### Chapter-4 Synthesis and characterization of bionanocomposites of natural rubber

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4.1 Introduction

The term “nanocomposite” refers to every type of composite material having fillers in the nanometer size range, at least in one dimension. For such nanocomposites the total interfacial phase becomes the critical parameter, rather than the volume fraction of the filler [1,2,3]. In recent years, hybrid organic–inorganic nanocomposites consisting of a polymeric matrix and a layered silicate has inspired scientists to a range of potential applications [4,5,6]. Due to their nanometer phase dimensions, nanocomposites exhibit significant improvements in physical and mechanical properties in relation to the polymer host [7,8,9]. The addition of just a low percentage of nanolayered inorganic fillers can increase the stiffness and strength with a minimal loss in ductility and impact resistance, decreases the permeability and swelling in solvents, improves the abrasion, flame resistance and thermal endurance, with an enhancement in electrical conductivity and optical properties [10]. Rubber nanocomposites with an exfoliated morphology have been successfully prepared by several methods, in situ polymerization, solution blending, latex compounding and direct melt intercalation. Consequently, the main advantage of nanocomposites is that the enhanced properties can be obtained with a smaller filler amount [11,12,13].

The inclusion of nanosized particles, in particular layered silicates (nanoclays) [14], enables the enhancement of properties in polymers with even small amounts of fillers, a feature not possessed by conventional composites. It was found that the inclusion of 10 phr (parts per hundred of rubber) of nanoclay greatly improves the mechanical properties of NR compounds over the conventionally filled systems [15]. Nevertheless, the mechanism of the reinforcement is still poorly understood. For example, why does it make NR-nanoclay materials stronger than conventionally filled rubbers without sacrificing properties like elongation at break, resilience, or compression set? According to the molecular models of conventional rubber compounds, for filled and crystallizable vulcanized rubbers, the main reason for the rise in the tensile strength at low deformations (below crystallization) has been considered as the formation of additional cross-links resulting from the filler-elastomer interactions due to the presence of fillers. Regarding the effect of nanoclay, we note that for the same weight/volume fraction of filler the nanosized platelets would lead to 4-6 orders of magnitude more particles per
volume than conventional fillers [16]. A large amount of surface area will be exposed to
the rubber molecules, leading to a huge interfacial volume around the nanofillers.
Another important issue, mentioned above, is the assumption of the strength increase in
NR-nanocomposite has often been attributed to rubber-filler interactions [16].
The concept of reinforced polymer materials with polysaccharide nanofillers has known
rapid advances and considerable interest in the last decade owing to their renewable
color, high mechanical properties, low density and diversity of the sources [17].
Starch nanocrystals have been used as filler in a synthetic polymeric matrix and proved to
be an interesting reinforcing agent [18,19,20,21,22]. In this context, waxy maize starch
nanocrystals have been considered as potential filler for natural rubber, which is one of
the most important elastomers widely used in industrial and technological areas [23].
However most of the composites have been prepared by solution blending.
Since the first publication related to the use of cellulose nanocrystals (CNs) as reinforcing
fillers in poly(styrene-co-butyl acrylate) (poly(Sco-BuA))-based nanocomposites by
Favier et al. [24] CNs have attracted a great deal of interest in the nanocomposites. This
is due to their appealing intrinsic properties such as nanoscale dimensions, high surface
area, unique morphology, low density and mechanical strength. Cellulose nanocrystals
have been incorporated into a wide range of polymer matrices, including polysiloxanes
[25], polysulfonates [26], poly(caprolactone) [27], styrenebutyl acrylate latex [28],
poly(oxyethylene) cellulose acetate butyrate [29], carboxymethyl cellulose [30],
poly(vinyl alcohol) [31], poly(vinyl acetate) [32], poly(ethylene-vinyl acetate) (EVA)
[33], polypropylene [34], poly-(vinyl chloride) [35], polyurethane [36], and water-borne
polyurethane [37]. Their incorporation into biopolymers, such as starch-based polymers
[38, 39,40], soy protein [41], chitosan [42], or regenerated cellulose [43], and
biopolymer-like poly(lactic acid) [44], poly(hydroxyoctanoate) [45], and
polyhydroxybutyrates [46] have also been reported. Recently, cellulose nanocrystals have
also been used to form nanocomposites with natural rubber [47].
We have mainly concentrated on studying the reinforcement ability of starch by
employing commercial mixing methods. Both native starch as well as starch
nanoparticles are found to induce excellent reinforcement in natural rubber [21,48].
Moreover, there is a growing interest in organically modified derivatives of
polysaccharides for different applications [49]. The hydrophobic derivatives (described in chapter 3) were used for the development of bionanocomposite of natural rubber by commercial mastication process. A comparison was made with mechanical and thermal properties of conventional composite counterparts.

