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THERMAL BEHAVIOR OF CHITOSAN/NATURAL RUBBER LATEX BLENDS

TG and DSC analysis

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The thermal behavior of chitosan (CS)/natural rubber latex (NRL) blends has been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Decomposition behavior of CS changes with the addition of NRL. The effect of blend composition on the amount of residue remaining at various temperatures has been studied. Activation energies of degradation have been calculated using Horowitz–Metzger equation. From the activation energy values, it is found that among the series of the blend compositions, $CS_{15}NRL_{85}$ exhibits better thermal stability. DSC studies reveals that the CS/NRL blends are thermodynamically incompatible. This is evident from the presence of two glass transitions, corresponding to CS and NRL phases in the blend.

Keywords: *chitosan, natural rubber, polymer blends, thermoplastic elastomer*

Introduction

Thermal properties are relevant to the potential use of polymeric materials in many consumer oriented applications. Fabrication of a variety of articles and their end uses need a detailed understanding of the thermal degradation of polymers. Blending of polymers has been reported to have much influence on the thermal stability of individual polymers. The thermal stability of the blends depends strongly on the compatibility of the polymers [1, 2]. The assessment of thermal stability is one of the most important applications of TG in the study of polymers. Thermogravimetric curves provide information about the decomposition mechanisms for various materials [3]. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) will provide information about the nature and extent of degradation of the material. A comparison of the thermal properties of miscible and immiscible blends was reported by Lizymol and Thomas [1]. Compatibility of the polymer blends can also be predicted using differential scanning calorimetric method. This will measure the glass transition temperature (T_g) and melting temperature of the polymeric material. Miscible blends will show single, sharp transition peak (T_g) intermediate between those of the blend components. Separate transitions are obtained for immiscible blends.

One type of fast-growing thermoplastic elastomer which is easier to process is made by blending rubber and plastic in definite proportions. Characteristically, this is a family of material consisting of a rubber soft segment which gives rise to elastomeric properties and a crystalline hard segment which acts as cross-link and fillers [4]. In the present paper we report the thermal behavior of a new blend system of chitosan and natural rubber latex using thermogravimetry and differential scanning calorimetric analysis. Chitosan is a partially acetylated glucosamine obtained by deacetylation of chitin, one of the most abundant natural polymers [5–7]. As a polysaccharide of natural origin, chitosan has many useful features such as nontoxicity, biocompatibility, biodegradability, good mechanical strength and antimicrobial properties [8, 9]. Chitosan can be used in different areas from health care to agriculture and dyes for fabrics, and it is soluble in most dilute acids [10]. Chitosan has a high modulus of elasticity, owing to the high glass transition temperature and crystallinity [11, 12]. Natural rubber (NR), poly(*cis*-1,4-isoprene), occurs in several plant species, but its most important source is the ‘*Hevea brasiliensis’* tree, which accounts for over 99% of the world’s natural rubber production. Natural rubber is extracted as a latex or ‘milk’, viz. an aqueous emulsion or dispersion of the natural polymer (~96 mass% of solids) and other substances, such as proteins (~1%), lipids (~3%) and traces of potassium, magnesium and copper [13]. Recent work on the thermal analysis of chitosan includes the DSC analysis of PVP/chitosan blends by Karvas *et al.* [14] and kinetic study on the thermal behavior of chitosan by Lopez *et al.* [15]. We have already reported the effect of chitosan on the mechanical properties of natural rubber [16].

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Experimental

Materials

Purified chitin was purchased from HiMedia Laboratories Pvt. Ltd. Mumbai, India and its viscosity average molecular mass was 400000 g mol^{-1}. 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 is found to be 40%.

Preparation of chitosan and chitosan solution

Chitin was dispersed in 50 mass/mass% NaOH solution and heated at 100°C for 2 h. Then the mixture was cooled to room temperature, filtered, and washed with water several times until the filtrate was neutral. The chitosan sample obtained was dried in 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 mixture. The mixture was then casted on a Petri dish at 45°C for 48 h. The films were prepared by compressing these casted samples at 140°C and a pressure of 10 ton for 10 min in a hydraulic press. The resulting film thickness was 2–2.5 mm. The studies have been limited to $CS_{70}NR_{30}$, on exceeding the volume fraction of chitosan, the films were found to be brittle and unstable.

