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Fire-retardant and ductile clay nanopaper biocomposites based on montmorrilonite in matrix of cellulose nanofibers and carboxymethyl cellulose

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ABSTRACT

Nacre-mimetic clay bionanocomposites of high clay content show interesting properties although low strain to failure is a limitation. For this reason, three-component nanocomposite films were prepared based on sodium montmorrilonite clay (MTM), a water-soluble cellulose derivative (CMC) of fairly high molar mass, in combination with nanofibrillated cellulose (NFC) from wood pulp. The nanocomposite is cast from an aqueous colloidal dispersion. First, the effects of CMC content on CMC/MTM compositions with high volume fraction of MTM (36–83 vol.%) were studied by FE-SEM, XRD, UV, DMTA and TGA. In addition, fire retardance and oxygen permeability characteristics were measured. The effect of NFC nanofiber addition to the matrix phase was then evaluated. This two-phase CMC/NFC matrix phase results in significantly improved modulus, strength but also strain to failure. NFC has a favorable effect by shifting catastrophic failure mechanisms to higher strains.
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1. Introduction

Polymer/clay nanocomposites (PCNs) have been actively studied since 1967 [1], and were then developed for automotive applications [2,3]. Polyamide 6/clay nanocomposites were successfully developed at Toyota, and applications were demonstrated [2,3]. More than 10,000 papers related to PCN have since been published since. The incorporation of less than 5 wt.% clay dramatically improves gas barrier properties [4], flame retardancy [5], and mechanical properties [3]. Numerous efforts have been carried out in order to increase the clay content in the polymer matrix, but most of them failed because of the very high aspect ratio of clay platelets. If the processing approach leads to random in space platelet orientation, then the maximum theoretical clay content is very low and strong agglomeration effects are obtained. In addition, the hydrophilic surface and nanoscale size of clay platelets could make it difficult to achieve good dispersion of clay, in particular in hydrophobic polymer matrices.

Some papers have reported on PCNs with very high clay contents, from about 50 wt.% to 80 wt.%. The strength and modulus can be quite high. For example, Kotov et al. reported on MTM/polyelectrolyte nanocomposites with about 50 wt.% MTM (montmorrilonite) [6] prepared by elegant but fairly time-consuming layer-by-layer (LbL) deposition techniques [7]. Using a similar technique, greatly improved modulus and strength was reported for MTM–PVA (polyvinylalcohol) composites where the MTM–polymer interaction is strong [8]. In other studies [9,10], a much simpler preparation route was used which was inspired by papermaking filtration procedures. A hydrocolloidal dispersion of exfoliated silicate platelets was mixed with a water-soluble polymer solution. The polymer adsorbed to the clay platelets, which were coated by the polymer. In order to achieve control of the polymer matrix

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distribution, the excess polymer present in solution was removed. The stiffest and strongest composition with about 50 wt.% MTM showed a modulus of 45 GPa, tensile strength of 250 MPa and strain to failure of 0.9%. MTM platelets were also combined with nanofibrillated cellulose (NFC) from wood to produce 200 mm diameter flat clay nanopaper sheets by a semi-automatic paper-making procedure [11]. These NFC nanofibers from wood pulp have a diameter of around 15 nm and a length of several micrometers, and are flexible in bending although stiff and strong in tension. Clay nanopaper has considerable ductility due to the NFC network [12]. Addition of chitosan reduces filtration time and modifies mechanical properties [13]. The polymer adsorption method developed for true nanostructural control [9,10], was also used to prepare MTM/chitosan bionanocomposite films [14]. The hybrid films prepared by first adsorbing chitosan show improved optical transparency and mechanical properties compared with hybrid films prepared by directly mixing MTM and chitosan (without separate adsorption step).

Although direct mixing and filtration is disadvantageous in terms of nanostructural control, this processing route is simpler. In early work, PCNs with high content of synthetic smectite saponite clay were combined with CMC [15]. CMC (carboxymethyl cellulose) in sodium salt form is a water-soluble cellulose derivative used as a negatively charged polymeric additive in industrial papermaking. Flexible and transparent clay/polymer films showed high thermal resistance and good gas barrier properties with only 10 or 20 wt.% water-soluble polymer as a binder [15]. Clay platelets were highly ordered parallel to the film surface, and the oxygen transmission rate was extremely low at dry conditions. However, the tensile strength was only around 25 MPa with a strain to failure of 1.8%. Although most PCNs with high content of ordered clay are stiff and strong, a remaining challenge is to design materials with increased strain to failure. PCNs with high clay content rely on matrix failure processes [16] and platelet pull-out [17] as important mechanisms, which can increase strain to failure.

