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CHEMICAL MODIFICATION OF POLYETHENE AND IMMOBILIZATION OF CONDUCTING POLYANILINE

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ABSTRACT

Polyethene has many properties that make it a suitable support for the immobilisation of functional moieties. Chlorination provides a convenient route for the functionalization of, the otherwise chemically inert polyethene. An environmentally harmless procedure was developed for the controlled chlorination of PE. During this procedure the duration of chlorination as well as the partial pressure of chlorine gas were conveniently controlled. Through nucleophilic substitution and elimination, the CPE intermediate was further functionalized to obtain hydroxyl, amine and unsaturated derivatives of PE, which are useful for the immobilization of a wide range of moieties. Conducting polymers, despite their potential for application in diverse situations, are difficult to be fabricated as self-supporting films and sheets. By growing the polymer on a suitable substrate this processing difficulty may be overcome. A method for immobilizing a conducting layer of polyaniline on PE through graft-copolymerizaton is described in this paper.

Key words: Polyethene, polythene, chlorinated polyethene, chemically modified polyethenes, conducting polyaniline.

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1. INTRODUCTION

Polyethene (PE) is one of the most widely used materials in the world. It finds application in a wide range of situations due to its low bulk density, lightweight, wide-ranging performance and favourable cost. The glass transition temperature of PE is around 200 K while its crystals melts around 383 – 408 K. C-C bond energy is 250-334 kJ mol^{-1}. This high C-C bond energy makes polyethene highly resistant to degradation [1]. Polyethene can be produced either as a low-density material, low-density polyethylene (LDPE) or as a high-density material, namely, high-density polyethylene (HDPE). LDPE has 20-40 branches per 1000 carbon atoms, which results in the loss of structural regularity, thus hindering crystallization and thereby lowering the rigidity. HDPE, on the other hand; has 5-15 branches per 1000 carbon atoms making the material inclined to crystallize, thus imparting rigidity to the material [1]. These characteristics make polyethylene a material highly suitable for supporting a wide range of moieties, an area of application of polyethene, not significantly explored hitherto. With suitable chemical modification it should be possible to immobilize a variety of substances on polyethene. These substances may be complexing agents, which, preferably, bind appropriate analytes selectively. If such binding leads to colour changes, then the polyethene-complexing agent composite could be used as a suitable opto-chemical sensor material. It may also be possible to graft-copolymerize specialist polymers on polyethene to produce composite materials with interesting and useful properties.

Polyethene, though resistant to attack by many chemical reagents, can be functionalized through photochemical chlorination; a reaction characteristic of saturated hydrocarbons. The C-Cl bond, once introduced, opens up polyethylene for further functionalization through nucleophilic substitution as well as elimination. This paper describes work carried out in our laboratories that led to the

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functionalization of polyethylene through controlled chlorination.

Conducting polymers such as polyacetylene, polypyrole and polyanilines have potential uses as active electrodes in rechargeable batteries [2], electrochromic displays [3], information memories [4], antistatic materials [5], *etc.*. In a majority of these applications, it is imperative that the conducting polymer be fabricated as either thin sheets or films. Most conducting polymers suffer from the weakness of poor processibility due to their insolubility in most common solvents. Though thin films of conducting polymers may be prepared by electrochemical polymerisation of suitable monomers, the methodology demands the substrate to be conducting. When the polymer is soluble, as in the case of polyaniline in *N*-methylpyrrolidine, it may be spin coated on a suitable substrate [6]. However, in such cases, due to the physical nature of the interaction between the film and the substrate, the polymer film tended to 'peel off'. Polymerization of aniline on surface modified glasses produces sturdy films that withstand moderate mechanical stress [6]. In this case, however, the application of the conducting film is controlled by the rigidity of the glassy support. In this paper, for the first time, the immobilization of a conducting polyaniline film on highly flexible polyethene films through graft-copolymerization is reported.

2. EXPERIMENTAL

2.1 Chlorination of PE

PE was chlorinated using the well-known method of photochemical chlorination of saturated hydrocarbons. Chlorine gas was produced in a controlled manner by the reaction between $KMnO_4$ and hydrochloric acid. A piece of a commercial PE sample (3 cm x 2 cm) was hung in a 250 cm^3 conical flask containing $KMnO_4$ (1.00 g) and 7.0 cm^3 HCl (aq, 5 mol dm^{-3}). The flask was then tightly closed with a cork and placed under direct sunlight for two hours, whereupon the polyethene sample turned opaque. A glass discharge tube, to which a clamped piece of rubber tubing is attached, inserted through the cork permits the scrubbing of any unreacted chlorine without releasing it to the atmosphere. The chlorinated PE (CPE) sample was then removed, rinsed several times with distilled water (DW) and dried in a desiccator. FTIR spectra of PE and CPE were recorded.

