



# Acrylation of pre-irradiated polypropylene and its application for removal of organic pollutants

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## ARTICLE INFO

### Article history:

Received 20 March 2009

Accepted 15 September 2009

### Keywords:

Polypropylene

Pre-irradiation

Acrylic acid monomer

Basic dye

## ABSTRACT

Reactive extrusion of pre-irradiated polypropylene (PP) at different doses of gamma radiation was studied in the presence of different concentrations of acrylic acid monomer (AAc). Preliminary investigations study the feasibility or removal of organic pollutants. The optical properties and surface morphology of the grafted polypropylene were observed by FT-IR, UV/vis and scanning electron microscopy (SEM). The affinity of this membrane to the basic dye was found to be increased with increase in the dose of gamma irradiation and the ratio of acrylic acid monomer (AAc).

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## 1. Introduction

Great attention was focused on the wastewater treatment from heavy metal and toxic pollutants because of their severe contribution in the problems of environmental pollution. The effective removal of organic pollutants from industrial wastewaters is of great importance. Phenol and substituted phenols are common and high-priority pollutants because they are suspected as carcinogens as well as being extremely toxic to aquatic life and imparting a strong taste and bad odor to water, particularly after chlorination. The main sources of phenolic wastewater are industries such as petrochemicals, coal gasification, pesticide manufacture, electroplating and metallurgical operations. Among many sorptive materials, various forms of synthetic polymers containing complexing molecule, which are abundant at low cost, have emerged as one of the most important materials for the synthesis of new sorbents. Functionalized copolymers are promising materials that can be used for the wastewater treatment as they are capable of chelation or complexation with pollutants via their reactive functional groups such as carboxylic acid, amide, nitrile, oxime, quaternized pyridine groups, etc. The use of high-energy radiations in the grafting and copolymerization processes is known to improve the physicochemical qualities of many polymer products to expand their utilizations. In this respect, great efforts were focused on the search and development of new efficient materials for many applications such as separation and

purification purposes. Radiation grafting is one of the most promising modification methods because of its unmatched advantages, for example large penetration in polymer substrates, rapid and uniform formation of active sites for initiating grafting through the substrate, being free of chemical initiator, and so forth. Also, in this regard, Le Thuaud et al. (2000) reported that when polymers are subjected to ionizing radiation, trapped radicals or macromolecular peroxides and hydroperoxide that are capable of initiating graft copolymerization reaction are formed. Irradiation-induced graft can be realized either simultaneously, which is called co-irradiation, or after irradiation, which is called pre-irradiation.

In the pre-irradiation method, polymeric matrix is first irradiated either in inert atmosphere or in vacuum in order to generate active sites. The radicals have to be stable at ambient temperature in order to initiate covalent bonds with monomers after irradiation (Chen et al., 2000, 2004; Massa et al., 2005). The procedure results in elimination of homo-polymerization; however, the yield of grafting in this case is relatively low. Other variation of such a method is an application of air during exposure to ionizing radiation. Both techniques are suitable only if the formed radicals are stable enough to react with monomers in post-irradiation effect. In such a case, grafting, depending on the system, might be performed after long storage time.

Bettini and Agnelli (2002) reported that the most frequent method used for polymer research and development has gradually changed direction in the last few decades. There has been a significant reduction in the introduction of new polymers and the need to improve the performance of existing polymers has led to the development of commercially feasible techniques, such as

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chemical modification, blending and reinforcement, among others, to modify them.

The American Environmental Protection Agency (EPA) has regulated concentration of phenol in wastewater below 4 mg/l in order to protect human health from the potential toxic effects caused by exposure to phenol (Pan and Kurumada, 2007); therefore, serious attention has been devoted to their removal from water and other media. So far, charcoal, synthetic aromatic polymers having very high surface areas (such as macro-porous styrene-divinyl benzene copolymers), anion exchangers and polymers capable of hydrogen bonding such as poly (vinyl pyrrolidone), polyamides, polyphenols, etc. are used for these purposes. The sorption capacity, specificity and adsorption kinetics are influenced by chemical composition of the adsorbent, its specific surface area and accessibility of active centers (Hradil et al., 2000). The aim of this work is the preparation of PP-g-AAc by reactive extrusion of pre-irradiated polypropylene to improve its dyeability and investigate its applicability in the removal of phenol from its solution.