Methods

Thermogravimetric analysis (TG)

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

Differential scanning calorimetry (DSC)

The thermal behavior of the blends was studied using a Mettler Toledo DSC 822 thermal analyzer. The samples were inserted into the apparatus and the DSC scan was made from –100 to 300°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere. The mass of each sample was about 5 mg. The glass transition temperature of each sample was taken at the initial change in the slope of the heat capacity of the DSC curve.

Results and discussion

The TG/DTG curves of different compositions of CS/NRL blends are shown in Fig. 1. Chitosan exhibits poor thermal stability compared to natural rubber. According to Bolland and Orr in the temperature range 200–270°C, in rubber both scission and cross linking occur though no loss of unsaturation of the bulk rubber occurs [17]. Madorsky and coworkers reported that NR undergoes thermal degradation in the temperature range of 287–400°C to give 39% isoprene, 13.2% dipentene and small amounts of *p*-menthene [17]. In the temperature range 450–800°C, dipentene is the major degradation product and isoprene is the major degradation product in the temperature ranges 675–800°C. In our case at 300°C, 6.5% mass loss and at 700°C, 94.5% mass loss is observed. In the DTG curve the major peak is at 379°C.

Pawlak and Mucha [18] 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 a new cross linked material formed by thermal cross linking reactions occurring in the first stage of degradation process. TG of chitosan shows mass loss in two stages (Fig. 1). The first stage ranges between 35 and 215°C and shows about 24.6% loss of mass. This may correspond to the loss of bound water and acetic acid from the solvent. The second stage of mass loss starts at 216°C and continues up to 400°C during which there was 61.4% mass loss due to the degradation of chitosan. In the beginning, mass loss is faster but after 400°C it is noticed to be slow, may be due to cross-linking of chitosan in the earlier stage.

At 300°C, about 49% of chitosan undergoes degradation where as 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 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. Second peak near 375°C is due to NR degradation. On increasing the natural rubber content, the decomposition of the blend decreases.

From the Table 1, it is observed that up to 350°C, the mass 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 mass loss is mainly

