Characterization of Natural Rubber Latex/Chitosan Blends

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Abstract: In an attempt to prepare novel biodegradable materials, blends of natural rubber latex/chitosan (NR/CS) with different compositions have been prepared by solution casting followed by compression. The blends were characterized by thermogravimetry, Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction, and scanning electron microscopy (SEM) techniques. The effect of thermal stability on the percentage of natural rubber latex (NR) in the blend was studied. The percentage of bound rubber content and fraction of rubber dissolved in benzene was determined. Better interfacial adhesion between chitosan and natural rubber is achieved in the blend NR_{95} CS_5. This is reflected in the IR spectrum also. The water absorption behavior of the blends has also been studied. X-ray diffraction study shows a decrease in crystallinity in natural rubber with addition of chitosan.

Keywords: Blends; Chitosan; Natural rubber; Thermoplastic elastomers; X-ray diffraction

INTRODUCTION

Chitosan is a deacetylated product of chitin, which is obtained from the cuticle of marine crustaceans such as crabs and shrimps; it is also classified as a natural polymer because of the presence of a degradable enzyme, chitosanase.[1–6] Another environmentally friendly material is

cis-1, 4-poyisoprene rubber. It is a biodegradable elastomer. This polymer has a high degree of crystallinity, which leads to good strength at normal temperature and also at temperatures near or above the crystalline melting point, allowing easy processing of the polymer.[7,8]

Blending of two polymers usually gives rise to a new material having better balance of properties than obtainable with a single polymer.[9–12] The emergence of thermoplastic elastomers is one of the most important developments in the field of polymer science and technology in recent years. Thermoplastic elastomers are a new class of materials that combine the properties of rubber with the ease of processability of thermoplastics.[13–15] One type of fast-growing thermoplastic elastomer that is easier to process is made by blending rubber and plastic in definite proportions.[16] However, to explore newer applications, important properties must be investigated. We have already reported the effect of chitosan on the mechanical properties of natural rubber.[17] It was found that the mechanical property was enhanced with the addition of chitosan into natural rubber. Likewise, the assessment of thermal stability is one of the most important applications of thermogravimetry (TG) in the study of polymers. Thermogravimetric curves provide information about the decomposition mechanisms for various materials.[18] In this article we report the characterization of natural rubber latex/chitosan blends by thermogravimetry, X-ray diffraction, FT-IR, and scanning electron microscopy and also the estimation of bound rubber and water absorption.

EXPERIMENTAL SECTION

Materials

Purified chitin was purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India); its viscosity average molecular weight was 400000 g/mol. The natural rubber latex was used directly as extracted from the tree (*Hevea brasiliensis*), cultivated around the belt of Western Ghats, Karnataka, India. The latex was stabilized by adding 2.5% of a 28% ammonium hydroxide solution. The dry rubber content was determined by drying the emulsion in an oven at 110°C for 12 h and was found to be 40%.

Preparation of Chitosan and Chitosan Solution

Chitin was dispersed in 50% (w/w) NaOH solution and heated at 100°C for 2 h. The mixture was then cooled to room temperature, filtered, and

washed with water several times until the filtrate was neutral. The chitosan sample obtained was dried in an oven at $60°C$ for 48 h. The chitosan solution was prepared by dissolving chitosan in distilled water containing 2% (v/v) acetic acid.

Preparation of Chitosan/Natural Rubber Blends

The blends were prepared by mixing chitosan solution and natural rubber latex to get a homogeneous solution. The mixture was then cast on a petri dish at $45°C$ for 48 h. The films were prepared by compressing these cast samples at $140°C$ and at a pressure of 1 GPa for 10 min in a hydraulic press. The resulting film thickness was 2–2.5 mm. The studies have been limited to $CS_{50} NR_{50}$; on exceeding the volume fraction of chitosan, the films were found to be brittle and discontinuous.

