

Effects of Boron Nitride Nanopowder on Thermal, Chemical and Gas Barrier Properties of Starch

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Abstract Starch/boron nitride (starch/BN) bionanocomposites were prepared with the reinforcement of boron nitride nano powder by solution technique. The dispersion of BN in the starch was achieved by a continuous sonication process. The interaction between starch and boron nitride nanopowder was investigated by Fourier transform infrared (FTIR) spectroscopy. The structural properties of starch/BN bionanocomposites was studied by X-ray diffraction (XRD). The high resolution transmission electron microscopy (HRTEM) was used for the study of dispersion of boron nitride in starch matrix and diffraction patterns were studied by selected area electron diffraction (SAED). Thermal stability of the starch was increased with rising concentrations of boron nitride due to incorporation of rigid nano BN with starch matrix. The substantial reduction in oxygen permeability was obtained by increasing the concentration of BN. The biodegradability of synthesized bionanocomposites was measured by using activated sludge water. Further, it was noticed that, starch/BN bionanocomposites are resistant towards inorganic acids and bases. The tensile strength of starch/BN bionanocomposites was increased whereas; the water resistance property of the materials was decreased with increasing BN loading.

Keywords: Starch; Boron nitride; Bionanocomposites; Oxygen permeability.

INTRODUCTION

Shortage of non-renewable petroleum-based products has aroused a great deal of interest in materials, based on biopolymers and inorganic nanoparticles. A strong built increase in environmental pollution has been caused by covering a large area use of non-biodegradable materials^[1]. On the other hand biopolymers such as starch, protein and cellulose have been considered as unconventional materials to petroleum based plastics as they are renewable, inexpensive, plentiful, eco-friendly and non-toxic to animal kingdom^[2]. Bionanocomposites can be prepared from these biopolymers using nano sized fillers. They are applied in the production of biomedical and packaging materials as they have superior physical, thermal and easy processing characteristics^[3].

Among the natural biopolymers, starch is one of the most popular, cheap, nontoxic, environmental friendly, abundant and fully biodegradable polymers stored as granules in plants^[4]. It is composed of two microstructures consisting of linear water soluble amylose and branched insoluble amylopectin^[5]. Starch is hydrophilic and has been proven as a conventional composite with kaolinite^[6–8]. It is a promising raw material because of its annual availability from many plants and its low cost^[9]. Natural biopolymers and bio-fibres are used in engineering fields because of three factors. They include low compatibility with hydrophobic polymer matrices, thermal sensitivity at the temperature of compounding processes and flammability which struggles with safety requirements^[10]. Avella *et al.* studied the preparation and characterisation of compatibilized polycaprolactone/starch composites^[11]. In our earlier works, we have studied the preparation of starch/f-MWCNT nanocomposites

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and reported on improvement of their thermal, chemical and gas barrier properties^[12].

Hexagonal boron nitride (h-BN) appears very similar to that of graphite having layer like structure in nature with strong bonding in the planner, fused, six-membered rings and weak van-der Waals bonding in between layers^[13, 14]. It has low elastic modulus, excellent thermal shock resistance, chemical inertness, limited surface activity, non-wet ability, corrosion resistance and lubricating effect^[15]. Boron nitride can be hot pressed, layered and interposed to prepare different composites where boron nitride plays vital role. The substances made up of boron nitride have several uses in cosmetic application, functional coating in the automotive and glass industry^[16]. Some researchers studied on polymer-boron nitride composites with nonbiodegradable polymers like polyaniline, polystyrene, copolymer of vinylidene chloride and acrylonitrile, justifying the key role of boron nitride in terms of better thermal, chemical resistant and mechanical properties^[17, 18]. The non-cytotoxicity of boron nitride to human body was studied by Chen *et al*^[19].

In the present work, the nano BN has been incorporated into starch matrix to study the improvement of thermal, chemical and gas barrier properties along with mechanical properties, chemical and water resistant properties of starch/BN bionanocomposites in comparison with those of the starch matrix. It was found that, these properties of the bionanocomposites are substantially improved as compared to starch with little scarification of biodegradable properties.

EXPERIMENTAL

Materials

Starch, soluble was purchased from Fisher Scientific, Mumbai, India of analytical grade and it was used as such. Boron nitride nano powder of average particle size of 70 nm was obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India which was of 99.9% purity. The other chemicals used were of analytical grade and used without any further purification. All solutions were prepared using double distilled water.

