

## Dielectric study of surface modification of linear low density polyethylene treated with chromic acid and sodium carbonate

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The relative permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of linear low density polyethylene (LLDPE) sample of 60  $\mu\text{m}$  thickness treated successively with a highly oxidizing environment like chromic acid of normality N/5 to N/30 for time duration of 0.5 to 12 hr and sodium carbonate for 24 hr are measured using GRA 650A impedance bridge over 100 Hz to 10 kHz range at 303.16 $\pm$ 1K. The N/10 chromic acid treated sample exhibited increase in values of  $\epsilon'$  (from 3.2 to 4.3) and  $\epsilon''$  (from 0.48 to 0.75) relative to the virgin sample at 300 Hz while the rest of the samples recorded reduction. But these chromic acid treated LLDPE samples being further treated with N/10 sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), exhibit change in  $\epsilon'$  and  $\epsilon''$  values in as much as those for N/10 chromic acid treated sample drops while that of N/15 chromic acid treated sample increases significantly. This indicates intense polarization penetrating to reasonable depth of the surface of the material. The higher value of  $\epsilon'$  and  $\epsilon''$  in N/10 chromic acid treated sample may be due to intra-molecular three-dimensional network of H-bonding between PE-COOH species. Attempt is made to explain these features.

**Keywords:** Relative permittivity, Dielectric loss, Linear low density polyethylene, Polymers

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### 1 Introduction

Study of the dielectric behaviour of polymers enables the industry to elicit the characteristic information as regards to its use as insulator and for various other mechanical and electrical applications. The physical and chemical nature of the macromolecules, the molecular mobility of sub-molecules and various other properties could be ascertained from a study of the temperature and frequency variation of relative permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$ . The structure of solid organic polymers as well as the surface composition influence many of their properties and uses. In fact, surface composition of the polymers primarily influences many important industrial applications such as wetting, weathering, permeation, adhesion, friction, electrostatic charging and dye adsorption<sup>1</sup>. However, it is difficult to hypothesize the linkage of molecular structure of polymeric surface with its macroscopic surface properties because it has not been possible to obtain polymers with surfaces having well defined functionality<sup>2-4</sup>. The lack of precise information regarding three dimensional spatial distribution of functional groups and the surface region – a problem having no counterpart in material science is an

important impediment in this sphere. Linear low density polyethylene (LLDPE)—a low cost, higher tensile strength and percent elongation has penetrated into the markets like stretch film, merchandise bags and also non-packaging applications like industrial sheeting and agricultural film. Attempts are being made to determine the size of surface microcracks of the irradiated polyethylene terephthalate (PET) with X-rays and non-monotonous dependence of the dissolution rate of the polymer on the NaOH solution<sup>5</sup>. The modification in the chemical structure and physico-chemical properties of LLDPE with wood fibre, induced by ion-bombardment are being extensively studied<sup>6-8</sup>.

### 2 Experimental Details

The LLDPE samples of 60  $\mu\text{m}$  thickness were obtained from Central Institute of Plastics Engineering and Technology (CIPET) Extension Centre, Bhubaneswar, India. The samples were treated separately with N/5, N/10, N/15, N/20, N/25 and N/30 chromic acid for varying time durations, viz., 0.5-12 hr successively at regulated temperature of 303.16 $\pm$ 1 K. Each of this sample after chromic acid treatment was washed by acetone in order to remove traces of acid

from the surface of treated sample. Thereafter, the chromic acid treated sample was further treated by N/10  $\text{Na}_2\text{CO}_3$  for 24 hr. The relative permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) were determined by using the sample holder designed by Mishra and Swain<sup>9</sup> and a GRA 650A impedance bridge in 100 Hz to 10 kHz range. The value of  $\epsilon'$  was computed by using the relation:

$$\epsilon' = (C - C_0) / (C_a - C_0) \quad \dots (1)$$

where  $C_0$  is the stray capacitance of the instrument,  $C_a$  the capacitance with air dielectric and  $C$  is the capacitance with polymer dielectric.