Thermogravimetric Analysis (TGA)

A Perkin Elmer Diamond TG/DTG was used for the thermogravimetric analysis of the blended samples. A small amount (1–10 mg) of sample was taken for the analysis, and the sample was heated from $40°$ to $720°C$ at a rate of $10°C/min$ in nitrogen atmosphere. The TGA and differential thermogravimetry (DTG) curves are plotted for each sample.

Morphology

Scanning electron microscopy (SEM) was performed to investigate the morphology of the blended films with a JEOL JSM 5800LV instrument. The surface was sputter-coated with gold before examining under the microscope.

Estimation of Bound Rubber

The swelling experiments were more difficult to perform for unvulcanized materials since part of the sample could dissolve in benzene. Therefore the following analysis was performed for these samples. Thin discs of samples with diameter of 10 mm and around 2 mm thickness were first weighed (M_0) and then immersed in benzene for 48 h. The swollen portion (gel) remains insoluble. They were subsequently dried for 12 h at $55°–60°C$ and weighed again (M_1). The "gel" fraction (M_1/M_0) and relative weight loss ($W_{(rel)} = [M_0–M_1]/M_0$) were then determined.[19] From

this, the fraction of natural (NR) bound to the chitosan and the fraction of NR dissolved in benzene were estimated.

Water Absorption Test

Samples were immersed in distilled water at 30°C. Weight of the samples was recorded at different time intervals. Samples were wiped with tissue paper to remove surface water before weighing. Finally, the weight gain was calculated. Water absorption was determined using the following equation:

$$W_g = \frac{[W_e - W_0]}{W_e} \times 100$$

where W_g is the weight gain, W_e is the equilibrium weight, and W_0 is the oven dry weight before water treatment.

Infrared Spectroscopy

IR spectra were taken using a Thermo-Nicolet Avatar 370 Fourier transform-infrared (FT-IR) spectrometer. The films were placed in the holder directly in the IR beam. Spectra were recorded at a resolution of $4 \, cm^{-1}$ and for 32 scans.

X-Ray Diffraction Studies

X-ray diffraction patterns of the samples were recorded with a Bruker D8 Advance X-ray diffractometer. The angular range was from $10°$ to $40°$ (2θ). The operating voltage and current of the tube were kept at 40 kV and 20 mA respectively throughout the entire course of investigation.

RESULTS AND DISCUSSIONS

Thermogravimetric Analysis

The TG/DTG curves of different compositions of CS/NR blends are shown in Figure 1. Chitosan exhibits poor thermal stability compared to natural rubber. According to Bolland and Orr,[20] in the temperature range 200°–270°C, in rubber both scission and cross-linking occur, although no loss of unsaturation of the bulk rubber occurs. NR undergoes thermal degradation in the temperature range of 287°–400°C to give
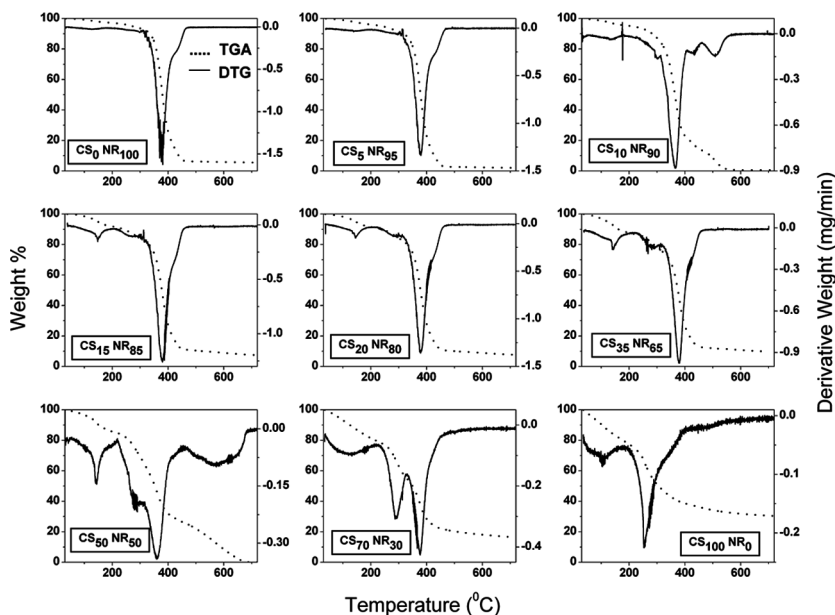
Figure 1. TGA and DTG plots of different NR/CS blends.