Preparation of Starch /BN Bionanocomposites

The series of starch/BN bionanocomposites were prepared by simple solution technique with variable percentage of boron nitride. The different wt% of boron nitride was dispersed in double distilled water by continuous stirring for 30 min at 50 °C and then sonication with ultrasound (120 W/180 kHz) for 30 min^[20–24]. The starch solution prepared in distilled water was then added to different wt% boron nitride solutions. Thereafter the prepared CuSO₄/glycine solution was added to the above mixture and stirred constantly for 3 h at room temperature^[25]. The product was cooled and 6 ml of acetone was added to it as a non solvent and kept overnight^[26, 27]. The viscous product obtained was filtered and washed time and again with double distilled water. The bionanocomposites obtained were dried in an oven for 24 h at a temperature of 50 °C. Then the dried samples were powdered and coded as SBN 0, SBN 2, SBN 3, SBN 5, SBN 8, and SBN 10 for loading of 0 wt%, 2 wt%, 3 wt%, 5 wt%, 8 wt%, 10 wt% of boron nitride nanopowder respectively for characterization and study of their properties.

Characterization of Starch/BN Bionanocomposites

The formation of composites was studied by Fourier transform infrared (FTIR) spectrophotometer using a Shimadzu IR Affinity-1 instrument in the range of 4000 cm⁻¹ to 400 cm⁻¹. X-ray diffraction (XRD) patterns of the nanocomposites and the raw material were obtained by using a Rigaku X-ray machine operating at 40 kV and 150 mA. The dispersion of the nano boron nitride in the starch matrix was studied using a Tec-nai 12, Phillips high resolution transmission electron microscope (HRTEM) operating at 20 kV.

The thermogravimetric analysis (TGA) of the prepared samples was carried out using a TGA apparatus of model DTG-60 by Shimadzu Corporation, Japan. The sample was heated under nitrogen purge with a heating rate of 10 K/min. Oxygen permeability of the bionanocomposites was measured with ASTM F 316-86 by using an Oxygen Permeation Analyzer (PMI instrument, model GP-201-A, Texas, NY, USA). For testing oxygen permeability, the prepared powdered bionanocomposites were changed into films of 5 mm thickness with the help of a polymer press at a pressure of 9 tons and at a temperature of 200 °C. The results were recorded as

average of the values obtained from five same samples. The biodegradability of the starch/BN bionanocomposites was studied for 180 days using sludge water. Further, resistance of the synthesized bionanocomposites towards dilute acid and alkali was investigated for 60 days.

The mechanical properties were measured with 5 samples for each composition by using an Instron machine (Canton, MA, USA) at room temperature with crossed-head speed of 1.5 mm/min. The samples were dried until constant weight in an oven to remove the moisture before measurements of water retention property by gravimetric methods. The water resistance of starch and starch/BN composites were calculated by the formula $[(W_f - W_i)/(W_i)] \times 100$. Where, W_i was the initial weight and W_f was the final weight of samples. The average values of five samples of same composition were taken into consideration.

RESULTS AND DISCUSSION

FTIR Analysis of Starch/BN Bionanocomposites

The FTIR spectra of starch/BN bionanocomposites are recorded in order to observe the functionalized groups present and the interaction between starch matrix and boron nitride (Fig. 1). Characteristic sharp peak of boron nitride at 812 cm^{-1} is due to B–N stretching vibration mode which is present in comparison to starch/BN bionanocomposites. The peak of starch at 3632 cm^{-1} is strong and broad because of the stretching vibration of –OH whereas, that of the peak at 1530 cm^{-1} is due to C–O bending. The characteristic peak of prepared bionanocomposites of starch and boron nitride is available around the same position with different intensities indicating the formation of composites. It is noticed that, the peak at 1530 cm^{-1} is shifted to left in starch/BN bionanocomposites. This may be due to the interaction of C–O–H groups of starch with boron nitride.

