J Mater Sci (2009) 44:4087–4094
DOI 10.1007/s10853-009-3589-2

# Thermal stability, morphology, and X-ray diffraction studies of dynamically vulcanized natural rubber/chitosan blends

**Jobish Johns · Vijayalakshmi Rao**

Received: 3 March 2009 / Accepted: 12 May 2009 / Published online: 2 June 2009

**Abstract** The thermal degradation behavior of cross-linked Natural Rubber/Chitosan (NR/CS) blends was studied by thermogravimetric analysis (TGA). Dicumyl peroxide (DCP) was selected as a cross-linking agent. Peroxide-cured NR/CS blends exhibit very good overall thermal properties. The activation energy of degradation was analyzed using the Horowitz–Metzger equation. Vulcanization of rubber phase in the blend increased the activation energy. From the activation energy values, it is found that among the series of the blend compositions, $NR_{85}CS_{15}$ blend vulcanized with 3 pphr DCP exhibits better thermal stability. Better adhesion between the two phases with the incorporation of DCP is achieved which results in an enhancement in the thermal stability. The DSC curve shows that, the $T_g$ of chitosan in the blend increased to 242 °C by dynamic vulcanization. The morphology of the vulcanized blends was studied by scanning electron microscopy. More uniform distribution was exhibited by the vulcanization of NR phase in the blend. X-ray diffraction (XRD) study shows an enhancement in the crystallinity by vulcanization.

## Introduction

The aim of polymer blending is to develop products with unique properties that can not be attained from individual constituents. The performance of a polymer blend is determined by various factors, including the nature of the individual components, type of vulcanizing agent, processing parameters, and to a certain extent, the application for which it is intended [1–3]. Natural rubber has long been considered as an excellent general purpose polymer with wide-ranging industrial applications. Also, its unique combination of properties has made it an elastomer of choice for many of the sophisticated engineering applications. However, one of the limitations of natural rubber is its low value of high temperature stability. Quite often, the additives such as plasticizers, fillers, curatives, flame-retardants, etc., used for compounding, affect the thermal stability of the base polymer, good information about which may be obtained from thermal analysis methods such as TGA, DTA, and DSC [4, 5]. 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 [6]. We have already reported the thermal, mechanical, and swelling behaviors of Chitosan/Natural Rubber (CS/NR) Latex blend system [7–9]. The chemical modifications of NR were carried out to improve the interfacial adhesion between the two components. If the elastomeric phase is sufficiently vulcanized, then the physical and chemical properties of the blend are generally improved [10, 11]. The presence of dicumyl peroxide (DCP) as the cross-linking agent for NR is expected to enhance the thermal stability of NR/CS blend. The dynamic vulcanization process was first claimed by Gessler [12] in 1962 and then further developed by Fischer [13], Coran and colleagues [14, 15]. Cross-linking rubber with peroxides has been well-known for more than 50 years. The general advantages of peroxides as cross-linking agents are: (1) their ability to cross-link unsaturated

J. Johns · V. Rao (✉)
Department of Materials Science, Mangalore University,
Mangalagangotri 574199, India
e-mail: vijrao@yahoo.com; vijraobrns@rediffmail.com

as well as saturated elastomers; (2) good high temperature resistance; (3) good elastic behavior, particularly at elevated temperature; (4) no moisture uptake; and (5) no staining or discoloration of the finished products [16]. 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 [17]. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) will provide information about the nature and extent of degradation of the material. The differential thermal analysis (DSC) 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. This article reports the result of a study carried out on the thermal stability and decomposition characteristics of vulcanized NR/CS blends using thermal analysis methods such as TGA, DTA, and DSC.

## Experimental

### Materials

Purified chitin was purchased from HiMedia Laboratories Pvt. Ltd. Mumbai, India and its viscosity average molecular weight was 400,000 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 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%. DCP was also purchased from HiMedia Laboratories Pvt. Ltd. Mumbai, India. The molecular structure of DCP is given in Fig. 1.

### Preparation and processing

Chitin was dispersed in 50% (w/w) 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. The blends were prepared by mixing chitosan and natural rubber latex to get a homogeneous solution. Chitosan cross-linked rubber blend was prepared by adding DCP to the blend solution. Then the mixture was casted on a Petri dish at 45 °C. Specimens for testing were compression molded using an electrically heated hydraulic press machine at 140 °C at a pressure of 10 ton for 10 min. The film thickness was 2–2.5 mm.