39% isoprene, 13.2% dipentene, and small amounts of p-menthene.[21] In the temperature range 450°–800°C, dipentene is the major degradation product and isoprene is the major degradation product in the temperature range 675°–800°C. In our case at 300°C 6.5% weight loss is observed and at 700°C 94.5% weight loss is observed. In the DTG curve the major peak is at 379°C.

Pawlak and Mucha[22] have confirmed the cross-linking of chitosan macromolecules following the destruction of amino groups. The second decomposition step, which appears at high temperature, may result from the thermal degradation of the new cross-linked material formed by thermal cross-linking reactions occurring in the first stage of the degradation process. TGA of Chitosan shows a weight loss in two stages (Figure 1). The first stage ranges between 35° and 215°C and shows about 24.6% loss in weight. This may correspond to the loss of adsorbed and bound water. The second stage of weight loss starts at 216°C and continues up to 400°C, during which there is 61.4% weight loss due to the degradation of chitosan. In the beginning, weight loss is faster, but after 400°C it is slow, which may be due to the cross-linking of chitosan in the earlier stage.

At 300°C, about 49% of chitosan undergoes degradation, whereas only 6.5% of natural rubber gets degraded. Below 300°C, solid rubber is quite stable. About 5.5% residue of natural rubber remains at 700°C

Table I. Weight loss of various CS/NR blends with temperature

Sample code	Percentage of weight loss at							
	100°C	200°C	300°C	350°C	400°C	500°C	600°C	700°C
$NR_{100} CS_0$	0.7	2.9	6.5	15.2	74.1	93.2	94.2	94.5
$NR_{95} CS_5$	1.0	3.9	8.6	18.4	77.2	97.3	97.7	98.0
$NR_{90} CS_{10}$	1.4	4.8	12.9	34.4	77.0	91.6	99.4	99.5
$NR_{85} CS_{15}$	1.4	8.2	15.7	25.8	72.7	89.6	91.1	92.4
$NR_{80} CS_{20}$	1.8	8.5	15.8	25.6	72.3	89.9	91.1	92.2
$NR_{65} CS_{35}$	3.0	12.4	21.9	32.0	73.7	88.0	89.2	90.4
$NR_{50} CS_{50}$	3.4	14.3	30.9	48.9	68.1	78.0	91.5	99.9
$NR_{30} CS_{70}$	6.9	18.5	37.0	50.2	71.6	79.7	81.8	83.5
$NR_0 CS_{100}$	9.5	22.6	49.0	57.1	61.4	65.8	68.2	69.4

and 30.6% residue remains for chitosan. As compared to the degradation of individual components, the degradation behavior of the blend is slightly different. The peak at about 145°C for the blends of CS/NR may be due to the liberation of volatile products. These blends show two DTG peaks, a minor and a major one. As the percentage of CS increases in the blend, the intensity of peak around 300°C increases. This is due to the degradation of CS. A second peak near 375°C is due to NR degradation. On increasing the natural rubber content, the decomposition of the blend decreases.

From Table I, it is observed that up to 350°C, the weight loss decreases with increase in the percentage of natural rubber in the blend. This shows that the blend samples are more stable than the pure chitosan below 350°C. Above 350°C the weight loss is mainly due to the degradation of the rubber. In the blend system, from 200° to 300°C as the percentage of chitosan increases, the increase in the weight loss may be due to the destruction of amino groups and the rate is found to be slow. Above 350°C, the weight loss is mainly due to the degradation of the newly cross-linked chitosan and natural rubber. Since degradation of the CS/NR blend (lower compositions) is negligible up to 150°C, the upper temperature limit for compression molding is 150°C. We have also observed that the blends have better mechanical properties than individual polymers.[17] Thus the rubber can be blended with chitosan and can be used for commercial applications.