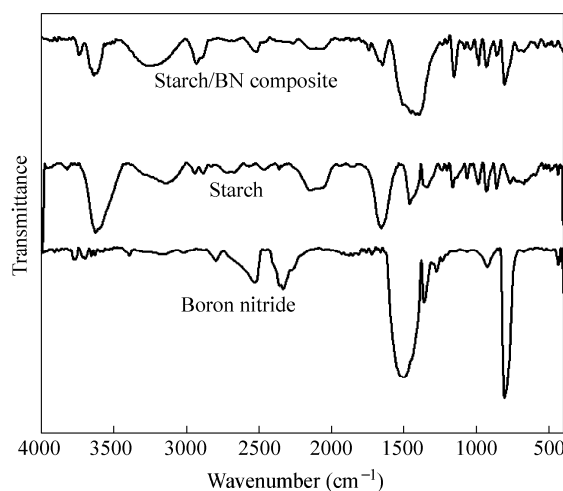


Fig. 1 FTIR spectra of starch, boron nitride and starch/BN bionanocomposite

XRD Analysis of Starch/BN Bionanocomposites

The XRD patterns of starch, boron nitride nanopowder and starch/BN bionanocomposites are compared in Fig. 2. The pure boron nitride shows high crystalline peaks at 2θ value of 26.7° and two peaks at 2θ values of 41.66° , 55.36° due to different phases of boron nitride. The X-diffraction of starch shows the characteristic crystalline peaks at 2θ values of 17° , 19° and 22° which demonstrated good crystallizability of starch. Similar results have been reported by the literature^[28]. In the synthesized bionanocomposites, the distinguishable peaks of both starch and boron nitride are present at about the same positions indicating the formation of composites by interaction of nano boron nitride with starch matrix.

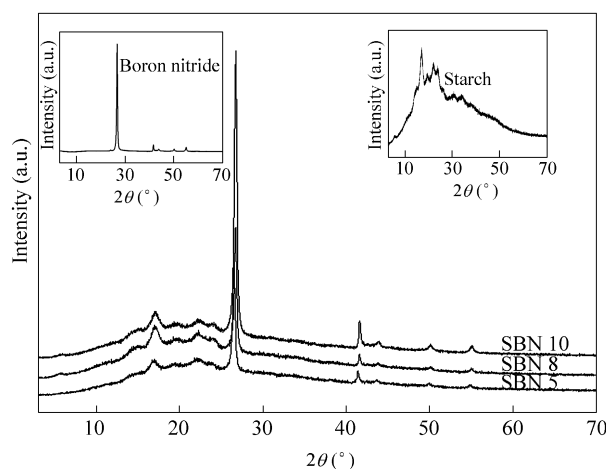


Fig. 2 XRD patterns of starch (inset), BN (inset) and starch/BN bionanocomposites as function of BN concentration

TEM Analysis of Starch/BN Bionanocomposites

The well dispersion of boron nitride within starch matrix is analyzed by TEM as is shown in Fig. 3. It is observed that the boron nitride nanopowders are distributed homogeneously in the starch matrix (Fig. 3a). The crystal structure of starch flakes are spread and partly dispersed in the TEM picture of starch/BN bionanocomposites. The black patches are due to agglomeration of boron nitride at bionanocomposites of 5 wt% which did not affect the physical properties of prepared bionanocomposites. The selected area electron diffraction (SAED) technique is taken to identify the boron nitride phase in the bionanocomposites. The quantitative *d*-spacing are calculated and presented in Fig. 3(b). The *d*-spacing values due to dispersion are 0.055 nm, 0.046 nm, 0.032 nm and 0.027 nm, in the SAED pattern of the starch/BN bionanocomposites.

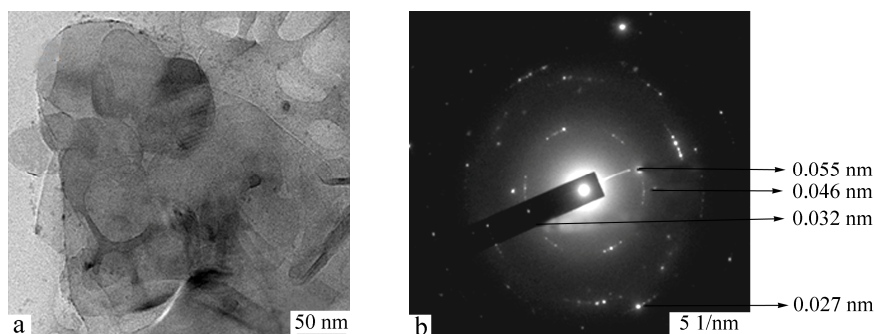


Fig. 3 (a) HRTEM image of starch/BN bionanocomposites (5 wt%) and (b) SAED pattern of starch/BN 5 wt%

