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➢ International Journals

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II Arup Mandal, Debabrata Chakrabarty: Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly(vinyl alcohol) and nanocellulose from sugarcane bagasse, *Journal of Industrial and Engineering Chemistry*, 2014, 20 (2), 462-473.


IV Arup Mandal, Debabrata Chakrabarty: Synthesis and characterization of nanocellulose reinforced full-interpenetrating polymer network based on poly(vinyl alcohol) and polyacrylamide (both crosslinked) composite films, *Polymer Composites*, 2015, DOI 10.1002/pc.23742.

V Arup Mandal, Debabrata Chakrabarty: Studies on flexible carboxymethyl cellulose supported nanocellulose films, 2016, communicated.

Other relevant publications not included in the thesis

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### International Conferences


II Arup Mandal, Debabrata Chakrabarty: Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly(vinyl alcohol) and nanocellulose from sugarcane bagasse. August 2014, *International Conference on Natural Fibers, The Indian Natural Fibre Society (TINFS)*, Kolkata, India.


### National Conference

I Arup Mandal, Debabrata Chakrabarty: Extraction of nanocellulose from waste sugarcane bagasse (SCB) and its application in polymer nanocomposites. August 2011, *National Conference on Nanoscience and Nanotechnology*, University of Madras, Chennai, India.
Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization

Arup Mandal, Debabrata Chakrabarty*

Department of Polymer Science and Technology, Calcutta University, 92 Acharya Prafulla Chandra Road, Kolkata 700 009, India

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A B S T R A C T

Nanocellulose obtained by acid hydrolysis of sugarcane bagasse (SCB) has been characterized by Fourier
transformed infrared (FTIR) spectra, thermogravimetric analysis (TGA), differential scanning calorimetry
(DSC), X-ray diffraction (XRD), dynamic light scattering (DLS), scanning electron microscopy (SEM) and
atomic force microscopy (AFM) and transmission electron microscopy (TEM) studies. Nanocellulose and
 cellulose exhibited identical FTIR spectra quite different from SCB. TG analysis shows that the bagasse
starts to degrade earlier than cellulose and the nanocellulose shows an even earlier onset of degradation
compared to SCB but leaves the maximum residue within the range of temperatures studied. DSC studies
revealed that SCB, cellulose and the nanocellulose differ in their loosely bound moisture content. The
nanocellulose exhibits an intermediate behavior between SCB and cellulose. The XRD shows enrichment
in the proportion of crystalline cellulose in nanocellulose, which manifests significant conversion of
 cellulose I to cellulose II. DLS studies show particle size distribution in the nanorange which has been
substantiated by SEM, AFM and TEM.

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1. Introduction

Cellulose, the major constituent of all plant materials including wood, cotton, flax, hemp, jute, ramie, cereal straws, rice straws and sugarcane bagasse, forms about half to one-third of plant tissues and is constantly replenished by photosynthesis. Thus it is the most abundant and renewable natural resource on earth (Goodger, 1976).

Sugarcane bagasse is a residue produced in large quantities every year by the sugar and alcohol industries, and is mainly used as a fuel to power the sugar mill (Simkovic, Mlynar, & Alfoldi, 1990). Several processes and products have been reported that utilize bagasse as a raw material for industrial applications. These include electricity generation, pulp and paper production, and products based on fermentation (Pandey, Soccol, Nigam, & Soccol, 2000). The utilization of this biomass for processing of novel composites has attracted growing interest because of their ecological and renewable characteristic (Cherian et al., 2010).

In the present investigation bagasse has been used for the production of microcrystalline cellulose and nanocellulose. About 40–50% of bagasse is the glucose polymer cellulose, much of which is in crystalline structure. Another 25–35% is hemicellulose, an amorphous polymer usually composed of xylene, arabinose, galac-

tose, and mannose. The remainder is mostly lignin (18–24%); plus lesser amounts of mineral, wax (<1%), and ash (1–4%) (Jacobsen & Wyman, 2002; Wyman, 1999). Normally it contains moisture to the extent of 40–50%. Chemically, cellulose is a linear, stereo-