Morphology

The properties of incompatible blend systems are strongly dependent on their morphology. The SEM micrographs of blends are shown in Figure 2.
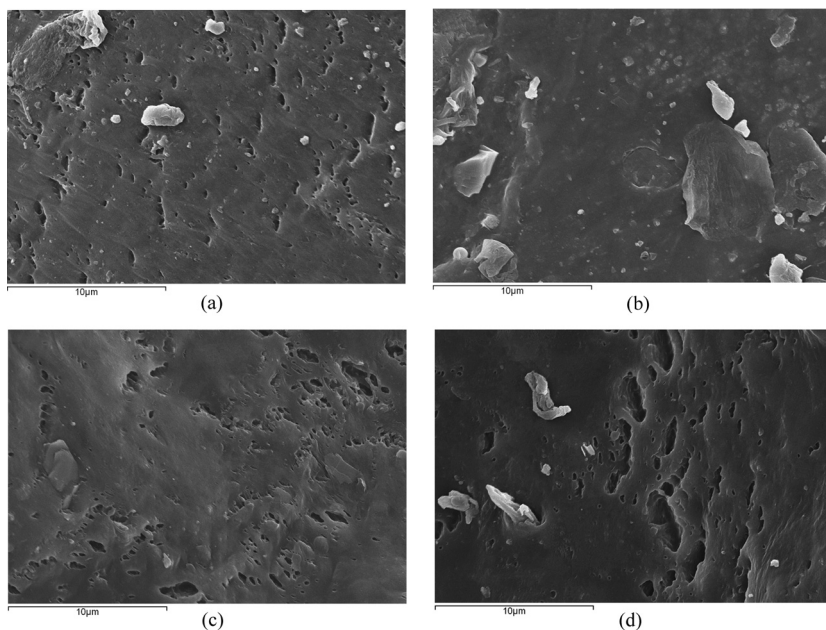
Figure 2. Scanning electron micrographs of natural rubber latex/chitosan blends: (a) pure NR, (b) NR_{95} CS_5, (c) NR_{80} CS_{20}, (d) NR_{50} CS_{50}.

The micrographs clearly show two distinct phase structures corresponding to NR and CS, indicating that the blends are incompatible. A uniform distribution of CS is observed in the blend NR_{95} CS_5. This morphology in NR_{95} CS_5 is reflected in the superior properties of this blend. On further increase in the amount of chitosan, discontinuity is again observed. NR_{50} CS_{50} blend shows almost a discontinuous morphology.

Estimation of Bound Rubber

The bound rubber content in the blend and the fraction of natural rubber dissolved were determined by immersing the samples in benzene. The relative weight loss (W_{rel}) and fraction of bound rubber (X_R) in the blends after 48 h of immersion in benzene are reported in Table II. The fraction of bound rubber is determined from relative weight loss data. The percentage of gel in the sample is given by

$$\%Gel = 1 - W_{rel} = W_c + (1 - W_{0(rel)})(1 - W_c) + X_R$$

where X_R is the fraction of bound rubber, and $W_{0(rel)}$ is the relative weight loss in pure rubber.