The value of  $\epsilon''$  was calculated by using the relation:

$$\tan \delta = \epsilon'' / \epsilon' \quad \dots (2)$$

where  $\tan \delta$  is the loss tangent.

### 3 Results and Discussion

The relevant data have been shown in Figures 1-4. Fig. 1(a and b) shows the variation of  $\epsilon'$  and  $\epsilon''$ , respectively measured at 300 Hz for the sample treated with chromic acid of different normalities over a time range. Fig. 2 shows its variation for the same specimens further treated with N/10  $\text{Na}_2\text{CO}_3$ . Fig. 3 gives the Cole-Cole plot for N/10 chromic acid treated sample. The Cole-Cole plot for the same specimen further treated with N/10  $\text{Na}_2\text{CO}_3$  is shown in Fig. 4. The relative permittivity  $\epsilon'$  of virgin LLDPE sample is 3.2 and that of  $\epsilon''$  is 0.48 at 300 Hz. It is observed that both values of  $\epsilon'$  and  $\epsilon''$  are the highest for N/10 chromic acid treated sample. A perusal of Fig. 1(a) shows that  $\epsilon'$  value for N/10 sample increases nearly 30% reaching as high as 4.33. The  $\epsilon''$  also exhibits similar trend reaching 0.75 which is nearly twice that of the virgin sample. This indicates an intense polarization penetrating into reasonable depth of the surface of the material. It is an indication of the probability of surface modification of the sample due to chromic acid treatment being significant for N/10 sample. Chromic acid is a relatively stronger oxidizing agent. Functionalisation of LLDPE is accomplished by oxidation with chromic acid, which produces a polyethylene film with functional groups attached to the surface. The film after chromic acid treatment is hereafter referred to as polyethylene carboxylic acid (PE-COOH). The higher value of  $\epsilon'$  and  $\epsilon''$  at N/10 chromic acid may be an indication of degree of oxidation due to intra-molecular three-dimensional network of H-bonding between PE-COOH species (Fig. 5).