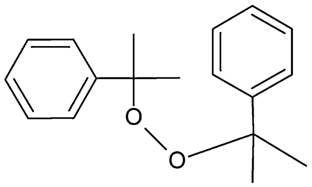

**Fig. 1** Structure of dicumyl peroxide

### Methods

### *Thermogravimetric analysis*

A Perkin Elmer, Diamond TG/DTG analyzer was used for the TGA of the blended samples. Small amounts (1–10 mg) of samples were taken for the analysis and the samples were heated from 40 to 720 °C at a rate of 10 °C/min 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 °C to 300 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The weight 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 thermogram.

### *Morphology*

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

### *X-ray diffraction studies*

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

## Result and discussion

### Thermogravimetric analysis

The TGA and DTA thermograms of vulcanized and unvulcanized NR/CS blends are shown in Figs. 2 and 3. NR is thermally more stable compared to chitosan. The addition of NR into chitosan improves the thermal stability. On dynamic vulcanization with DCP, the thermal stability of blends increases due to formation of crosslinks in the NR phase. 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 [18]. 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 [18]. 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. Pawlak and Mucha [17] have confirmed the cross linking of chitosan macromolecules following the destruction of amino groups. According to Coran [19] and Dluzneski [20], the formation of cross links by DCP in unsaturated polymers such as rubber can be explained by the free radical addition reaction between the DCP and that of the unsaturated carbon present in NR. The DTA peak, near to 150 °C disappeared for blends having above 15% chitosan by vulcanization. This suggests that even though the NR/CS blends are immiscible, the thermal stability can be improved by the addition of DCP. For $NR_{90}CS_{10}$, $NR_{85}CS_{15}$, $NR_{80}CS_{20}$, and $NR_{65}CS_{35}$ blends, the incorporation of DCP resulted in the improvement of thermal stability of the blends. The data derived from the figures are depicted in Table 1. Vulcanized natural rubber shows an increase in weight loss with temperature compared to unvulcanized rubber. It is seen from the table that the increase in weight fraction of chitosan into natural rubber decreases the weight loss by vulcanization, increasing the thermal stability of the blends. The thermal stability of $NR_{85}CS_{15}$ blend shows a maximum improvement by the vulcanization of natural rubber phase compared to the other blend series. The thermograms of blends especially $NR_{90}CS_{10}$, $NR_{85}CS_{15}$, $NR_{80}CS_{20}$, and $NR_{65}CS_{35}$ revealed that the addition of DCP has profound positive impact on the thermal stability. Above the weight fraction of 35% chitosan, the stability decreased. The enhancement in thermal stability is mainly due to the improvement in the interfacial adhesion between the components in the blend. But upon vulcanization, NR crosslinks with DCP forms a separate phase and extent of interaction between NR and CS decreases. This may be the reason why a decrease in thermal stability is observed for $NR_{50}CS_{50}$. At 300 °C the weight loss reduced to 27%, 43%, and 30% for the blends $NR_{90}CS_{10}$, $NR_{85}CS_{15}$, and $NR_{80}CS_{20}$, respectively, by dynamic vulcanization.

Activation energies for degradation have been calculated for the initial degradation stage using the Horowitz–Metzger equation [21].

The Horowitz–Metzger equation is,

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

where $\alpha$ represents weight fraction degraded in time $t$, $\theta = (T-T_s)$, $T_s$ 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 versus $\theta$. The slope and intercept of this graph are used for calculating the kinetic parameters by the least square method.

The pre-exponential factor $A$ can be calculated using the equation,

$$\frac{E}{RT_s^2} = \frac{A}{q\exp\frac{E_a}{RT_s}}$$

where $q$ is the linear heating rate.The entropy of activation can then be calculated using the equation,

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

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

Effect of vulcanization on the activation energy for the blends is shown in Table 1. It is important to note that an increase in activation energy indicates that more energy is required for the degradation, which in turn implies an improvement in thermal stability of the blends. The calculated values of pre-exponential factor $A$ is given in the Table 1. Maximum activation energy and most negative entropy value are observed for the vulcanized $NR_{85}CS_{15}$ blend. This can be attributed to the increased thermal stability of the blend arising from the improved interfacial adhesion leading to the formation of very strong interface upon vulcanization. Hence it becomes necessary that more energy should be given for decomposition of the blend.