Table II. Relative weight loss and fraction of bound rubber for different NR/CS blends

% of chitosan	Relative weight loss (W_{rel}) (%)	Fraction of bound rubber (X_R) (%)
0	78	0
5	29	45
10	31	39
15	41	25
20	42	20.4
35	48	2.7
50	38	1

The first term corresponds to the chitosan content, the second term $[(1-W_{0(rel)})(1-W_c)]$ to the insoluble part of the rubber, and the third term to the fraction of NR in strong interaction with chitosan. Table II shows that 78% of the pure NR dissolved in benzene. The low W_{rel} values are due to stronger interaction between NR and chitosan in these blends. As the percentage of chitosan increases, the relative weight loss of the sample increases. The fraction of bound rubber (X_R) is determined from relative weight loss data. It is interesting to see that the X_R value for the $NR_{95} CS_5$ is maximum and decreases with the increasing amount of chitosan. This may be due to the high degree of interfacial interaction between CS and NR in $CS_5 NR_{95}$. Scanning electron micrographs of the blend samples support this argument. In the blend $CS_5 NR_{95}$, no voids or surface discontinuities are observed. This means that at lower concentration, the interfacial interaction between NR and chitosan is high and with increase in the amount of chitosan, the interaction becomes less important and, at last, it is negligible.

Water Absorption Test

Figure 3 shows the water absorption behavior with different time intervals for different blend ratios of NR/CS. At a similar absorption time, blends with higher concentration of chitosan exhibit higher water absorption. One of the physical properties of chitosan is its hydrophilic nature. In the blend samples, the water is absorbed mainly by chitosan because rubber is hydrophobic and its water absorbability can be neglected. Pure chitosan absorbs water immediately but as the percentage of NR increases, time to reach the equilibrium increases. The water absorption can also be minimized by vulcanizing the blends. The water absorption
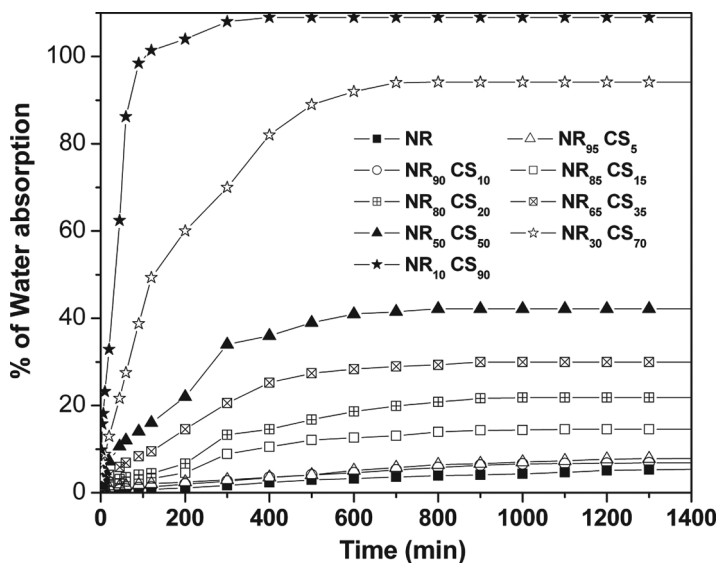
Figure 3. Water absorption behavior of different NR/CS blends.

of vulcanized samples in boiling water was also studied. The percentage of water absorption in the vulcanized sample is negligible. Therefore, it can be useful for the production of steam lines.
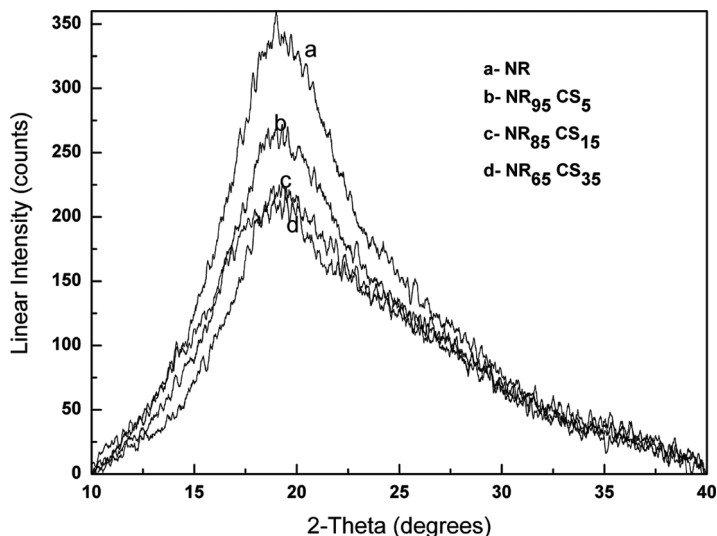

Figure 4. X-ray diffraction patterns of natural rubber and its blends with chitosan.