TGA Analysis of Starch/BN Bionanocomposites

The thermogravimetric analysis of starch, boron nitride and starch/BN bionanocomposites are compared in the temperature range of 30–800 °C (Fig. 4). The thermal decomposition of starch occurred in three steps. In first step was the initial weight loss at 100 °C due to loss of water on the surface of starch. The second step degradation of starch was at about 250 °C due to its thermal decomposition and the third step degradation was more marked in the region between 260 °C and 380 °C and then charring due to oxidation. From TGA analysis, it was observed that starch decomposed completely at 480 °C where as about 15%, 25%, 35% of residue left in the case of bionanocomposites with 2 wt%, 5 wt% and 8 wt% of boron nitride loading respectively. Hence, the thermal stability of the bionanocomposites of starch/BN was increased due to well distribution of thermally stable boron nitride. The existence of thermal stable boron nitride may cause the enrichment of thermal resistant property of these bionanocomposites. Similar result has been also reported during the study of thermal properties of starch composites with reinforcement of multi-walled carbon nanotubes^[29].

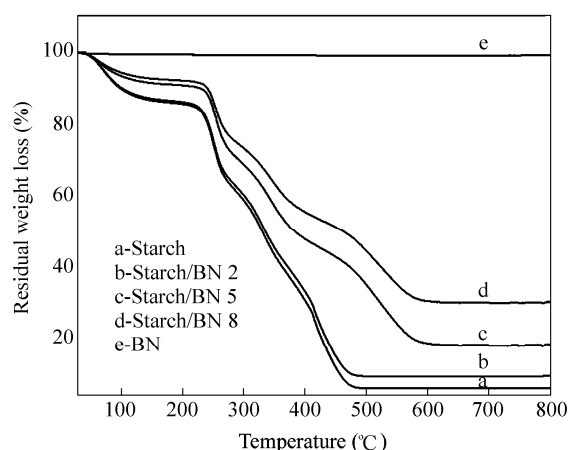


Fig. 4 TGA curves of starch, BN and starch/BN bionanocomposites of 2 wt%, 5 wt% and 8 wt% of BN

Oxygen Barrier Properties of Starch/BN Bionanocomposites

The oxygen permeability of the starch/BN bionanocomposites was observed and compared in order to study the effect of boron nitride nanopowder loading (Fig. 5). At constant pressure, the flow rate was decreased with increase in percentage of boron nitride loading (Fig. 5a). At different pressure, the oxygen barrier property was measured and compared (Fig. 5b). The substantial reduction in oxygen permeability may be due to the uniform distribution of boron nitride nanopowder within starch matrix blocking the voids for oxygen penetration. In the present study of starch/BN bionanocomposites the penetration reduction is six times than the corresponding virgin matrix where as our earlier work on starch/SiC bionanocomposites reduction reported four times at 10 wt% loading^[30]. Hence, the reduction of oxygen permeation is the suggestion for packaging application.