Chlorination can be carried out in a controlled manner by controlling the amount of chlorine gas produced as well as the duration of chlorination. The amount of chlorine produced was controlled by replacing HCl with stoichiometric quantities of KCl and excess conc. H_2SO_4. The extent of chlorination could be monitored using FTIR spectroscopy.

The following reactions were then effected with CPE.

a) With a view to introduce C-C double bonds a small piece of CPE (1 cm x 2 cm) was placed in a 100 cm^3 conical flask and 5 cm^3 of alcoholic KOH was added. The flask was shaken for two minutes while heating gently. The sample (UPE), which turned yellow/brown, was rinsed first with dilute HCl and then with distilled water to remove any physisorbed hydroxyl ions, dried in a desiccator and characterized by FTIR spectroscopy.

   The pale yellow sample (UPE) obtained above was then treated with a dilute Br_2/water solution upon which, the Br_2/water solution was decolourized and the sample turned clear and transparent. The sample thus obtained (BPE) was then treated with alcoholic KOH, which turned the polymer, again, to a yellow/brown colouration. This yellow/brown sample (BAPE) was rinsed first with dilute HCl and then with distilled water to remove any physisorbed hydroxyl ions, dried in a desiccator and characterized by FTIR spectroscopy.

b) In another experiment, the CPE sample was allowed to react with ammonia by hanging the sample in a stoppered 250 cm^3 conical flask containing 10.00 cm^3 of concentrated ammonia.

c) A small piece of CPE sample was placed in a 100 cm^3 conical flask containing 2 cm^3 of distilled aniline and gently heated while shaking for two minutes. The sample (APE) was then thoroughly washed with distilled water, dried in a desiccator, and characterised using FTIR.

d) Polymerisation of aniline was carried out using a procedure previously developed in our laboratories [6]. In an attempt to graft-copolymerize conducting polyaniline on PE, a sample of APE [from (c) above] was placed in a 250 cm^3 beaker containing 50 cm^3 of 0.1mol dm^{-3} aniline solution (prepared by dissolving distilled aniline in 0.1mol dm^{-3} HCl solution). Maintaining the temperature of the mixture at 298 K, 50 cm3 of a 0.05 mol dm^{-3} $(NH_4)_2S_2O_8$ solution was added drop-wise from a burette over a period of one hour while continuously stirring the mixture. This experiment was also repeated at 273 K.

e) For comparison, the procedure in (d) above was carried out with samples of PE, chlorinated poly(etheneterephthalate) (PET) and chlorinated polystyrene.

3. RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of PE (spectrum B) and CPE(spectrum A) samples recorded under identical conditions. The comparison of the two spectra clearly reveals that the CPE sample contains two additional peaks at 667 $cm^{-1}$and 608 cm^{-1}, which are attributed to C-Cl stretching vibrations. The broad features appearing around 1250 and 3500 cm^{-1} indicate the presence of C-O bonds and H-bonded OH groups, respectively. These may have been formed by the reaction of water vapour with the free radicals formed on the polyethene backbone.

The C-Cl stretching bands are present in PE samples treated for more than one hour in direct sunlight. These bands are, however, absent when the treatment time is less than one hour indicating that, at least a one hour of treatment is required for the chlorination of PE to a detectable extent.

The concentration of chlorine, as expected from simple chemical kinetic considerations, has a direct effect on the rate of reaction as shown in Figure 2. The higher the initial concentration of chlorine gas, the greater is the extent of chlorination, in a fixed time, as evident from the enhancement of peak heights at 667 $cm^{-1}$and 608 cm^{-1}.

The chlorination of PE makes it susceptible for attack by many nucleophilic reagents, as the chloride ion is a good leaving group. Thus CPE undergoes ready nucleophilic substitution reactions with ammonia, hydroxyl ion, *etc.*. In addition, the elimination of HCl moieties from CPE can lead to the formation of olefinic bonds in the polymer backbone. These olefinic bonds can be used in the further chemical modification of polyethene.

The CPE sample turned brown when treated with alcoholoic KOH and heating increased the brown colour of the sample. Although the CPE sample turned brown, it had some transparency. This colour change is consistent with the formation of conjugated double bonds on the polymer backbone by the elimination of Cl from alternate C atoms along the chain. This is confirmed by the FTIR spectrum (Figure 3, spectrum B).

