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Synthesis, characterization and electrospinning of corn cob cellulose-graft-polyacrylonitrile and their clay nanocomposites

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ABSTRACT

This study aims at evaluation of cellulose recovered from agricultural waste (corn cob) in terms of synthesis of graft copolymers, polymer/clay nanocomposites, and nanofibers. The copolymers and nanocomposites were synthesized in aqueous solution using Ce^{4+} initiator. Conditions (concentrations of the components, reaction temperature, and period) were determined first for copolymer synthesis to obtain the highest conversion ratio. Then found parameters were used to synthesize nanocomposites adding clay mineral to reaction medium. Although there was a decrease in conversion in nanocomposites syntheses, thermal and rheologic measurements indicated enhancements compared to pristine copolymer. Obtained polymeric materials have been successfully electrospun into nanofibers and characterized. Average diameter of the nanofibers was about 650 nm and was strongly influenced by NaMMT amount in the nanocomposite sample.

1. Introduction

Disposal of non-degradable petroleum-based polymeric wastes is one of the greatest challenges for a clean environment. Thus investigations are being made to produce environmentally friendly alternatives (Simkovic, 2008). Industrial crops leave lignocellulosic wastes as renewable raw material resource for biodegradable polymer syntheses (Cyras, Soledad, & Analía, 2009; Karaaslan et al., 2011Karaaslan, Tshabalala, Yelle, & Buschle-Diller, 2011; Lynd et al., 2005Lynd, Van Zyl, McBride, & Laser, 2005). Corn cobs, as lignocellulosic waste and renewable raw material, contain approximately 40–50% cellulose, 30–40% hemicellulose and 8–10% lignin and are the largest group contributing to environmental pollution significantly (El Seoud & Heinze, 2005; Sun & Cheng, 2002). Cellulose is mainly linear biodegradable polymer composed of β-D-glucose units linked through β-glycosidic bonds at positions 1–4; it is also the main component of the agricultural wastes forming cell walls of plants, fibers, and wood.

Copolymers of naturally occurring materials are labile to biodegradation as they have biodegradable parts (Maiti, Sain, Ray, & Mitra, 2013). This type of biodegradable graft copolymers are synthesized using various methods including ceric ion initiated redox polymerization reactions. Ceric ions are versatile reagents which are used for oxidation of many organic functional groups (Nagarajan & Srinivasan, 1998; Pottenger & Johnson, 1970) through radicalic pathway; thus they can be used as redox initiators in aqueous solutions for copolymerization of vinyl monomers (acrylonitrile, acrylamide, etc.) (Galioğlu Atıcı, Akar, Ayar, & Mecit, 1999; Lutfor, Sidik, Haron, Rahman, & Ahmad, 2003; Mino & Kaizerman, 1958). Reaction conditions (including temperature, components' concentrations, acid catalyst) affect the resulting conversion ratio and properties of the copolymer. Radicals are produced from interaction among ceric ion and reducing agents (i.e. alcohol, polyol) in several steps. Polysaccharides can also be employed as reducing agent for graft copolymerization using ceric ions (Galioğlu, Soydan, Akar, & Saraç, 1994; Mishra, Clark, Vij, & Daswal, 2008; Ünlü, Günister, & Atıcı, 2012; Gürdağ & Sarmad, 2013; Rana, Singha, Thakur, & Thakur, 2015).

Research on polymer/clay nanocomposites is another popular subject and has been studied extensively in recent years (Fahmy & Mobarak, 2008; Lagaly, Reese, & Abend, 1999; Pavlidou & Papaspyrides, 2008; Sinha Ray & Okamoto, 2003). There is a rising trend to use clay in nanocomposites as it costs low and is supplied easily. Nanocomposites are produced generally dispers-

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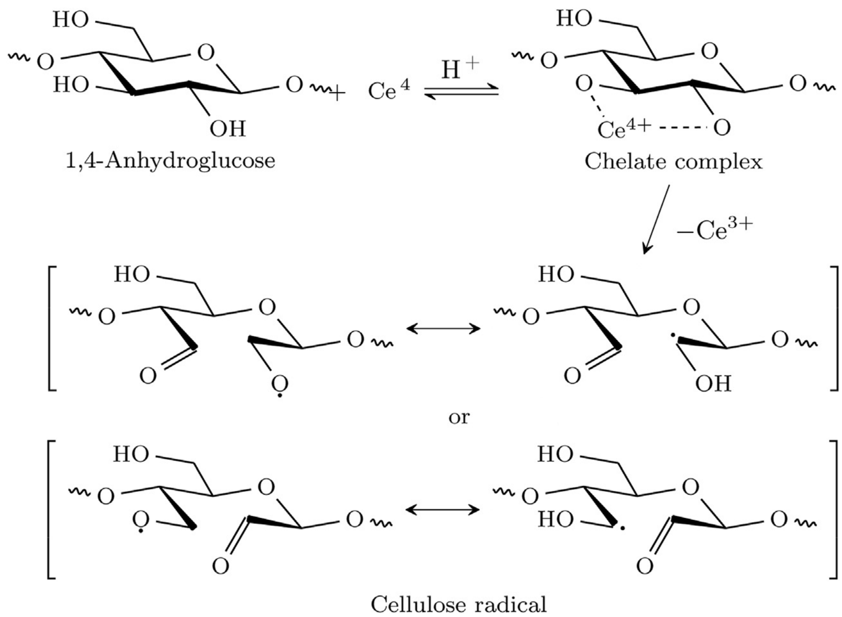