**Starch-natural rubber bionanocomposites**

4.2 Experimental

4.2.1 Materials
Waxy corn starch was purchased from Sigma Aldrich, Mumbai.

4.2.2 Preparation of bionanocomposites
The bionanocomposites of NR were prepared on two roll mixing mill (as shown in scheme-1). Four sets of bionanocomposites were synthesized using each of waxy corn starch (Waxy starch), starch nanocrystals (StNPs), HMDI modified starch nanoparticles (StINPs) & acetylated starch nanoparticles (StAcNPs) as reinforcing fillers in NR by dry process on two roll mixing mill [50]. Upto 40 phr of fillers were added along with the along with other additives viz., sulphur (1.8 phr), tetramethylene thiuram disulphide (0.5 phr), mercaptobenzo thiazyl disulphide (1 phr), zinc oxide (5 phr), and stearic acid (1 phr). The mastication was continued until homogenous composites were obtained. This was followed by vulcanization at 150 °C and ~300 k Pa pressure for 7-8 min to obtain composite sheets with 1 mm thickness. Composites with carbon black (C-black/NR) were also prepared for comparison.
4.2.3 Characterization of bionanocomposites

**Hardness**
See section 2.2.3

**Mechanical properties**
See section 2.2.3

**Scanning Electron Microscopy (SEM)**
See section 2.2.3

**Thermal analysis**
**Thermal Gravimetric Analysis (TGA)**
See section 2.2.3
Differential Scanning Calorimetry (DSC)
See section 2.2.3

Water sorption studies:
Water sorption was determined by a method reported elsewhere [51].

Dynamic Mechanical Analysis
Dynamic mechanical tests were carried out using NETZSCH DMA 242. The specimen was a thin rectangular strip (15 x 5.1 x 0.959). The range of temperature in which the analysis was carried out between -80 ° to 0 °C at the frequencies of 1, 5 and 10 Hz in nitrogen atmosphere. The setup measured the complex tensile modulus $E^*$, i.e., the storage component $E'$ and the loss component $E''$. The ratio between the two components, $\tan \delta$ was also determined.

X-ray diffraction:
X-ray diffraction (XRD) was determined by using PANalytical ‘X’PERT-PRO XRPD.

4.3 Results and discussion

4.3.1 Mechanical properties

Hardness
The results of hardness of the various nanocomposites are expressed in Figure 4.1. It is observed that in all the nanocomposites the hardness increases with increase in concentration of fillers. Up to 30 phr all the four fillers showed superior hardness than C-black. After this the hardness imparted by waxy starch and StNPs is less than that of C-black whereas, that imparted by StINPs and StAcNPs is more than that of C-black. This is due to hydrophobic nature of modified StNPs the interaction with hydrophobic rubber is better which results in increase hardness. Among the biofillers StINPs imparted best hardness properties followed by, StAcNPs, StNPs and Waxy starch.
Figure 4.1 Mechanical properties of NR composites

![Stress-Strain Curve with Graphs](image)

**Scheme 4.2 Structure of allophanate formation**

**Stress-Strain Curve**

Typical stress vs. strain curves for the NR nanocomposites at 40 phr are shown in Figure 4.1. For each measurement, it was observed that the strain was macroscopically homogenous and uniform along the sample until it breaks. The lack of any necking phenomenon confirms the homogenous nature of these nanocomposites. The samples
exhibit an elastic behavior at \( T > T_g \). The stress continuously increases with strain and the amount of fillers as shown in Figure.4.1. Incorporation of nanofillers leads to an increase in strength as well as elongation at break. These results are contradictory to the observations of Angellier et al. [20] who recorded a decrease in elongation as the amount of filler increases. The behavior is consistent with respect to all the nanofillers. Thus we can say that the nanofillers used retain the elastic property of natural rubber which is also concluded by dynamic mechanical analysis (described later). The initial high stress is due to the reinforcement of the rubber with nanofillers [52]. As the strain increases, stress induced crystallization comes into role, which increases proportionally along with strain [30]. The dispersion of nanofillers leads to an efficient reinforcement, which leads to improved stiffness. The unmodified starch nanoparticles (StNPs) showed lower strength as compared to modified starch nanoparticles. Due to hydrophilic nature of StNPs and hydrophobic nature of NR the adhesion between the two is poor. As a result the stress transfer from the matrix to the filler is poor and the mechanical properties of nanoparticles are not fully utilized.