Nanofibrillated cellulose (NFC) from plant cell walls is an interesting building block for new nanocomposites. NFC networks have been used to reinforce a variety of polymer matrices [18–21]. In contrast to pure bacterial cellulose [22], NFC based on enzymatically pretreated wood pulp [23] forms stable hydrocollodial dispersions [24]. The reason is not completely clear although it may be due to weakly charged hemicelluloses at the surface of NFC. Due to the stability of the NFC hydrocolloid, water-soluble polymers can be readily combined with NFC.

In a previous study [12], NFC nanofibers were directly used to provide a nanofibrous matrix to MTM platelets and formed clay nanopaper structures. The clay content was as high as 89% by weight with maintained mechanical robustness. This clay composition had a strain to failure as high as 2%, due to the load-carrying function of the continuous, web-like cellulose nanofiber network. A later study combined electronegative NFC with clay in exceptionally thin films of very high mechanical performance [25]. The very low film thickness may contribute to the favorable properties obtained.

Encouraged by the interesting characteristics of three-component clay nanopaper containing clay, NFC and chitosan [13], (strength 103 MPa and strain to failure 2.4%) we proceed to study a nanocomposite system based on MTM, NFC and CMC. The main technical objective is to aim for improved ductility, since it is very difficult to combine high MTM content (>25 vol%) with ductile deformation behavior. This has not been achieved in previous studies. Since both CMC and the MTM surface are electronegative, weak interaction is expected which may increase strain to failure. First, structure–property relationships in MTM–CMC nanocomposite films are studied with MTM content in the range 36–83% by volume. The properties will be compared with a previous chitosan study [14] (strength 99 MPa, strain to failure 2.3%). Secondly, the effect of adding a small amount of NFC is studied. Mechanical properties, thermal stability, gas barrier properties, optical transparency and fire-shielding characteristics are evaluated.

2. Experimental

2.1. Materials

Carboxymethyl cellulose sodium salt (CMC) with an average molecular weight of 250,000 and a DS of 0.7 was obtained from Sigma Aldrich Co., 1.0 wt.% CMC was dissolved in de-ionized water by vigorous stirring before using.

The MTM (Cloisite Na^+, Southern MTM Products) was a sodium montmorillonite (MTM) with a cation-exchange capacity (CEC) of 92 meq/100 g. The average width of the platelets is 110 nm as described by the manufacturer, with a thickness of about 1 nm. 1.0 wt.% hydrocolloidal MTM dispersion was prepared by dispersing 10 g of MTM in 1 L of de-ionized water under vigorous stirring.

A nanofibrillated cellulose (NFC) hydrocolloid dispersion was prepared as described in previous work [26]. Degree of polymerization (DP) was estimated to be 480 after homogenization, as determined from the average intrinsic viscosity of the dissolved polymer [26]. An NFC aqueous suspension with a concentration of 1.6 wt.% was obtained and stored at 4 °C. The NFC suspension was diluted to 0.2 wt.% in de-ionized water and stirred before use.

2.2. Preparation of CMC/MTM hybrid films

CMC/MTM hybrid films were prepared as follows: 1.0 wt.% CMC solution was added slowly to the MTM dispersion and the mixture was stirred for 24 h. Then it was poured into a Teflon mold and dried in the oven at 55 °C. CMC/MTM hybrid films with a thickness in the range 60–70 μm were obtained with initial CMC–MTM weight ratio of 10:90, 20:80, 30:70, 40:60 and 50:50, coded as CMC10–MTM90, CMC20–MTM80, CMC30–MTM70, CMC40–MTM60, CMC50–MTM50, respectively.

2.3. Preparation of NFC/CMC nanocomposite films

CMC nanocomposite films were prepared as follows: 0.2 wt.% NFC solution was added slowly into the 1.0 wt.%

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