regular natural homopolymer composed of anhydroglucose units linked at one and four carbon atoms by β-glycosidic bonds. This is confirmed by the presence of three hydroxyl groups (secondary OH at the C-2, and at the C-3 and primary OH at the C-6 position) with different reactivities (Kadla & Gilbert, 2000). These hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystal packing and also governing the physical properties of cellulose. In cellulosic plant fiber, cellulose is present in an amorphous state, but also associated with crystalline phases through both intermolecular and intramolecular hydrogen bonding for which cellulose does not melt before thermal degradation (Fengel & Wegner, 1989; Klemm, Heublein, Fink, & Bohn, 2005). Cel-

lulose is organized into fibrils, which are aligned parallel to each other, surrounded by a matrix of lignin and hemicelluloses. The properties of cellulose including good mechanical properties, low density, and biodegradability (Zimmerman, Pöhler, & Schwaller, 2005) depend on the type of cellulose present. There are several types of celluloses (I, II, III, IV, and V) and type I shows the best mechanical properties. At present, it seems generally accepted that cellulose I has a parallel chain orientation, while in cellulose II, the chains are anti-parallel (Lennholm & Iversen, 1995).

Cellulose nanoparticles have been synthesized in spherical form (Pu et al., 2007; Zhang, Jiang, Dang, Elder, & Ragauska, 2008),...
Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly(vinyl alcohol) and nanocellulose from sugarcane bagasse

Arup Mandal, Debabrata Chakrabarty

Department of Polymer Science and Technology, Calcutta University, 92 Acharya Prafulla Chandra Road, Kolkata 700 009, India

Abstract

Nanocomposites from poly(vinyl alcohol) [PVA] in linear and crosslinked state were synthesized using varying proportions of bagasse extracted nanocellulose. These were characterized by tensile, thermal, X-ray diffraction (XRD), moisture vapor transmission rate (MVTR), and morphological studies. Crosslinked PVA and linear PVA nanocomposite exhibited highest tensile strength at 5 wt.% and 7.5 wt.% of nanocellulose respectively. Thermogravimetric analysis (TGA) studies showed higher thermal stability of nanocomposite made of crosslinked PVA and nanocellulose with respect to linear PVA and nanocellulose. TEM and AFM studies confirm the formation of nanocomposites while the SEM images show the dispersion of nanocellulose particles in them. © 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

Polymer nanocomposites are made up of nanometric particles (nanofillers) dispersed in a polymer matrix. The incorporation of a small amount of nanometer-sized filler can yield composites with enhanced properties earnestly required for many industrial and technological applications [1]. The conventional polymer–inorganic filler composites have improved stiffness, strength, hardness and high temperature creep resistance compared to the unfilled polymers [2–6]. These nanocomposites have recently become an issue of great concern from environmental, economic and performance point of view. This can be alleviated by the replacement of inorganic fillers with natural ones [7].

Cellulose, synthesized mainly in biomass by photosynthesis, is the most abundant natural biopolymer in the world. Natural cellulotic fibers, particles, fibrils (micro and nano scale), and crystals/whiskers are used as reinforcement while making environmental friendly products. These cellulotic materials have many advantages including, renewability, low cost, low density, low energy consumption, high specific strength, modulus, biodegradability and biocompatibility with less susceptibility to fracture during processing due to their high aspect ratios in composites [8,9]. In addition, the waste disposal becomes easier by combustion for lignocellulosic filled composites (that can be completely converted into water and CO₂) [10]. That is why, the possibility of using lignocellulosic fillers in the plastic industry have received considerable attention. Automotive applications display strong promise for natural fiber reinforcements as well [11–14]. Potential applications of lignocellulosic fiber based composites in railways, aircraft, irrigation systems, furniture industries, and sports and leisure items are currently being researched [15].

Cellulose fibers modified at nanometer size induce much higher mechanical properties to polymer matrices as regards to common cellulose fibers because of their higher crystallinity and mechanical properties combined with higher surface area and active interfaces [16]. Crystalline cellulose nanofibers often referred to as nanowhiskers display an elastic modulus of 120–150 GPa [17]. Due to their strongly interacting surface hydroxyl groups [18], cellulose nanowhiskers have a significant tendency for self-association, which is advantageous for the formation of load-bearing percolating architectures within the host polymer matrix [19]. The spectacular reinforcement of polymers observed for this class of materials is attributed to the formation of rigid nanowhisker networks in which stress transfer is facilitated by hydrogen-bonding between the nanowhiskers [20]; Van der Waals interactions also have been shown to play a significant role [18]. However, these same nanowhisker–nanowhisker interactions can also lead to aggregation during the nanocomposite fabrication [21], which significantly reduces the mechanical properties of the resulting