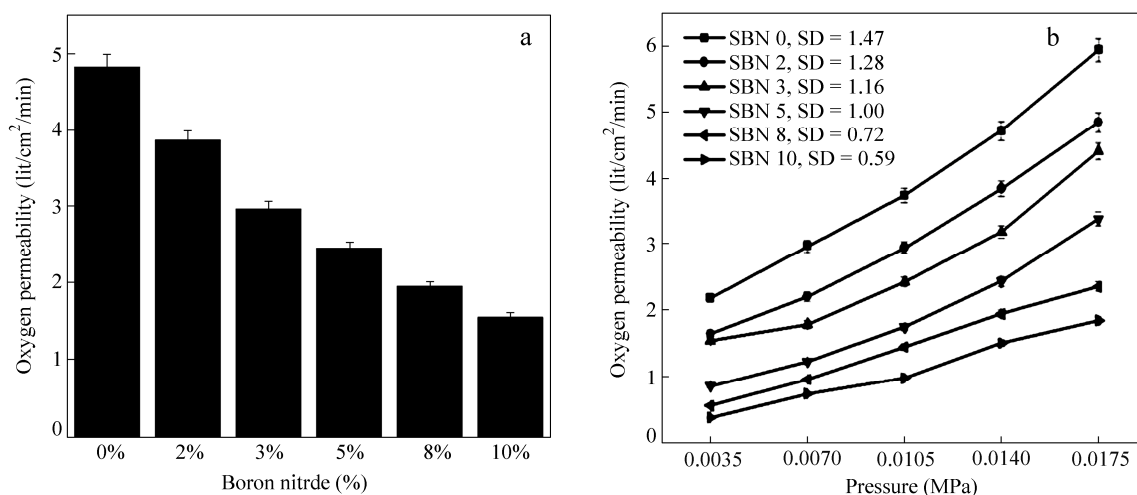


Fig. 5 Oxygen permeability of starch and starch/BN bionanocomposites at constant pressure (a) and different pressures (b) (SD-Standard deviation)

Biodegradation Properties of Starch/BN Bionanocomposites

The biodegradation of starch and prepared starch/BN bionanocomposites using activated sludge water was studied and compared with virgin starch for a period of 180 days at an interval of 30 days (Fig. 6). It was found that the percentage of weight loss in bionanocomposites decreased with increase in percentage of boron nitride loading. However, biodegradation of starch/BN bionanocomposites as well as virgin starch was increased with increase in time duration with sludge water^[31].

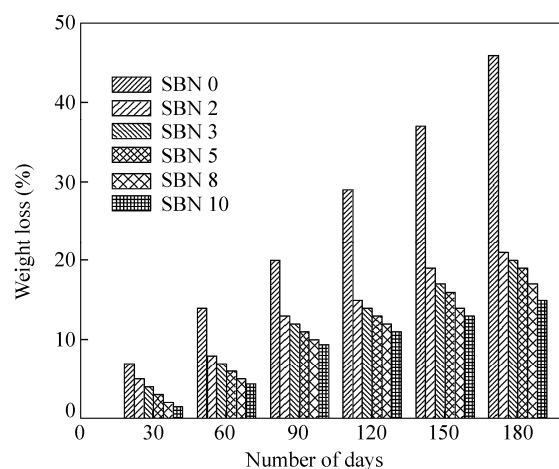


Fig. 6 Weight loss % of starch and starch/BN bionanocomposites due to biodegradation in activated sludge water at different intervals of time

Chemical Resistance Properties of Starch/BN Bionanocomposites

The resistivity of the bionanocomposites towards chemicals like dilute acids and alkalis was studied using dilute HCl (1 mol/L) and NaOH (1 mol/L) for 60 days with an interval of 10 days (Fig. 7)^[32]. The weight loss of bionanocomposites was increased by increasing the time period. The resistance of starch/BN bionanocomposites towards alkali as well as acid significantly increased as compared to virgin starch due to chemical inertness of boron nitride present in the starch matrix. Hence, these starch/BN bionanocomposites may be suitable for packing mild acidic and alkaline products.