The FTIR spectra of BPE under different experimental conditions are shown in Figure 4 (D, E, and F). These spectra show significant changes in the C=C vibration range when compared to UPE. The intensity of the band around 1650 cm^{-1} has decreased drastically whereas the bands around 1300, 1400, and 1550 cm^{-1} have gained intensity indicating the formation of $Br\text{-}CH_2$ groups.

FTIR spectrum of CPE treated with with NH_3 is given in the Figure 5 B. The spectrum shows characteristic N-H stretching vibrations around 3200-3500 cm^{-1} and primary amine C-N absorption at around 1100 cm^{-1}. The result thus shows that CPE can be conveniently converted to an amino derivative. A wide range of compounds such as those containing alkyl carbon-halogen bonds, carboxylic acids and their derivatives etc., may be then immobilized on PE without much difficulty.

When a CPE sample was treated with aniline, the sample turned colourless from translucent white. The FTIR spectrum of CPE treated with distilled aniline (Figure 6A) shows absorptions at around 3380 cm^{-1} due to N-H stretching of aromatic amines, at 1620 cm^{-1} due to N-H deformation of secondary amines and at 1500 cm^{-1} due to C-C skeletal vibration of the aromatic nucleus. This is strong evidence for chemical immobilization of aniline on CPE.

When an aniline solution (in HCl) containing PE pre-treated with aniline was polymerised, with persulphate ions as the oxidant, a uniform layer of the green emaraldine-salt form of polyaniline was formed on the modified CPE. This green emaraldine salt form is the conducting form of polyaniline [6]. The sample showed a satisfactory resistance to abrasion. The average point-to-point resistance at 1 cm for the sample prepared at 298 K was found to be 426 S^{-1} whereas that for the sample prepared at 273 K was 28

S^{-1}. When the polymerisation was carried out in the presence of untreated PE, at 273 K, a thin green emaraldine-salt layer was formed on it. This layer appeared in patches and peeled away easily from the PE substrate. The coating exhibited a wide range of point-to-point resistance, at 1 cm, varying from 630 S^{-1} to 1960 S^{-1}. The FTIR spectrum of polyaniline graft-copolymerized on CPE is shown in Figure 6B. Figure 6C shows polyaniline physisorbed on PE.

The polymerization of aniline was carried out, separately, in the presence of PET and chlorinated PET for the purpose of comparison. On the chlorinated PET, a thin green film was deposited but this film showed a high point-to-point resistance. There was no significant deposition of the polymer on PET. Polystyrene when chlorinated gave a brittle material and no attempt, therefore, was made to deposit a polyaniline film on it. The untreated polystyrene sample when placed in aniline underwent dissolution.

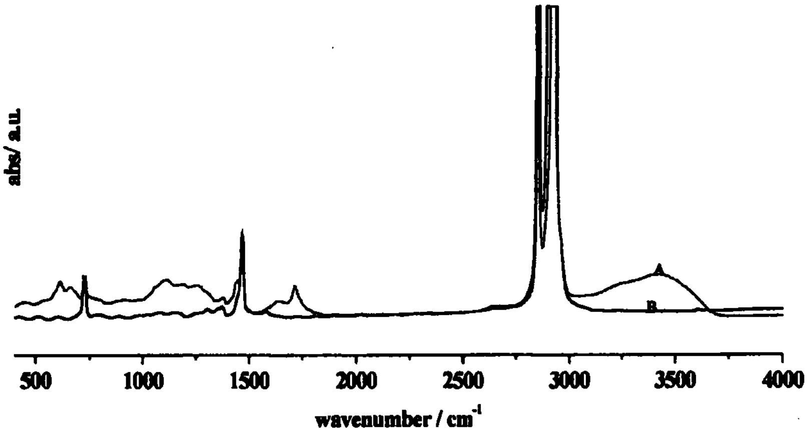

Fig.1 FTIR spectra of (A) CPE obtained after 2 hour chlorination (B) PE before chlorination.