* Corresponding author. Tel.: +91 9830773792.
E-mail address: chakrabarty.deb@yahoo.com (D. Chakrabarty).
Characterization of nanocellulose reinforced semi-interpenetrating polymer network of poly(vinyl alcohol) & polyacrylamide composite films

Arup Mandal, Debabrata Chakrabarty

Department of Polymer Science and Technology, Calcutta University, 92 Acharya Prafulla Chandra Road, Kolkata 700 009, India

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ABSTRACT

Semi-interpenetrating polymer network (semi-IPN) of poly(vinyl alcohol)/polyacrylamide was reinforced with various doses of nanocellulose. The different composite films thus prepared were characterized with respect to their mechanical, thermal, morphological and barrier properties. The composite film containing 5 wt.% of nanocellulose showed the highest tensile strength. The semi-interpenetrating polymer network of poly(vinyl alcohol)/polyacrylamide; and its various composites with nanocellulose were almost identical in their thermal stability. Each of the composites however exhibited much superior stability with respect to the linear poly(vinyl alcohol) and crosslinked polyacrylamide. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies exhibited phase separated morphology where agglomerates of nanocellulose were found to be dispersed in the matrix of the semi-IPN. The moisture vapor transmission rate (MVTR) was the lowest for the film containing 5 wt.% of nanocellulose.

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1. Introduction

Intercalating polymer networks (IPNs) are synthesized with the objective of imparting one or more mechanical advantages of one component polymer to the other and vice versa. In this way the deficiencies of one polymer are removed by the other. In some cases, entirely some new special features are exhibited by the IPNs which are not observed in either of the two single network alone. This novel tool of blending provides a means of mixing crosslinked polymers with the least possibility of phase separation. Sometimes it helps in mixing incompatible polymers without any phase separation.

A semi-IPN consists of linear polymer chains of one component thread or interwoven with a crosslinked polymer network of the other without any covalent bonds being formed between the chains of the two different types of polymers. However the possibility of formation of some covalently bonded compounds or graft copolymers can not be ruled out totally in this technique.

Poly(vinyl alcohol) [PVA] is a water soluble, non-toxic, highly crystalline, non-immunogenic and a unique synthetic biopolymer with remarkable film forming property (Chan, Hao, & Heng, 1999; Hassan & Peppas, 2000) and a high degree of swelling in aqueous solution. The use of this polymer is important in many applications, such as controlled drug delivery systems, membrane prepa ration, recycling of polymers and packaging. It has been used together with starch in the field of paper and textile sizing (El-din, El-Naggar, & Ali, 2003). PVA can be used as an absorbent for pollutants because it is a highly hydrophilic polymer. Poly(vinyl alcohol)/silk fibroin (PVA/SF) blends have been implicated as functionally important in a wide range of biological phenomena (Cuculo, Smith, Sangwatanaroj, Stejskal, & Sankar, 1994; Iijima et al., 1996).

Polyacrylamide (PAAm) is well known for its hydrophilicity and inertness that make it a material of choice in large number of applications (Bajpai & Bhanu, 2004). PAAm and its derivatives provide the most common system for hydrogels due to their non-toxic and biologically inert, long chain lengths, capacity for preserving their shape and mechanical strength in the gelled state even. A convenient adjustability of mechanical, chemical and biophysical properties can be achieved from it (Hynd, Turner, & Shain, 2007; Lin, Yurke, & Langrana, 2004). Hence, PAAm hydrogels have a wide variety of applications in agriculture (Kazanskii & Dubrovskii, 1992), drilling fluids (Maitland, 2000), tissue engineering (Calvert, 2009; Drury & Mooney, 2003), and waste treatments (Chauhan, Chauhan, Kumar, & Kumari, 2008; Yi & Zhang, 2008). However, highly swollen hydrogels of PAAm are normally very brittle because of lack of an efficient energy dissipation mechanism and irregular distribution...
Synthesis and Characterization of Nanocellulose Reinforced Full-Interpenetrating Polymer Network Based on Poly(vinyl alcohol) and Polyacrylamide (Both Crosslinked) Composite Films

Arup Mandal, Debabrata Chakrabarty
Department of Polymer Science and Technology, Calcutta University, Kolkata, India

