

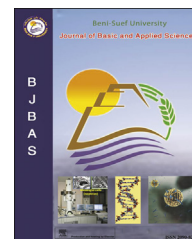
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Full Length Article

Enhancing both the mechanical and chemical properties of paper sheet by graft copolymerization with acrylonitrile/methyl methacrylate



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ABSTRACT

The chemical graft copolymerization reaction of acrylonitrile (AN) and methyl methacrylate (MMA) binary mixture onto paper sheet was performed. The effect of initiator concentration, monomer concentration and temperature on the reaction rate was studied. The reaction rate equation of the graft copolymerization reaction is found to be $RP = K_2 [\text{Initiator}]^{0.795} [\text{Monomer}]^{2.007}$. The apparent activation energy (E_a) of the copolymerization reaction is found to be 75.01 kJ/mol. The infrared characteristic absorption bands for cellulosic paper structure and the paper gr-AN-MMA are investigated. Tensile break load, porosity and burst strength were measured for the grafted and pure paper sheet. It was found that the mechanical properties are improved by grafting copolymerization. The chemical resistance of the graft product against a strong acid a strong alkali, polar and nonpolar solvents was investigated. It was found that the resistance to these chemicals is enhanced by grafting.

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1. Introduction

The paper manufacture is an ancient industry in EGYPT, which developed quickly to change the paper properties according to their usages. The graft copolymerization of vinyl monomers onto natural and synthetic polymers by chemical or radiation induced polymerization has been suggested as potentially good means of alternating the properties of the

base polymer (Yoshitaka et al., 1967; Hirose and Hatakeyama, 1982).

The graft copolymerization of acrylonitrile (AN), methyl methacrylate (MMA) and styrene onto paper sheet, cotton and silk was reported (Minoru et al., 1966). Paper sheets were grafted by copolymerization with styrene-divinylbenzene mixture, methyl acrylate or other monomers using benzoyl peroxide (Bz_2O_2) as free radical initiator (Lenka et al., 1980). Only a small number of studies have been carried out

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concerning the use of polymeric materials for the consolidation and protection of paper (Humphrey, 1984 and Burstall et al., 1984).

The grafting copolymerization of AN onto cellulose using the cellulose xanthate-Cr⁶⁺ system proceeds rapidly at normal temperature (0–20 °C) (Majid and Chowdhury, 1987). No ungrafted homopolymers in solution was formed. The activation energy for this grafting copolymerization was found to be 0.45 kJ/mol and the reaction order was 1.3.

Graft copolymerization reactions of acrylic acid, acrylates and acrylonitrile on cellulosic materials have been investigated (Vita et al., 1985, 1986; Okieimen and Ebhoaye, 1986a, 1986b, 1986c; Okieimen, 1987 and Yousef, 1990; Saikia and Ali, 1999; Qiu and Hu, 2013) by the use of ceric ammonium nitrate in aqueous medium at different temperatures. The variation in the level of incorporation of poly(acrylic acid) grafts on the cellulosic substrate and the dependence of the water and saline retentions of the graft copolymers on the graft level were examined.

Graft copolymerization of vinyl monomers onto cellulose has been previously studied (El-Sisi, 1995); acrylic monomers appear particularly suitable because they show high filmability, transparency, optical clarity, good adhesive properties, water-repellance and stability to atmospheric oxygen and UV light; thus their use makes possible to achieve the consolidation and protection of the cellulosic materials leading to the improvement of the restoration treatment (Alessandro et al., 2001; Sayyah et al., 2011; Kalia and Sabaa, 2013 and Ibrahim, 2013).

The chemical graft copolymerization reaction of acrylonitrile onto paper sheet and characterization of the obtained product was studied.

The aim of the present work is to study the chemical graft copolymerization reaction of acrylonitrile and methyl methacrylate binary mixture onto paper sheet to protect the documents which was written by pencil from long time ago against damage or bacterial action and forgery. Moreover it is also interesting to increase their preservation time. The effect of initiator concentration, monomer concentration and temperature on the reaction rate are performed. The thermodynamic parameters of activation are given. The obtained grafted paper sheet is characterized by IR spectroscopy, electron microscopy, X-ray diffraction and TGA and DTA analysis. The chemical and mechanical behavior of the obtained paper sheet grafted with AN/MMA mixture is described.

2. Experimental

2.1. Materials

The paper sheets (A4) Japan NPI; grammage 80 g/m² made largely from mechanical pulp which contains bleached cellulose, a noticeable amount of fillers (CaCO₃) (ash 18%). The paper sheet was cut into small pieces of the diameters 3.3 cm length, 2.8 cm width and 0.1 cm thickness. The paper sheets were treated with different polar and non-polar solvents to remove any fats from the paper sheet surface or organic additives present in the paper structure or polymeric additives.

Acrylonitrile (AN) was a product of Koch light Ltd. Company and has specific gravity of 0.806 g/cm³ inhibited with 35–45 ppm hydroquinone monomethyl ether. Methyl methacrylate (MMA) was a product of Merck-Schuchardt yield 99% established with 100 ppm hydroquinone, the density is equal to 0.942–0.944 g/cm³ at 20–24 °C. The monomers were washed with a few drops of 10% sodium hydroxide solution followed by small amount of distilled water. The monomers were fractionated using a fractionating column of 15 theoretical plates. Methyl methacrylate was separated with a separating funnel.

The initiator for the free radical graft copolymerization reactions was benzoyl peroxide (Bz₂O₂) provided from El-Nasr pharmaceutical chemical company, Egypt. It was purified and activated by dissolving in chloroform, then filtered, dried and kept under vacuum.

Ferrous ammonium sulfate hexahydrate, 1,2-dichloroethane, acetone, cyclohexane, petroleum ether, xylene, hydrochloric acid, ethyl alcohol, sodium hydroxide (pellets) were products of B.D.H Chemical Company, England. Benzene (thio-phene free), dimethyl formamide (DMF), chloroform and methanol were of chemical pure grade from El-Nasr Pharmaceutical Chemical Company, Laboratory Chemical Division, Egypt.

2.2. Instrumental analysis

2.2.1. Infrared spectroscopy

The infrared measurements on paper sheet, AN-MMA copolymer and grafted paper sample with AN-MMA copolymer were carried out by Shimadzu FTIR-430 Jasco Spectrophotometer using KBr disk technique.

2.2.2. Electron microscopic and X-Ray diffraction analysis

The electron microscopic analysis was carried out using JSM-T20 Scanning electron microscope, (JEOL, Japan) after metalization of the specimen with very thin layer of gold to obtain a good conductivity and the ESM picture was taken with magnification 1:1500. The X-ray diffractometer type Philips 1976 Model 1390 was operated at the following conditions that were kept constant overall the analysis processes;

X-ray tube: Cu
Scan speed: 8 (dg/min.)
Current: 30 mA
Voltage: 40 kV
Preset time: 10 (s)

2.2.3. Paper testing

Since the physical properties of the paper change with variation of its moisture content, it is necessary to standardize it at a definite temperature and humidity values in order to obtain a standard test results. The process was carried out at 60% relative humidity and at a temperature range from 18 to 20 °C.

The tensile break load was measured by a Loyed LR10 universal testing machine. A paper strip of 15 mm width was clamped between two jaws and an increasing load was applied by swinging pendulum from its vertical resting position by a motor. The tensile break load was taken as the force (N/mm²) required to break the strip.

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