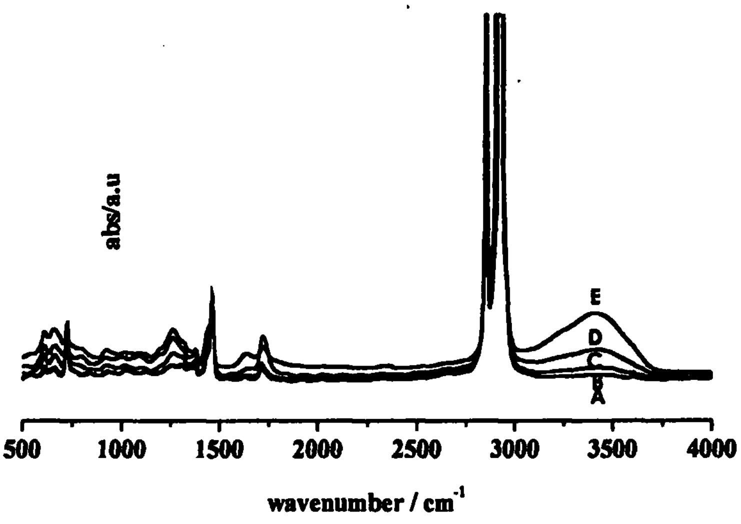

Fig.2 The variation of the extent of chlorination with the concentration of chlorine, monitored using FTIR spectroscopy. The amount of Chlorine was varied by using stoichiometric amounts of solid KCl and excess concentrated H_2SO_4. The amounts are (A) 0.25 g, (B) 0.50 g, (C) 1.00 g, (D) 1.50 g, and (E)2.00 g, respectively.

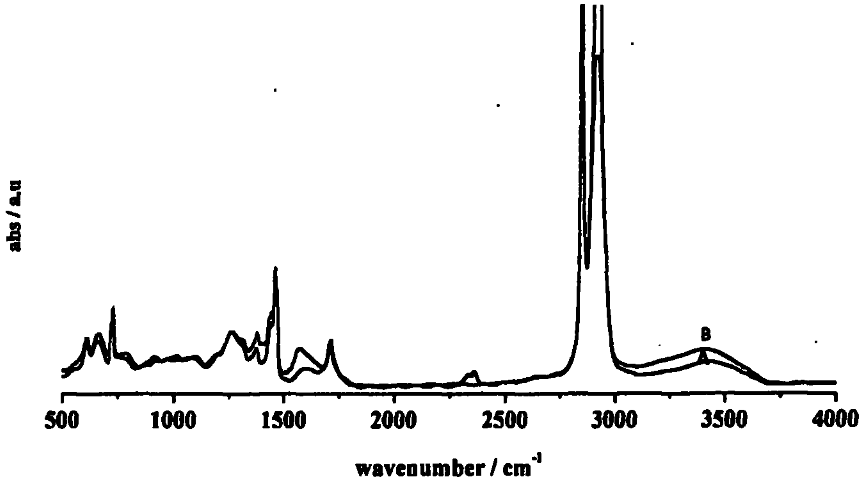

Fig.3 FTIR spectra of A: CPE, B: CPE treated with alcoholic KOH

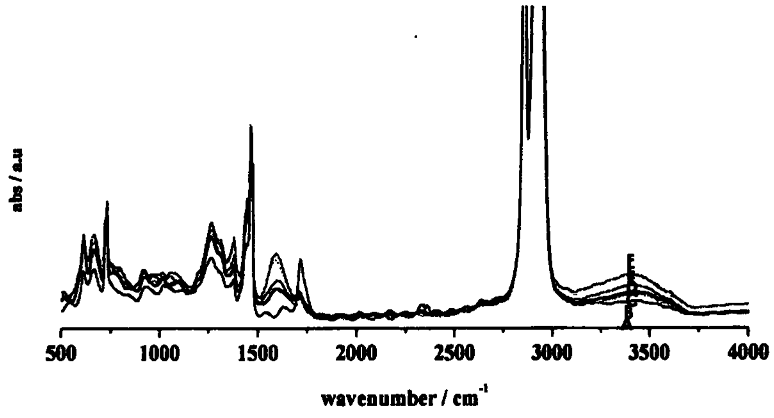

Fig.4 FTIR spectra of A: CPE, B: CPE treated with alcoholic KOH, C: CPE treated with KOH and washed with diluted HCl, D: CPE treated with alcoholic KOH and BR_2/H_2O, E: CPE treated with alcoholic KOH, Br_2/H2O and again with KOH, F:. CPE treated with alcoholic KOH, Br_2/H2O and again with KCH then washed with distilled water.