### Differential scanning calorimetry

The DSC method is one of the convenient techniques to measure the $T_g$. A base-line step in a DSC curve appears due to different heat capacity below and above the $T_g$ of a polymer [22]. 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 base line step in the DSC curve. DSC results of the peroxide vulcanized blends compared with unvulcanized blends are shown in Fig. 4. All vulcanized blends have almost the

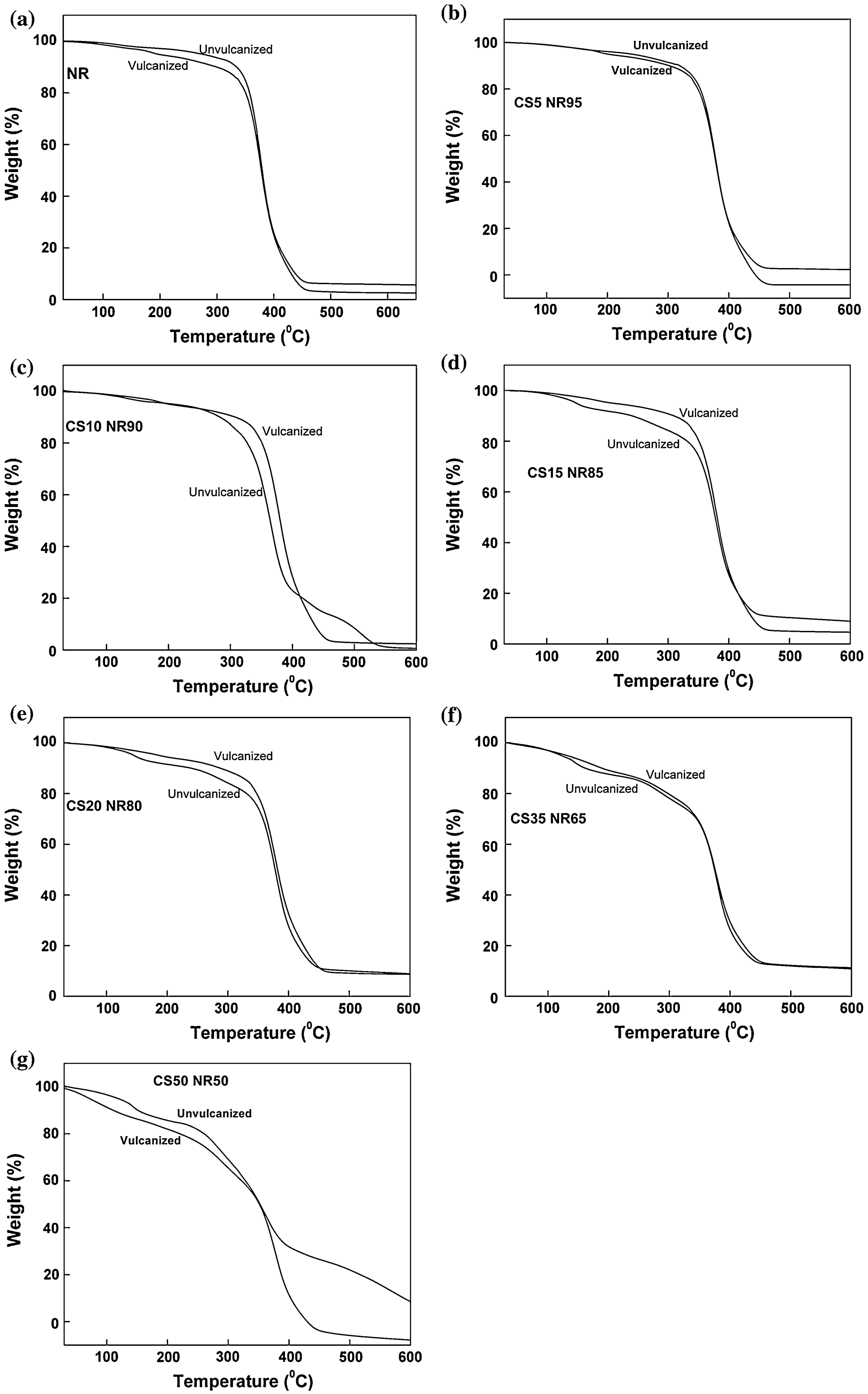

**Fig. 2** The TGA thermograms of vulcanized and unvulcanized NR/CS blends

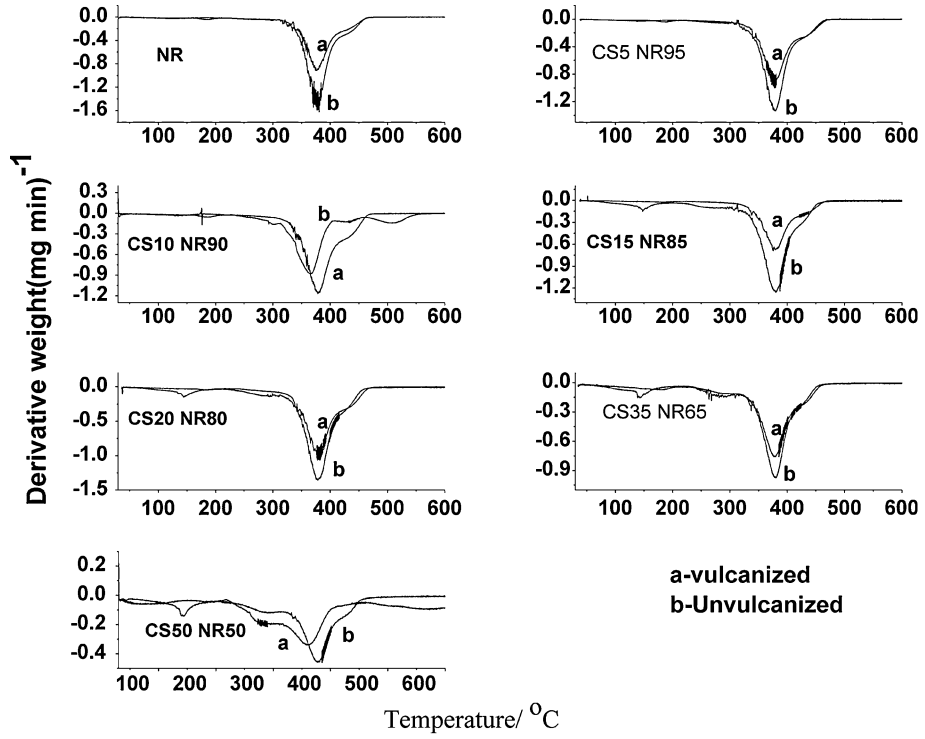

**Fig. 3** The DTA thermograms of vulcanized and unvulcanized NR/CS blends

**Table 1** Weight loss, activation energy, pre-exponential factor, and entropy change of various vulcanized and unvulcanized NR/CS blends