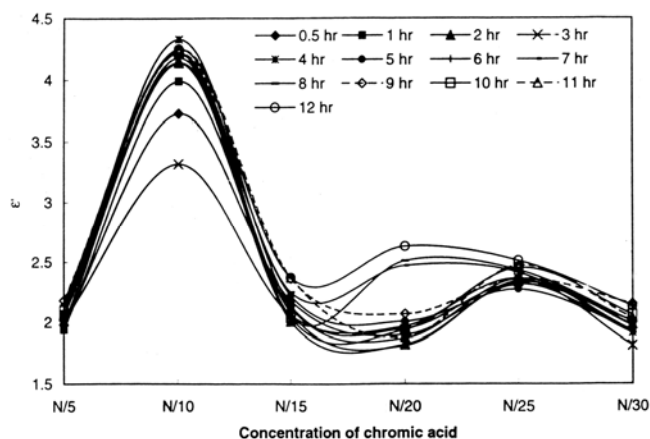


Fig. 1(a)—Variation of  $\epsilon'$  with Chromic acid concentration

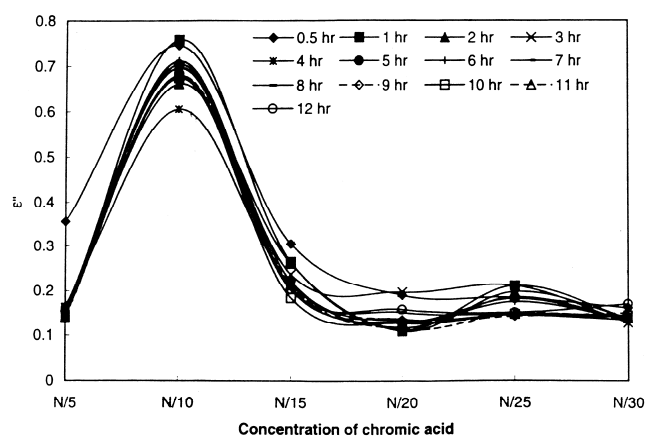


Fig. 1(b)—Variation of  $\epsilon''$  with Chromic acid concentration

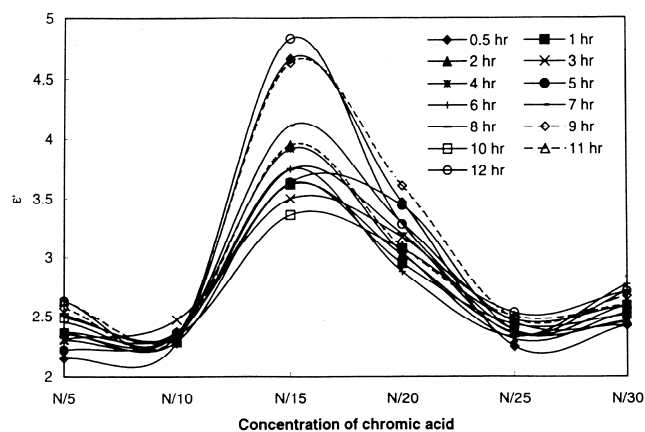


Fig. 2—Variation of  $\epsilon'$  with Chromic acid concentration washed by N/10 Sodium Carbonate

Sample treated with acid of higher concentration (N/5), however, shows reduction in the value of  $\epsilon'$  and  $\epsilon''$ . At higher concentration, oxidation penetrates into greater depth generating more functional groups in inner layers. In such a situation, the probability of

interaction between the surface PE-COOH groups with those in the inner layer groups is likely to cause more of inter-layer inter-molecular network. This is analogous to one existing in a wood-pile structure<sup>10</sup>, whereas that existing on a single-layer can be viewed as end-on structure<sup>10</sup>. The enhanced interaction being directed in a near transverse plane is likely to adversely affect the bulk dielectric property of the sample.

With increasing dilution i.e., N/15, N/20 though both penetration depth as well as the surface functionalisation diminishes the resultant inter-layer interaction might be contributing to reduction in the value of  $\epsilon'$  and  $\epsilon''$ . But at chromic acid concentration of

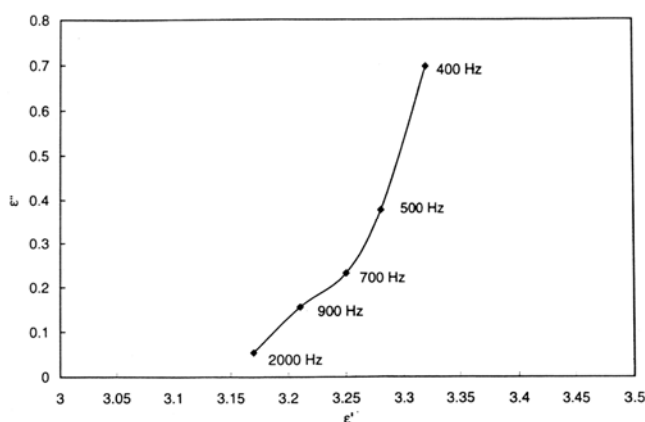


Fig. 3—Cole-Cole plot for N/10 Chromic acid treated sample

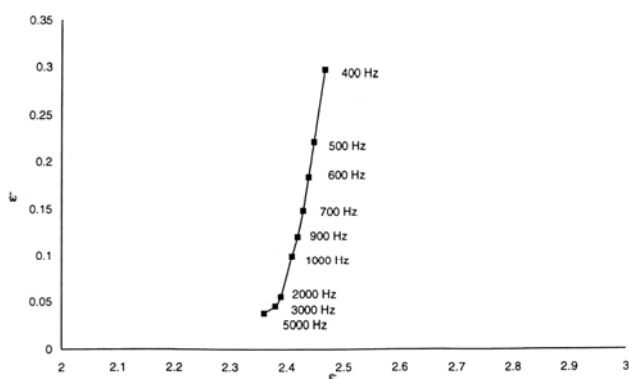


Fig. 4—Cole-Cole plot for N/10 Chromic acid treated sample washed by N/10 Sodium Carbonate

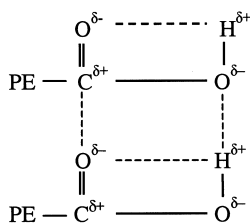


Fig. 5—Intramolecular three dimensional network of H-Bonding between PE-COOH species

N/25, there is a slight increase in  $\epsilon'$  probably due to the dilution factor coming into play. Greater dissociation in the dilute environment liberates more free  $H^+$  ions which might be adhering to the polarized surface rendering it more perforated and hence slight increase in dielectric values.