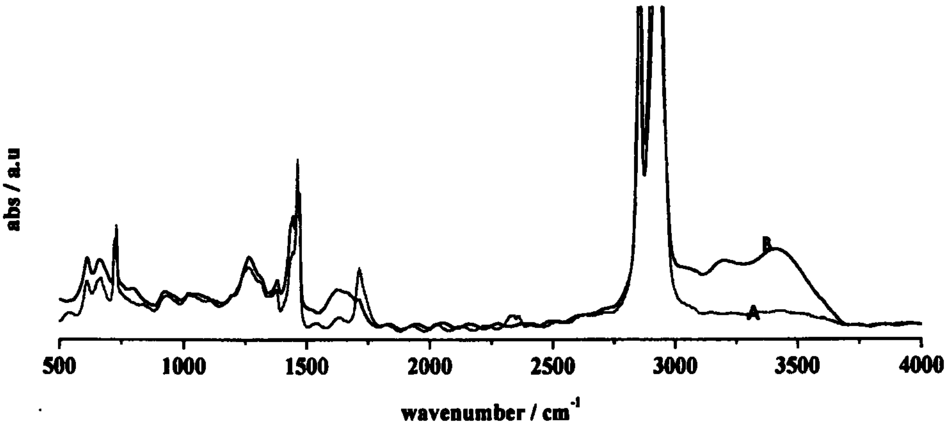

Fig. 5 FTIR spectrum of A: CPE, B: CPE contacted with concentrated NH_3 vapour.

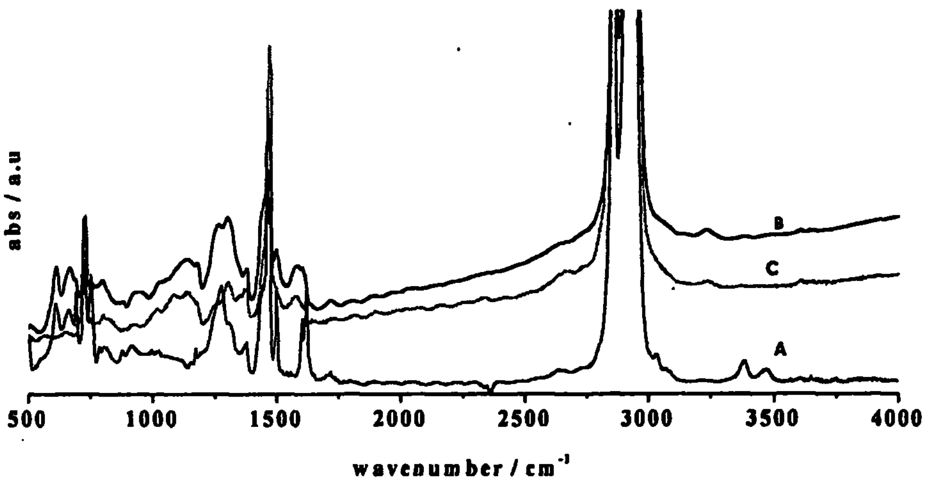

Fig.6 FTIR spectrum of A: CPE treated with aniline, B: CPE treated with aniline and polymerised in an aniline solution with persulphate, C.: PE treated with aniline and then polymerised with persulphate.

4. CONCLUSION

The chemically stable backbone of polyethene makes it a material suitable for immobilization of various functional moieties. In this work it has been demonstrated that polyethene could be conveniently functinalized through a chlorinated intermediate. Controlled photochemical chlorination of PE was achieved through an environmentally safe procedure. The functionalized forms of PE can serve as a substrate for the immobilization of compounds with a variety of functionalities. C=C double bonds can be introduced to the polymer backbone by the treatment of chlorinated PE with alcoholic KOH. This unsaturated compound can then serve as an intermediate for further chemical modification, such as hydroxylation, of PE. The chlorinated PE was converted to an amino derivative by the simple treatment with ammonia. Various types of acid derivatives can then be immobilized on this material. Aniline could be conveniently bound to the chlorinated PE. These bound aniline moieties were then used as anchoring points for attaching conducting polyaniline strands to the PE substrate. This gave a uniformly spread, highly conducting layer of the emaraldine-salt form of polyaniline with a point-to-point resistance as low as 28 S^{-1}. The material showed significant resistance to abrasion. One of the major problems of developing devices employing conducting polyaniline has been the difficulty of fabricating it in the form of thin films. We believe that conducting polyaniline immobilized on PE, prepared by us in our laboratories, being a lightweight and highly flexible-conducting material with significant chemical stability, should make a significant contribution to the use of polyaniline as a conducting material in particular, and the field of conducting polymers in general.

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