An interpenetrating polymer network (IPN) is a novel blend of two polymers at least one of which is synthesized or crosslinked in the immediate presence of the other so that there is the least possibility of any gross phase separation. Full-IPNs, prepared from poly(vinyl alcohol) and polyacrylamide, have shown superior performances over the conventional individual polymers. The ranges of applications have grown rapidly for such class of materials. Cellulose nanoparticles extracted from sugarcane bagasse in-house are used to reinforce this PVA/PAAm (80:20) full-IPN in different proportions during the synthesis of IPN. The characteristics of this new series of IPN composite materials have been evaluated by Fourier transform infrared spectroscopic analysis, mechanical, thermal (thermogravimetric analysis and differential scanning calorimetry), and scanning electron microscopy techniques. A loading of 5 wt% of nanocellulose lead to the highest tensile strength amongst the different IPN composite films. Although the non-reinforced full-IPN and the various reinforced composites with nanocelluloses are almost identical in their thermal stability, they prove to be much superior compared to the neat polymers. POLYM. COMPOS., 00:000–000, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

Now-a-days an ever growing demand for unique polymer properties has paved the way for development of the blending of polymers [1, 2]. Full interpenetrating polymer networks (full-IPNs) are a special class of polymer blends in which the individual polymer forms three-dimensional crosslinked network either by chemical crosslinking process or through some physical forces in the immediate presence of one another. These materials are characterized by the presence of two networks strongly interwined ideally only by topological constraints [3, 4]. An IPN can be distinguished from polymer blend in the way that an IPN swells but does not dissolve in solvents and creep properties are suppressed to a great extent [5]. Interpenetrating polymerization is a mode of blending of two polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise [6]. However, IPNs synthesized so far exhibit various degrees of phase separation depending mainly on the miscibility of polymers [7]. With highly incompatible polymers, the thermodynamically driving force phase separation is so powerful that gross phase separation occurs before gelation. Crosslinking, mutual chain entanglement, and eventual internetworks grafting [8–10] in IPNs produce finer dispersion of one polymer into the other.

There are two types of IPNs: (i) based on method of synthesis and (ii) based on chemical bonding.

(i) IPNs based on method of synthesis:
(a) Sequential IPN: In this type of IPN a polymer network of monomer (I) is formed by initiating with suitable monomer and a crosslinking agent. This network (I) is then swollen in the second combination of monomer (II) and its crosslinking agent. The resulting swollen network on polymerization gives rise to a sequential IPN [11].
(b) Simultaneous IPN: An IPN is formed by polymerizing two different monomers and their crosslinking agents together in one step [11, 12]. Here, the two components must polymerize simultaneously by reactions that will not interfere with one another.
(c) Latex IPN: In latex type IPN both networks are included in a single latex particle, usually by polymerization of the second monomer together with the crosslinking agent and activator in the original seed latex of the first crosslinked monomer [11]. Latex IPNs are formed from a mixture of two lattices, frequently exhibiting a “core” and “shell” structure [13].
(d) Thermoplastic IPN: The thermoplastic IPNs are combination of two physically crosslinked polymers [11, 12]. Typical physical crosslinks arise from ionic groups, crystallinity, or glassy domains. Thus, these materials flow at elevated temperatures, similar to the thermoplastic elastomers,
Studies on Synthesis and Characterization of Poly(methyl methacrylate)-Bentonite Clay Composite by Emulsion Polymerization and Simultaneous \textit{In Situ} Clay Incorporation

Sadhan Kumar Modak, Arup Mandal, Debabrata Chakrabarty
Department of Polymer Science and Technology, Calcutta University, Kolkata 700 009, India