Scheme 1. Reaction mechanism of ceric oxidation.

ing some inorganic material in a polymer matrix with a gain in various physical properties including thermal stability, gas barrier properties, and mechanical strength. Smectite type clay minerals are widely used as additive to obtain polymer/clay nanocomposites. Montmorillonite, which is a member of the smectite group, has a 2:1 layered structure, and it is the most widely used layered silicate in polymer/clay nanocomposites due to its negatively charged large surfaces and with high aspect ratios. The polymer and montmorillonite interact according to the ionic properties of the polymer. The ionic polymers induce electrostatic interactions, but non-ionic polymers are adsorbed on the larger surface of clay minerals via steric interactions (Bergaya, Theng, & Lagaly, 2006). As a result of these interactions clay mineral can disperse uniformly as monolayers in polymer matrix causing some enhancements in physical properties.

Aim of this study is evaluating corn cobs which are considered as waste material. Corn cob cellulose was used as a reducing agent and acrylonitrile was grafted on corn cob cellulose via redox polymerization (P). Corn cob cellulose-*graft*-polyacrylonitrile/montmorillonite nanocomposites (NCP) were produced through in-situ polymerization method. Then nanofibers were prepared by electrospinning from this resultant acrylonitrile based copolymers (NF). Obtained products were investigated by spectroscopic, thermal, rheologic and morphologic characterizations.

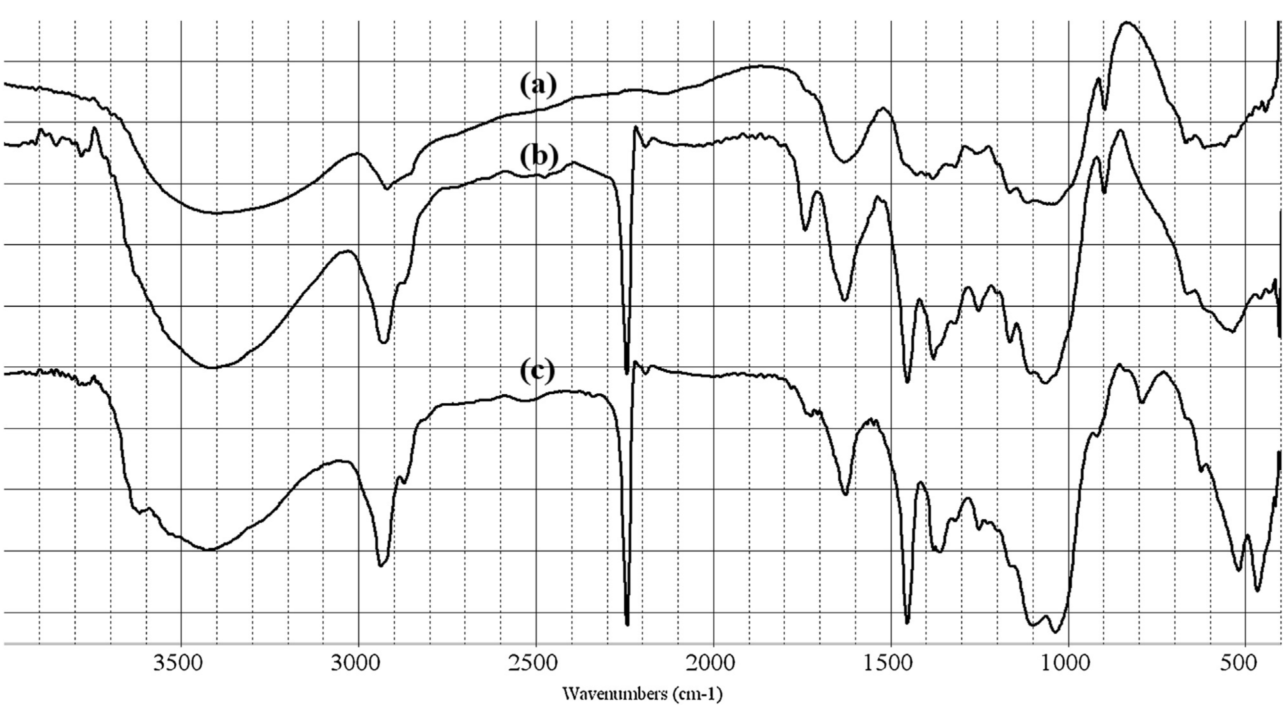

Fig. 1. FTIR spectra of corn cob cellulose (a), P (b), and NCP_5(c).