X-Ray Diffraction Studies

Figure 4 shows the X-ray diffraction patterns of natural rubber and its blends. The X-ray patterns of all the samples exhibited rubber's characteristic peaks at around 19°. The intensity of the peak decreases with the addition of chitosan in NR. The crystallinity of natural rubber decreases with the addition of chitosan.

FT-IR Spectral Analysis

Figure 5 gives the FT-IR spectra of NR, CS, and blends. All the characteristic peaks of NR and CS are seen in the blend systems. There is no peak shifting/additional peak in the blends except in NR_{95} CS_5. The additional peak in NR_{95} CS_5 at 2370 cm^{-1} may be due to the stretching
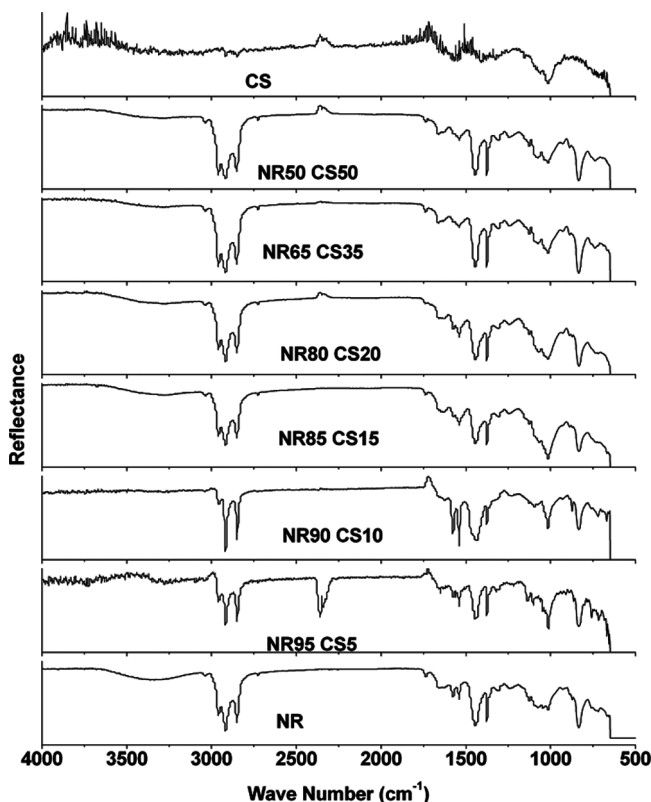

Figure 5.   FT-IR spectra of NR, CS, and its different blend compositions.

of NH_2 because this peak is a characteristic of N−H stretching. N−H bond stretching may be due to better interfacial adhesion between NR and CS in NR_{95} CS_5 blend. Improvement in interfacial adhesion in NR_{95} CS_5 is also confirmed from the fraction of bound rubber analysis, thermal stability, and water absorption.

CONCLUSIONS

The characterization of NR/CS blend has been studied using thermo-gravimetry, FT-IR, SEM, and X-ray analysis. Blending improved the thermal stability of chitosan. The amount of bound rubber in the blend $NR_{95}CS_5$ shows the maximum value. This could be an indication of comparatively stronger interfacial interaction between the independent components. This is also confirmed by FT-IR spectrum. The water absorbability of blends increases with the percentage of chitosan. This can be minimized by vulcanizing the blends. The water absorption in boiling water shows that the percentage of water uptake in the vulcanized samples is negligible. X-ray diffraction study shows that the crystallinity of natural rubber decreases with increase in the amount of chitosan.

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