| Sample | % of DCP | Percentage weight loss at (°C) | | | | | | | | Activation energy (kJ/mol) | $A$ (s$^{-1}$) | Entropy of activation energy (J/degree/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 50 | 100 | 200 | 300 | 350 | 400 | 500 | 600 | | | |
| $CS_0NR_{100}$ | 0 | 0.07 | 0.74 | 2.9 | 6.47 | 15.2 | 74.1 | 93.2 | 94.2 | 44.31 | $4.7 \times 10^5$ | −201 |
| | 3 | 0.33 | 1.41 | 5.2 | 10.1 | 19.7 | 75.1 | 97 | 97.4 | 38.5 | $7.3 \times 10^4$ | −138 |
| $CS_5NR_{95}$ | 0 | 0.17 | 0.98 | 3.93 | 8.59 | 18.4 | 77.2 | 97.3 | 97.7 | 43.08 | $3.2 \times 10^5$ | −202 |
| | 3 | 0.21 | 1.07 | 5 | 9.9 | 20.5 | 77.7 | – | – | 38.7 | $7.4 \times 10^4$ | −140 |
| $CS_{10}NR_{90}$ | 0 | 0.28 | 1.4 | 4.78 | 12.85 | 34.4 | 77 | 91.6 | 99.4 | 52.51 | $1.5 \times 10^7$ | −185 |
| | 3 | 0.35 | 1.2 | 4.98 | 9.4 | 19.6 | 71.6 | 97 | 97.6 | 66.83 | $1.01 \times 10^9$ | −216 |
| $CS_{15}NR_{85}$ | 0 | 0.1 | 1.44 | 8.15 | 15.7 | 25.8 | 72.7 | 89.6 | 91.1 | 55.89 | $2.2 \times 10^7$ | −123 |
| | 3 | 0.22 | 0.96 | 4.7 | 9.2 | 19.6 | 71.1 | 94.9 | 95.3 | 70.58 | $4.4 \times 10^9$ | −337 |
| $CS_{20}NR_{80}$ | 0 | 0.33 | 1.76 | 8.47 | 15.83 | 25.63 | 72.3 | 89.9 | 91.1 | 42.02 | $2.2 \times 10^5$ | −158 |
| | 3 | 0.34 | 1.45 | 5.6 | 11.1 | 21.1 | 67.4 | 90.9 | 91 | 49.24 | $2.7 \times 10^6$ | −240 |
| $CS_{35}NR_{65}$ | 0 | 0.47 | 3.03 | 12.37 | 21.87 | 31.95 | 73.68 | 88 | 89.2 | 44.24 | $4.7 \times 10^5$ | −151 |
| | 3 | 0.7 | 3 | 10.9 | 20.3 | 31.5 | 70.7 | 87.8 | 88.7 | 45.92 | $8.7 \times 10^5$ | −173 |
| $CS_{50}NR_{50}$ | 0 | 0.65 | 3.39 | 14.31 | 30.9 | 48.88 | 68.14 | 78 | 91.5 | 30.83 | $8.3 \times 10^3$ | −186 |
| | 3 | 2.32 | 8.7 | 18 | 34.6 | 49.4 | 88.7 | – | – | 23 | $2.9 \times 10^2$ | −112 |
| $CS_{100}$ $NR_0$ | 0 | 2.1 | 9.5 | 22.6 | 49 | 57.1 | 61.4 | 65.8 | 68.2 | 28.5 | $4.06 \times 10^5$ | −183 |

same pattern of the heating thermogram and shows an exothermic peak around 190 °C in the DSC curve. The blends show two glass transition temperatures, which reveals that the blends are incompatible and phase separated. The $T_g$ of NR is found to be −65 °C, and in vulcanized blends also it appears at the same temperature. For pure blend, an endothermic peak appears around 150 °C and $T_g$ is found to be 224 °C corresponding to chitosan. But in case of vulcanized blends, this peak vanishes and an exothermic peak is observed around 190 °C. This may be due to the degradation or melting of DCP in the blend. The $T_g$ of chitosan in the blend increased to 242 °C for the vulcanized samples. This is an evidence for the enhanced thermal stability during vulcanization. The C–C bonds that are formed between the molecular chains during cross linking increases the thermal stability of the blend. The

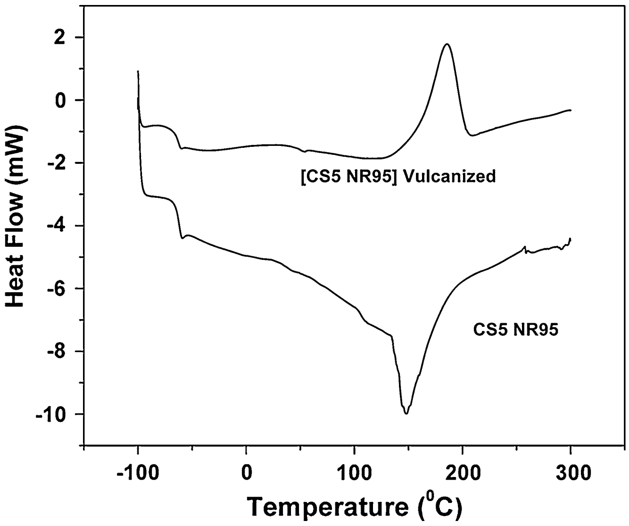

**Fig. 4** DSC curves of the peroxide vulcanized and unvulcanized blends

change of inclination of the base line for chitosan was small, because chitosan is a partially crystalline polymer and also due to the small specific volume of rigid chain [22].