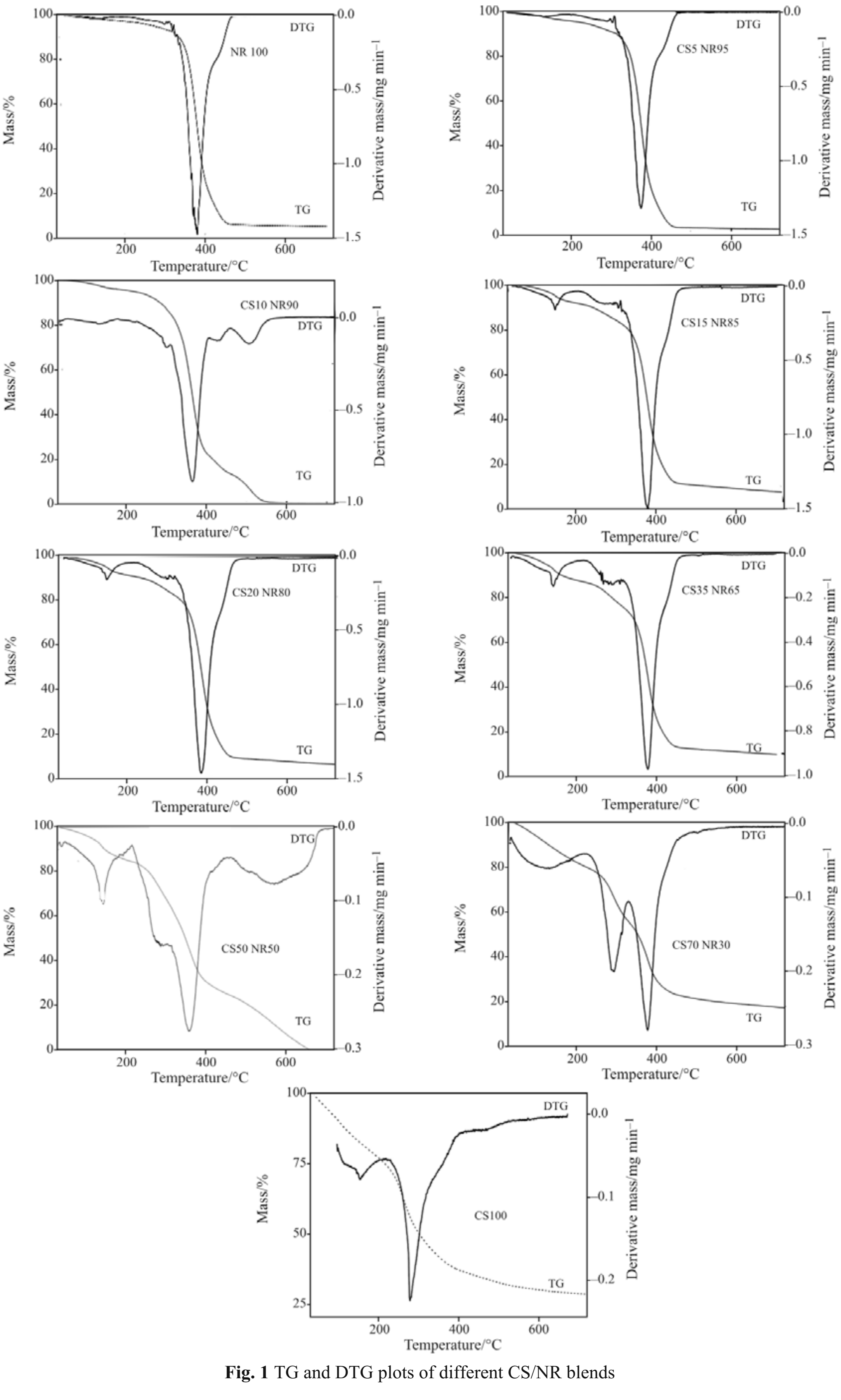

Fig. 1 TG and DTG plots of different CS/NR blends

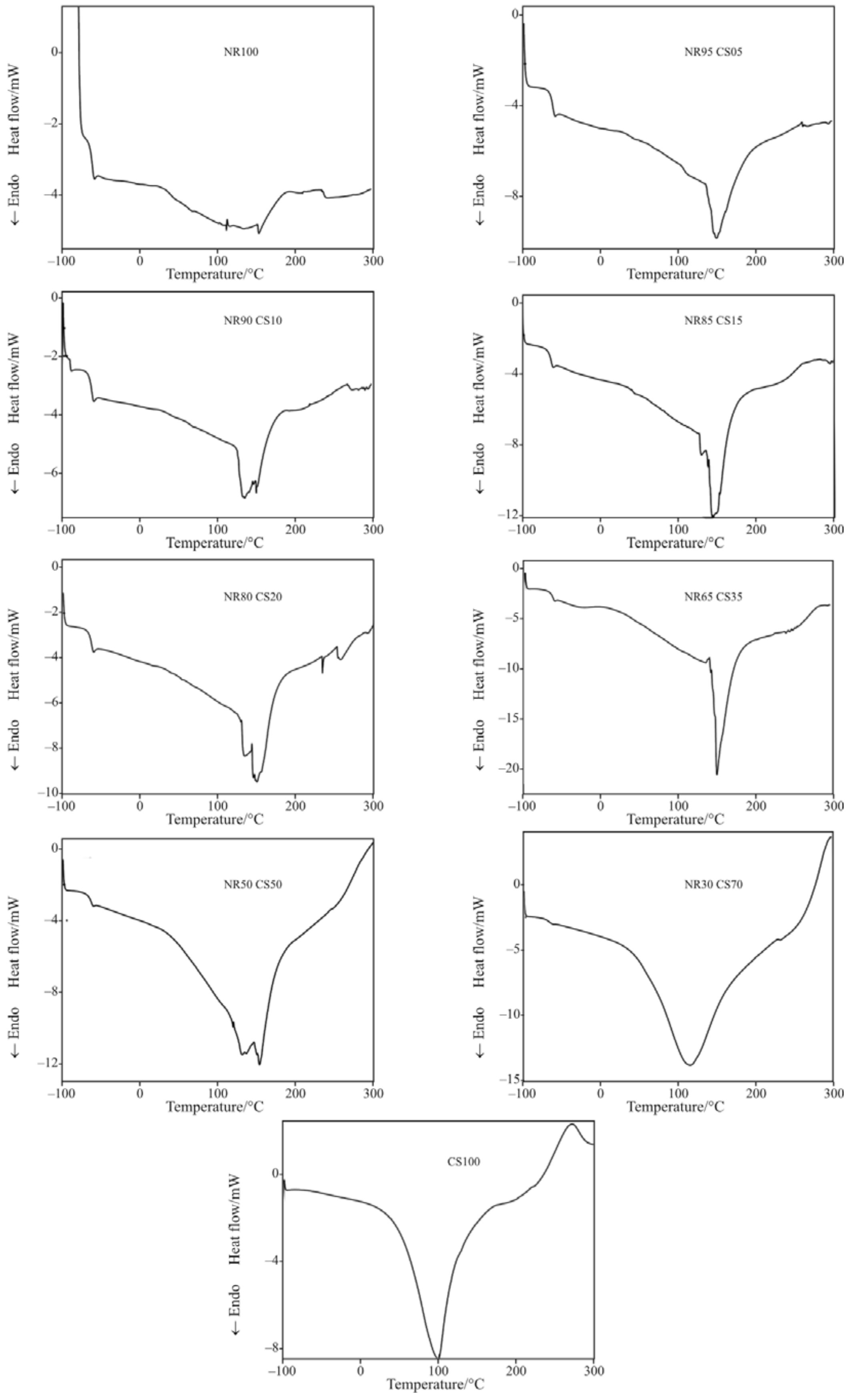

Fig. 2 DSC curves of different CS/NR blends

due to the degradation of rubber. In the blend system, from 200–300°C as the percentage of chitosan increases, the increase in the mass loss may be due to the destruction of amino groups and the rate is found to be slow. Above 350°C the mass loss is mainly due to the degradation of the newly crosslinked chitosan and natural rubber. Since degradation of CS/NR blend (lower compositions) is negligible till 150°C, the blend can be moulded by compression. Also we have observed that the blends have better mechanical properties compared to individual polymers (under publication). Thus rubber can be blended with chitosan and can be used for commercial applications.

Activation energies for degradation have been calculated for the initial degradation stage using the Horowitz-Metzger equation [2].

The Horowitz–Metzger equation is,

$$\ln[-\ln(1-\alpha)]=-\frac{E_a\theta}{RT^2}+C \text{ (For } n=1)$$

where α represents mass fraction degraded in time t, $\tau=(T-T_s)$ where T_s is the DTG peak temperature, R is the gas constant and E_a is the apparent activation energy of decomposition. A straight line graph will be obtained if we plot the left hand side (LHS) of this equation *vs.* $1/T$. The slope and intercept of this graph are used for calculating the kinetic parameters by the least square method.

A can be calculated using the equation,

$$\frac{E}{RT_s^2}=\frac{A}{q\exp\left(\frac{\Delta S}{R}\right)}$$

The entropy of activation can then be calculated using the equation,

$$A=\frac{kT_s}{h}\exp\left(\frac{\Delta S}{R}\right)$$

where k is the Boltzmann constant and h is the Planck's constant.