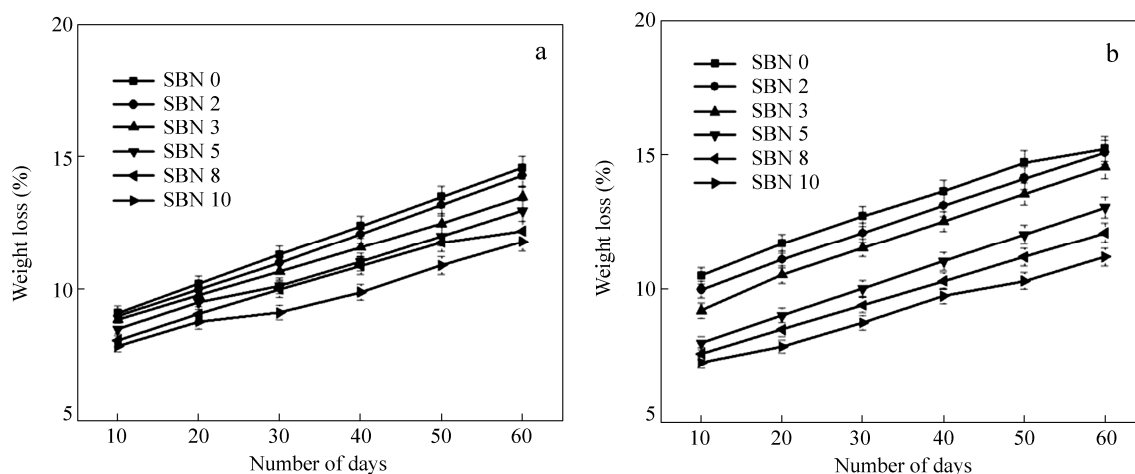


Fig. 7 Chemical resistance of starch and starch/BN bionanocomposites (a) in dilute NaOH and (b) in dilute HCl

Water Resistance Properties of Starch/BN Bionanocomposites

The water resistance property of starch and starch/BN bionanocomposites is compared in Fig. 8. It was noticed that water resistance property of starch was reduced with increasing percentage of boron nitride. The hydrophobicity of starch was increased by three times due to dispersion of boron nitride nano powder. This is attributed to the decrease in chain mobility of starch. After mixing with nano boron nitride, the decrease in hydrophilicity of starch may due to increase in barrier properties by the formation of tortuous path of boron nitride.

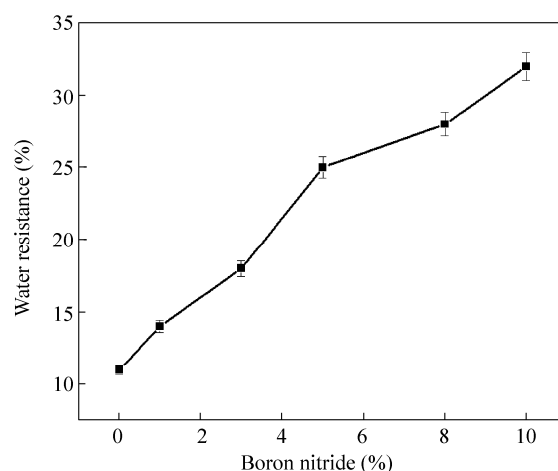


Fig. 8 Water resistance of starch and starch/BN bionanocomposites at different concentrations of BN

Tensile Strength of Starch/BN Bionanocomposites

The tensile strength of starch/BN bionanocomposites as a function of boron nitride content was measured (Fig. 9). The tensile strength of starch was found to be 6 MPa. It was found that the tensile strength of the bionanocomposites increased with increase in boron nitride content. The tensile strength of the bionanocomposites at 10 wt% of boron nitride was found to be more than three times as compared to that of the starch. It was due to the presence of boron nitride platelets which increased the tensile modulus of starch. The result of mechanical property evidenced that boron nitride platelets act as reinforcing nano filler to the starch matrix.

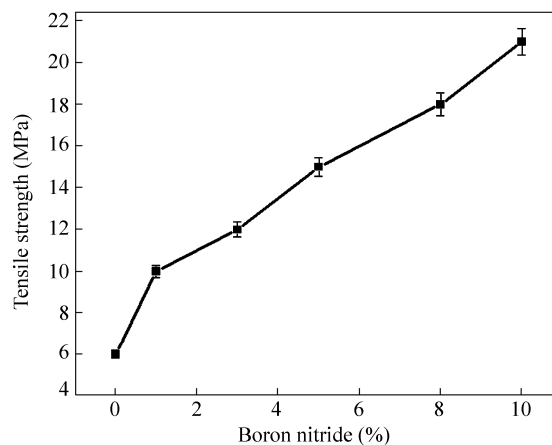


Fig. 9 Tensile strength of starch and starch/BN bionanocomposites at different concentrations of BN

CONCLUSIONS

Nano boron nitride reinforced starch bionanocomposites are synthesized by low cost green solution technique. The nanostructural dispersion of starch/BN bionanocomposites was achieved by HRTEM and SAED. Prepared bionanocomposites have thermal resistant property with reduction in oxygen permeability by six times as compared to virgin starch. Starch becomes acid and alkali resistant with dispersion of nano boron nitride however biodegradation ability of starch/BN bionanocomposites was sacrificed with improvement in other properties. The thermal, chemical resistant starch bionanocomposites with substantial improvement in gas barrier property can make the prepared material suitable for packaging application.

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