## SEM analysis

Figure 5 shows the scanning electron microscopy (SEM) microphotographs of CS/NR blend samples in the absence and in the presence of DCP. The unvulcanized blend (Fig. 5a) shows a large number of voids and discontinuity on the surface of the samples. This is an indication of uncompatibility or heterogeneous phase structure of the blend. Figure 5b shows the NR/CS blends that are dynamically vulcanized with peroxide, and reveal the finer morphology. The presence of cross links in the rubber phase limits the flow and mobility of rubber particles. More uniform phase distribution was exhibited by the vulcanization of rubber phase in the blend. This means that cross links enhances the interfacial interaction between NR and CS. According to Sariatpanhi et al. [23], DCP, a well-known cross-linking agent can also be used to compatibilize blends containing cross-linkable constituents, through dynamic vulcanization. Compatibilization by covalent cross linking reaction has been reported [24–26]. There are some established methods widely used for compatibilizing immiscible polymer systems. These includes dynamic vulcanization, addition of third polymer partially miscible with all blend systems, addition of reactive fillers as compatibilizers, addition of low molecular weight compounds, and solid state shear pre-vulcanization. Dynamic vulcanization is a cost effective technique to achieve better properties which involves vulcanizing the elastomer during blending with a non-vulcanizing thermoplastic polymer.

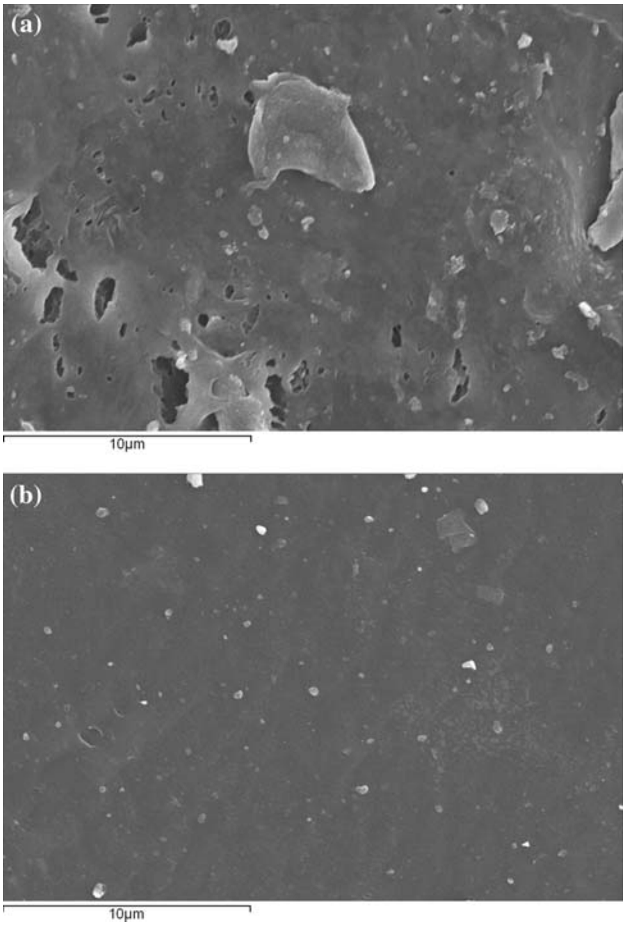

**Fig. 5** SEM microphotographs of **a** unvulcanized $NR_{85}CS_{15}$ blend and **b** vulcanized $NR_{85}CS_{15}$ blend

Improvements in properties include reduced permanent set, improved ultimate mechanical properties fatigue resistance, and high temperature utility, greater fluid resistance, melt strength and phase stability, and more reliable thermoplastic fabricability. The introduction of cross links into one of the phases increases the viscosity of this phase leading to a change in the morphology of the blend [27]. There is an effective interaction between NR and CS leading to better adhesion and thermal stability. The SEM analysis is in agreement with the thermal analysis results and supports the observed changes in the NR/CS blend properties by dynamic vulcanization. The FTIR analysis (Fig. 6) shows a decrease in the intensity of peaks at 1540 and 1576 $cm^{-1}$ corresponding to double bond by the vulcanization of NR phase in the blend.