From Table 1, it is observed that the activation energies of blends increase in both stages as the natural rubber content increases and it is maximum for the blend $CS_{15}NR_{85}$. This shows that the increase in natural rubber phase makes the system more resistant to thermal degradation and the $CS_{15}NR_{85}$ blend is most stable among the blend ratios. From Table 1, it is clear that the entropy of activation has negative values. The magnitude of entropy is lower in first stage in all the cases.

The DSC method is one of the convenient techniques to measure the T_g. A baseline step in a DSC curve appears due to the different heat capacity below and above the T_g of a polymer [19]. Generally, the glass transition temperature is read at the initial change in the slope of the heat capacity of the DSC curve, i.e. the temperature at the onset of a baseline step in the DSC curve. The thermal behavior of chitosan/natural rubber latex blends with different compositions and the pure blend components were analyzed by DSC. Figure 2 shows the DSC traces of homopolymers and the blends of these two components. The T_g of pure natural rubber latex is found to be –65°C. The DSC traces of chitosan film gives an endothermic peak at about 100°C, which attributes to absorbed moisture and another step around 222°C is due to the glass transition though the baseline step is somewhat small. Sakurai *et al.* [19] reported the T_g of chitosan to be around 203°C using the DSC analysis. T_g values of various blends are given in the Table 2. The blends show two T_gs, which reveals that the blends are incompatible and phase separated.

Table 1 Mass loss, activation energy and entropy of various CS/NR blends

Sample code	Mass loss/%								Activation energy, E_a/kJ mol^{-1}		Entropy change, ΔS/J °C^{-1} mol^{-1}	
	100°C	200°C	300°C	350°C	400°C	500°C	600°C	700°C	I stage	II stage	I stage	II stage
CS_0NR_{100}	0.7	2.9	6.5	15.2	74.1	93.2	94.2	94.5	44.3	—	–201	—
CS_5NR_{95}	1.0	3.9	8.6	18.4	77.2	97.3	97.7	98.0	43.1	—	–202	—
$CS_{10}NR_{90}$	1.4	4.8	12.9	34.4	77.0	91.6	99.4	99.5	52.5	12.3	–185	–268
$CS_{15}NR_{85}$	1.4	8.2	15.7	25.8	72.7	89.6	91.1	92.4	55.9	27.0	–123	–231.6
$CS_{20}NR_{80}$	1.8	8.5	15.8	25.6	72.3	89.9	91.1	92.2	42.0	26.7	–158	–231.9
$CS_{35}NR_{65}$	3.0	12.4	21.9	32.0	73.7	88.0	89.2	90.4	44.2	24.1	–151	–237
$CS_{50}NR_{50}$	3.4	14.3	30.9	48.9	68.1	78.0	91.5	99.9	30.8	22.8	–186	–238
$CS_{70}NR_{30}$	6.9	18.5	37.0	50.2	71.6	79.7	81.8	83.5	35.3	7.3	–204	–272
$CS_{100}NR_0$	9.5	22.6	49.0	57.1	61.4	65.8	68.2	69.4	28.5	6.0	–183	–269

Table 2 Glass transition temperature of different CS/NR blends

Sample code	T_g/°C
CS_0NR_{100}	–65
CS_5NR_{95}	–65, 231
$CS_{10}NR_{90}$	–65, 217
$CS_{15}NR_{85}$	–65, 224
$CS_{20}NR_{80}$	–65, 232
$CS_{35}NR_{65}$	–67, 222
$CS_{50}NR_{50}$	–66, 239
$CS_{70}NR_{30}$	–71, 228
$CS_{100}NR_0$	222

Conclusions

Thermogravimetric analysis and differential scanning calorimetric analysis were carried out to study the thermal behavior of CS/NRL blends. The effect of blend composition on the thermal behavior of blends was analyzed. It was found that blending has improved the thermal properties of chitosan. The mass loss for the blends was found to be lower than that of pure chitosan. It is found that the blend $CS_{15}NR_{85}$, shows good thermal stability among the other blend compositions studied. DSC studies reveal two glass transitions for the blends and hence CS/NRL blends are thermodynamically incompatible.

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