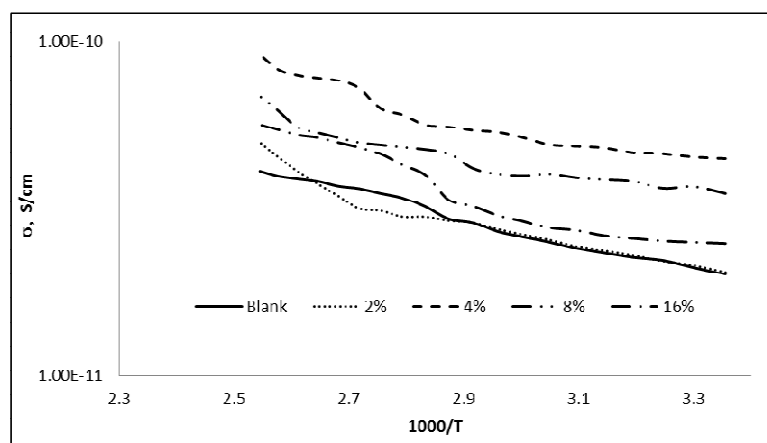


Fig. 5: Temperature dependence of dc electrical conductivity of the copolymers and the copolymer/adduct

Fig.6. shows the conductivity dependence on the concentration of the adduct. The figure shows that σ of the all composites is higher than that of the neat copolymer. The best values of σ is obtained for 4% PS co-MA/adduct composite, however 8% and 16% PS co-MA/adduct composite have lower values of σ

than that of 4%. In absence of electric field the dipole moment of the composites are randomly oriented. Applying electric field to the composites causing alignment of these dipoles so conductivity increases. At higher adduct concentrations, the free volume of the copolymer system decreased so

retarding the internal movement of the dipole moments then conductivity decrease (Motawie *et al.*, 2014; Abulyazied *et al.*, 2014). This results in

accordance with the previous data of the TGA which confirm that this concentration (4%) give the best results.

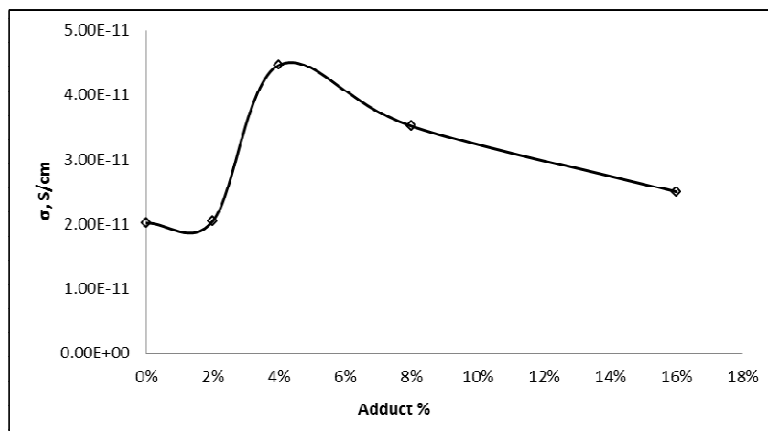


Fig. 6: Effect of the concentration of the adduct on the dc conductivity

Concolusion:

Styrene-methylacrylate copolymer was prepared and new adduct (hexachloro- cyclopentadiene HCP with allyl p-bromo phenylether) was added to the copolymer with different wt% (2, 4, 8 and 16). The composition of St/ MA copolymers and its composites with the adduct was estimated with FTIR and ¹HNMR analysis. From the thermogravimetric analysis results we concluded that the thermal stability of the prepared composites was improved in compared with the pure copolymer and the concentration of 4 wt% adduct is the optimum concentration for enhancing the thermal stability of the samples. It was found that the electrical conductivity is slightly increased with the increasing of the temperature. Moreover, the electrical conductivity of the all composites is higher than that of the neat copolymer. The best values of σ are obtained for 4 wt% PS co-MA/adduct composite which in accordance with the data of the TGA.

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