A perusal of Fig. 2 unfolds a different scenario. The N/10 chromic acid treated sample after undergoing N/10  $Na_2CO_3$  treatment loses its distinctive character in as much as the  $\epsilon'$  comes down to nearly 2.4. However, though the values of  $\epsilon''$  in general reduces, it does not confirm to a particular trend. On the other hand, N/15 chromic acid treated sample which showed  $\epsilon'$  value around 2.3 earlier, shows a significant rise to nearly 4.8, while its  $\epsilon''$  value decreases. It is known that a process of hydrolysis of amorphous LLDPE occurs in alkalis. The rate of the hydrolysis changes with variation of alkali concentration. The formation of conjugated polyene system on the polymer matrix due to alkalis shows that either H atoms from adjacent carbon atom in the main chain are lost and/or some of the  $CH_3$  groups on side chains are knocked out<sup>11</sup>.

The reduction in the value of  $\epsilon'$  in N/10 chromic acid treated sample after treatment in N/10  $Na_2CO_3$  may be due to removal of loosely bound proton species from the surface of LLDPE through acid-base neutralization process. The process of dissolution of polymers is limited by diffusion of active particles through the bulk of the polymer and the diffusion of products of dissolution to the surface of the polymer. For LLDPE polymer, the process of dissolution proceeds in the external diffusion-kinetic area, thickness of which is very close to that of monolayer<sup>12</sup>. The lowering of the rate of dissolution is associated with ionization of the ester bond in the solution. Independent diffusional motion of water and alkali molecules is typical of LLDPE, a hydrophobic polymer<sup>13-16</sup>. However, when the N/15 chromic acid treated sample is treated with N/10  $Na_2CO_3$  the alkali medium dominates over acid medium resulting in the formation of PE-COONa species on the surface of LLDPE sample (Fig. 6).

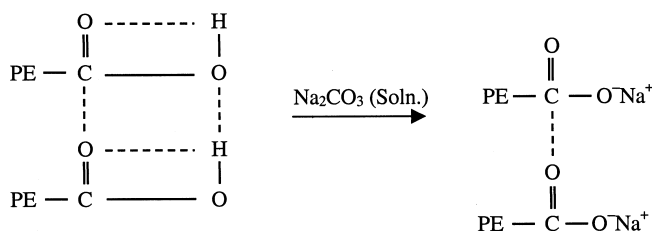


Fig. 6—Formation of PE-COONa species on the surface of LLDPE sample

The process may leave the LLDPE surface in the most polarized state which favours for higher value of  $\epsilon'$ . Further, with decrease of acid concentration the rate of oxidation on the surface of LLDPE gradually decreases and availability of PE-COOH species also reduces due to multimerization for which the probability of formation of hydrogen bonding becomes scarce and supports in the reduction of  $\epsilon'$  value. The Cole-Cole plot (Fig. 3) drawn for  $\epsilon'$  versus  $\epsilon''$  for N/10 chromic acid treated sample and (Fig. 4) for the same sample treated with N/10  $\text{Na}_2\text{CO}_3$  are not usual arc type. The patterns are similar to one observed by Banhegyi *et al.*<sup>17</sup> for moist  $\text{CaCO}_3$  filled polyethylene composites. From our earlier FTIR studies<sup>18</sup>, it is observed that there appears two absorption bands having  $\nu_{\text{abs}}$  in the range  $1307\text{-}1213\text{ cm}^{-1}$  and  $1464\text{-}1377\text{ cm}^{-1}$  arising out of C-O stretching ( $1320\text{-}1210\text{ cm}^{-1}$ ) and O-H bending ( $1440\text{-}1395\text{ cm}^{-1}$ ) of COOH group. The deviation from the theoretical values may be attributed to the intra-molecular hydrogen bonding that occurs on the surface functionality of LLDPE.

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