## XRD analysis

Figure 7 depicts the XRD pattern of NR and blends of NR/CS vulcanized with 3 pphr DCP. The XRD patterns of all the samples exhibited rubber's characteristic peaks at around

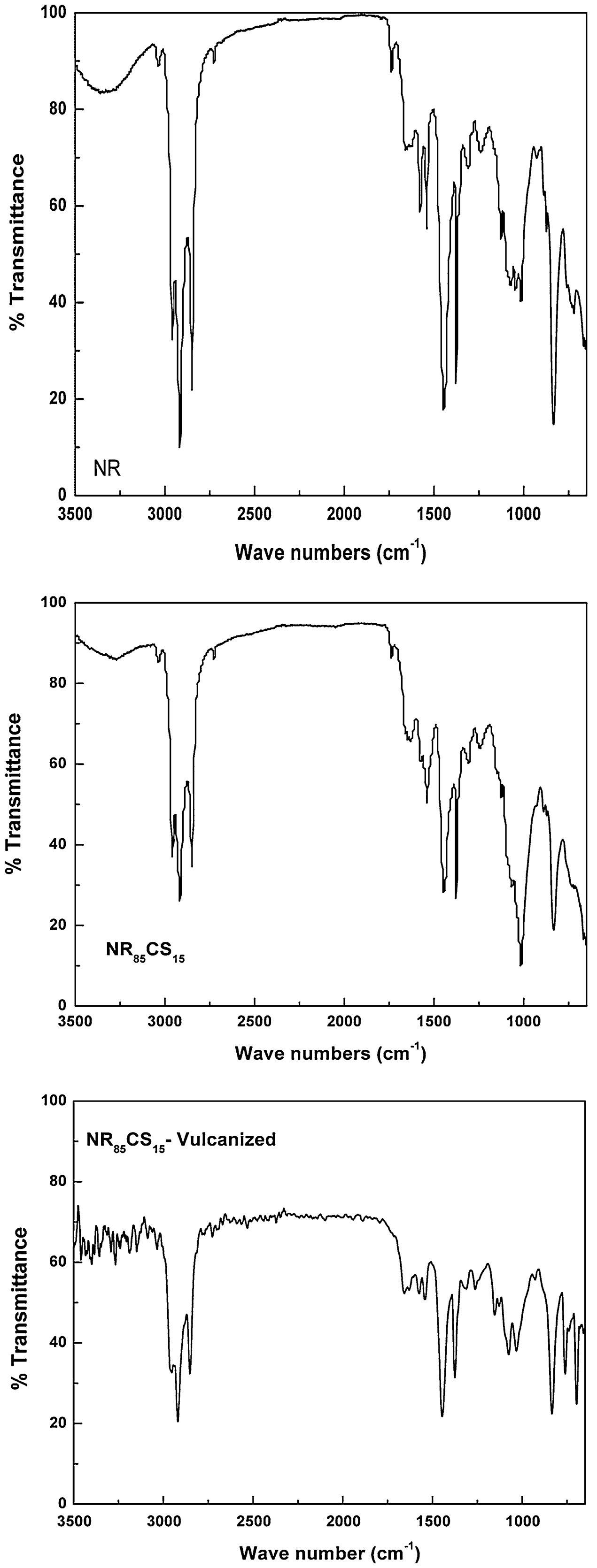

**Fig. 6** FTIR spectra of NR, NR$_{85}$CS$_{15}$, and vulcanized NR$_{85}$CS$_{15}$ blends

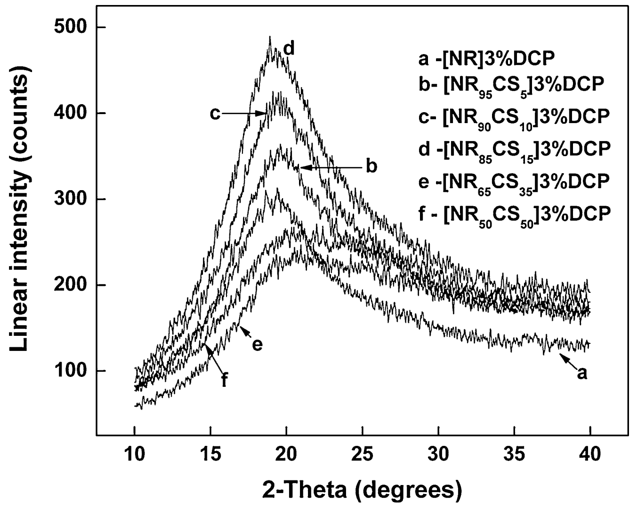

**Fig. 7** X-ray diffraction pattern of NR and blends of NR/CS vulcanized with 3 pphr DCP

19°. The intensity of the peak increases with the addition of DCP in the blend. It shows a maximum intensity for the blend NR$_{85}$CS$_{15}$ vulcanized with 3 pphr DCP. Above this volume fraction, the intensity decreased, may be due to a decrease in the cross-linking efficiency of the blend.

## Conclusions

The thermal stability and degradation behavior of cross-linked NR/CS blends were studied using TGA. NR/CS blend vulcanized with DCP exhibits enhanced thermal stability. Maximum activation energy is observed for the vulcanized NR$_{85}$CS$_{15}$ blend. Thermal decomposition temperature increases with the addition of DCP in the blend. The enhancement in thermal stability of blends is explained in terms of the physical compatibility of the two phases during blending even though the two phases are immiscible. The C–C bonds that are formed between the molecular chains during cross linking increases the thermal stability of the blend. The improvement in thermal stability is also confirmed from the DSC thermograms of cross-linked NR/CS blends by the positive deviation of $T_g$ value. The scanning electron macrographs show an increase in the uniformity by vulcanization. The XRD study shows an improvement in crystallinity by vulcanizing the blend. Finally it can be concluded that vulcanization of rubbery phase in the blend makes the system thermally stable.