## 2. Experimental

### 2.1. Materials

Isotactic PP in the form of pellets with melt flow rate of 9 dg/min at 230 °C and specific gravity of 0.9 g/cm<sup>3</sup>, and laboratory grade chemicals were supplied from Aldrich Chemicals Co.; the monomer used throughout this work was acrylic acid (AAc) of laboratory grade chemicals supplied by Prolabo Chemicals (France). The monomer was used without further purification. A laboratory grade methanol was supplied by British Drug House Ltd., England. Sandocryl Golden yellow B-RLS (basic water soluble dye), Sandoz, Switzerland.

### 2.2. $\gamma$ -Irradiation

Irradiation to the required doses was carried out in a 60-Co  $\gamma$  cell (made in Russia) at the National Center for Radiation Research and Technology, Cairo, Egypt. Irradiation was carried out under atmosphere at a dose rate of 6.92 kGy/h.

### 2.3. Preparation of grafted pre-irradiated polypropylene

The melting of pre-irradiated PP granules at different doses of gamma radiation (5–20 kGy) was accomplished in Brabender Plasticorder PL 2100 mixture at 180 °C and 60 rpm for 3 min.

Thereafter, different amounts of the acrylic acid monomer (AAc) (1, 3, 5 and 7 wt%) were added gradually to the molten sample and mixing was continued for another 2 min. The molten mixture of polymer/monomer was immediately transferred from the mixer to an open roll-mill to sheet. The sheet of the completely homogeneous mixture of the PP-g-AAc was then pressed under hot press at 180 °C for total 5 min (2 min preheating and 3 min at 15 MPa) to obtain a rectangular sheet of 0.70–0.75 mm thickness. The molded sheet was then immediately transferred to water-cooled press at the same pressure.

### 2.4. FT-IR spectroscopic analysis

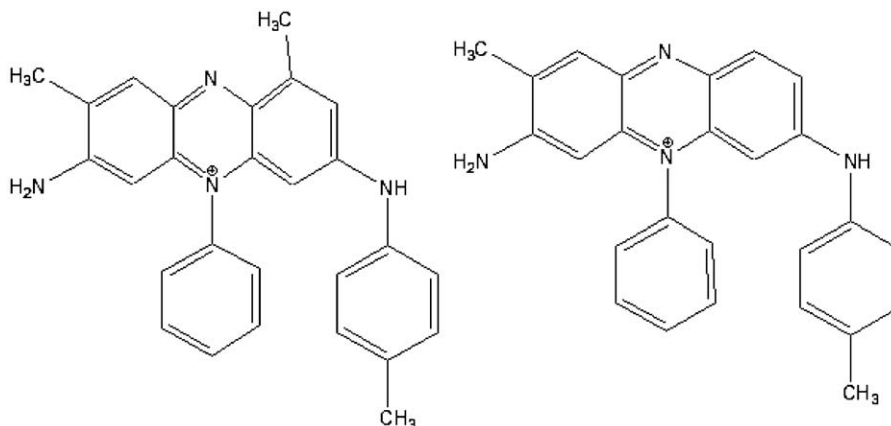
The infrared spectra of the unmodified polypropylene and modified polypropylene were performed on a Mattson 5000 FT-IR spectrometer (Mattson Instruments, Madison, WI) over the 500–4000 cm<sup>-1</sup> range. The samples for IR analysis were dried in a vacuum oven.

### 2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) micrographs were obtained using a JSM-5400 instrument (JEOL, Japan). The investigated samples were kept for 1 h in liquid nitrogen prior to fracture. A sputter coater was used to pre-coat conductive gold onto the surface before observing the microstructure at 15 kV. The morphology of the surface of the unmodified and modified polymer PP was examined.

### 2.6. Dyeing of the modified polymer by basic dye

The dye bath was first prepared by pasting the required concentration using acetic acid and then dissolved, and then boiling water was added to bring it in solution. The usual additive such as 10% sodium sulfate (Glauber salt) was then added to the dye bath and the pH of the bath was adjusted at 6.5. The prepared samples were swelled in methanol/water mixture (of composition 80/20 wt%) and then soaked in the dye bath for 1 h. The dye temperature was then increased gradually to boiling temperature within a period of 30 min and continued for another 60 min at boiling. At the end of the dyeing process, the dyed sheets were removed from the dye bath, rinsed with hot and cold water, soaped with a solution containing 2 g/L anionic wetting agent, rinsed again with cold water and finally air dried (Scheme 1).



**Scheme 1.** The structure of basic dye (Sandocryl Modified Basic Dyes).

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