Well-dispersed poly(methyl methacrylate) (PMMA)–bentonite clay composite was synthesized by emulsion polymerization using methyl methacrylate (MMA) monomer and 3% sodium carbonate treated bentonite clay. The composite lost its transparency normally encountered with the neat PMMA. The composite was characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), vicat softening point (VSP), dynamic mechanical thermal analysis (DMTA), and tensile studies. The morphology was investigated by scanning electron microscopy (SEM) and atomic forced microscopy (AFM) as well. The crystallography was studied to estimate the changes in crystallographic planes by X-ray diffraction (XRD) analysis. The particle size distribution was compared amongst neat bentonite clay, neat PMMA and the composite. The FTIR spectra reveal the fact that no new primary valence bond is formed between the clay and PMMA. The thermal stability of the composite is significantly improved, as indicated by the TGA and VSP studies. A substantial increase in glass transition temperature ($T_g$) approximately, 10$^\circ$C was recorded from the DMTA as both the storage modulus and tan $\delta$ values underwent inflexion at higher temperatures in case of the composite compared with the pristine PMMA. The XRD pattern indicates increase in basal $d$ spacing for the composite. The morphology from both the SEM and AFM is quite supportive to well-dispersed exfoliation. The incorporation of nanosized activated clay particles in PMMA during its \textit{in situ} polymerization from MMA led to the formation of nanocomposites.

INTRODUCTION

Composites based on layered inorganics offer an alternative to conventionally filled polymers and composites. Due to the very small phase dimensions of the reinforcements, the composites exhibit new and improved properties. These include increased stiffness and strength without sacrificing impact resistance, reduced permeability and swelling in solvents, increased barrier properties and flame resistance [1, 2]. This type of organic–inorganic composite can potentially exhibit hybrid system synergistically derived from both the host (clay) and the guest polymer [3]. These nanocomposites find extensive application in antiballistic, anticorrosion, and dental purposes [4, 5]. Poly(methyl methacrylate) (PMMA)/methyl methacrylate (MMT) nanocomposite has been prepared by melt intercalation, solvent intercalation, and \textit{in situ} intercalative polymerization which may proceed by solution, suspension, or emulsion technique. Intercalated and partially exfoliated or fully exfoliated composite structures have been obtained by the various methods [6–8].

Montmorillonite, one of the major constituents of Indian bentonite—a smectic clay consists of octahedral aluminate sheet sandwiched between two tetrahedral silicate layers. The layer charge can easily be generated by replacement of cations in the layer with cations of different charges: e.g., Al$^{3+}$ in the aluminate sheet with the Mg$^{2+}$ or Fe$^{2+}$ produces negatively charged aluminate layers and cations like Na$^+$ or K$^+$ are newly incorporated into the interlayer spaces to maintain charge neutrality. The hydrophilic property of MMT is attributed to the presence of such Na$^+$ or K$^+$ ions incorporated in the interlayer spaces of the TOT structure [2]. This enhanced hydrophilic characteristic leads to easy penetration and high degree of water swelling. Thus, it can be presumed that these structural characteristic of MMT present in bentonite can possibly provide an effective method for the preparation of a hybrid composite if an aqueous system is involved in the intercalation or exfoliation process, the two different processes for lamella reinforcement.

In the present investigation, in accordance with the above theory an emulsion system has been chosen to find out the extent of reinforcement, the bentonite clay can offer to the guest polymer PMMA and modify its properties. The logic behind such expectation of enhancement in properties lies in the fact that the hydrophilic unmodified
Modifying influences of micro crystalline and nanocellulose on the gelling characteristics of poly(Methacrylic acid-co-2-hydroxyethylmethacrylate)

Rabin Bera, Ayan Dey, Arpita Mandal, Arup Mandal, Debabrata Chakrabarty *

Department of Polymer Science and Technology, University of Calcutta,
92, APC Road, Kolkata-700009, India

* Corresponding author: email id- chakrabarty_deb@yahoo.com

Abstract

Cellulose dispersions were incorporated in the methacrylic acid (MAc) - 2-hydroxyethyl methacrylate (HEMA) copolymer hydrogel matrix formed in situ and the effects of such incorporation on various properties of the resulting hydrogel were investigated by means of swelling-deswelling study, morphological study and rheological characterization. The absorption capacity of the hydrogels decreases on increasing HEMA content in the copolymer network. The introduction of cellulose, particularly nanocellulose in the MAc-HEMA co-polymer network enhances remarkably the swelling efficiency of the hydrogels. Such incorporation also affects the rheological and morphological characteristics of the hydrogels. The deposition or adsorption of cellulose in and around the pores of the polymer matrix is clearly revealed by SEM images. The cellulose based hydrogels are found to be efficient particularly in respect of removal of cationic dyes and heavy metal ions (Cu$^{2+}$ and Fe$^{3+}$) from aqueous solution also.

Key words

Hydrogel, swelling, SEM, rheology, dye removal, nanocellulose