## References

1. Favis BD, Chalifoux JP (1988) Polymer 29:1761
2. Rappaport M (1985) Plast Eng 41:33

3. Utracki LA (1982) Polym Eng Sci 22:1166
4. Budrugeac P, Segal E (1994) Polym Degrad Stab 46:203
5. Qu X, Wirsen A, Albertsson AC (2000) Polymer 41:4841
6. Jha A, Bhowmick AK (1997) Polymer 38:4337
7. Rao V, Johns J (2007) J Appl Polym Sci 107:2217
8. Johns J, Rao V (2008) Int J Polym Anal Charact 13:280
9. Rao V, Johns J (2008) J Therm Anal Calorim 92:801
10. Datta S, Naskar K, Jelenic J, Noordermeer JWM (2005) J Appl Polym Sci 98:1393
11. Basuli U, Chaki TK, Nasker K (2008) J Appl Polym Sci 108:1079
12. Gessler AM, Haslett WH (1962) US Patent 3037954, 5 June 1962
13. Fisher WK (1973) US Patent 3758643, 11 Sept 1973
14. Coran AY, Das B, Patel RP (1978) US Patent 3130535, 19 Dec 1978
15. Coran AY, Patel RP (1980) Rubber Chem Technol 53:141
16. Palys L, Callais P, Novits M, Moskal M (1998) Rubber Chem Technol 71:820
17. Pawlak A, Mucha M (2003) Thermochim Acta 396:153
18. Mathew AP, Pakrisamy S, Thomas S (2001) Polym Degrad Stab 72:423
19. Coran AY (1989) In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI (eds) Encyclopedia of polymer science and engineering, 2nd edn, vol 17. John Wiley & sons, Canada, p 666
20. Dluzneski PR (2001) Rubber Chem Technol 74:451
21. Rao V, Ashokan PV, Shridhar MH (2000) Polym Degrad Stab 70:11
22. Sakurai K, Maegawa T, Takahashi T (2000) Polymers 41:7051
23. Sariatpanahi H, Nazokdast H, Dabir B, Sadaghiani K, Hemmati M (2002) J Appl Polym Sci 86:3148
24. Santra RN, Samantaray BK, Bhowmick AK, Nando GB (1993) J Appl Polym Sci 49:1145
25. Manoj NR, De PP, De SK (1993) J Appl Polym Sci 49:133
26. Manoj NR, De PP, De SK (1993) Rubber Chem Technol 66:550
27. Usachev SV, Zakharov ND, Kuleznev VN, Vetoshikin AB (1980) Introd Polym Sci Technol 7:T48