**Tensile Strength**

It can be seen from Figure.4.1 that as the amount of nanofillers increases the tensile strength (T.S.) goes on increasing as expected. It follows the order StINPs/NR > StAcNPs/NR > StNPs/NR > Waxy starch/NR. In case of C-black composites the initial lower T. S. value rapidly increases from 10 to 40 phr loading but remains lower than nanocomposites at all levels. Nanocomposites of modified StNPs showed greater strength and elongation due to their improved dispersion and better compatibility with NR due to its hydrophobic nature and small particle size. Among the modified StNPs, StINPs showed higher mechanical properties which can be explained on the basis of chemical reactions that are likely to occur during the process of vulcanization. At this high temperature the free NCO groups of isocyanate terminated StINPs may react further to form three-dimensional allophanate structure (Scheme 4.2) thus leading to increased chemical crosslinking [53] which imparts higher mechanical strength to the nanocomposite.
% Elongation

Figure.4.1 shows that as the amount of nanofillers in NR goes on increasing the elongation increases along with T.S. which is also seen in C-black composites. This is an interesting observation as generally elongation and T.S. show opposite trend. Also the increase in % elongation in case of modified StNPs is more progressive than C-black composites. High nanofiller content seems to preserve the elastic behavior of NR-based nanocomposites. In case of Waxy starch/NR the increase is obtained because it has high amylopectin content and hence higher molecular weight. Waxy starch imparts lower mechanical strength than other nanofillers due to poor compatibility with hydrophobic NR.

4.3.2 X-ray diffraction pattern

The XRD of nanocomposites at 40 phr loading (Figure.4.2) showed no diffraction peak corresponding to pure NR unlike other reports [54,55]. This is because the filler loadings in the present case are much higher than those reported by Huang et al., and Pojanavaraphan et al. for nanoclays (10 phr or less). On the other hand, for high filler loadings Dufresne et al. have observed that the processing by casting and evaporation at 40 °C did not affect the crystallinity of starch in nanocomposite [20]. While the vulcanization process in the present case may have led to change in the structure of the nanocrystals from crystalline to amorphous. This accounts for the absence of peaks corresponding to modified and unmodified starch in XRD of present nanocomposites.

4.3.3 Morphology studies

The results of the mechanical properties can be explained on the basis of morphology. The SE micrographs of fractured samples of biocomposites at 40 phr loading are shown in Figure.4.3(a-e). It can be seen that all the bionanofillers are well dispersed into polymer matrix without much agglomeration. Uniform distribution of modified and unmodified StNPs into NR matrix is observed. This is due to the compatibility between the modified StNPs and the NR matrix (Figure.4.3a and b). While in case of unmodified StNP the reduction in size compensates for the hydrophilic nature (Figure.4.3c), in case
of waxy maize starch it seems to be lack of interfacial adhesion (Figure.4.3d). The lack of any evidence of agglomeration combined with the significant increase in mechanical properties indicates even distribution of nanofillers in NR. In case of CB composites (Figure.4.3e) relatively coarse, two-phase morphology is seen.

Figure. 4.2 XRD spectra of nanocomposites at 40 phr loading.

4.3.4 Thermal analysis

Thermo gravimetric analysis
Typical TG curves (Figure.4.4(a)) of the nanocomposites at 40 phr loading showed an initial mass loss from temperature 150-250 ºC attributed to elimination of volatile components such as water [18]. At 350 ºC the percentage of weight retained is higher for nanocomposite (Table-1). This increase in thermal stability of the hybrid may result from the dispersion of the nanoparticles and strong interaction between the nanoparticles and rubber molecules. High vulcanization temperatures may have resulted in crosslinking within the polysaccharide network which led to unusual thermal stability of the nanocomposites.
Figure. 4.3 SE Micrographs of NR composites at 40 phr loading of (a) StINPs, (b) StAcNPs, (c) StNPs, (d) Waxy starch and (e) C-black.

**Differential scanning calorimetry**

DSC curves of NR composites at 40 phr filler loading (Fig. 4.8) shows that all the nanocomposites have Tg comparable with that of C-black/NR composites, while that of unfilled NR is around -66°C [18]. The Tg also goes on increasing with the nanofillers loading as expected (Fig. 4.9). The Tg of StINPs/NR is highest followed by StAcNPs/NR, StNPs/NR, Waxy starch/NR and C-black/NR composites. The results of
thermal properties support the observation that increased hydrophobicity and reduced particle size of filler imparts rigidity and strength to the network. Also isocynate modification leads to a greater increase in Tg due to increased crosslinking as already explained for enhanced mechanical strength.

Figure. 4.4 TG curves of (a) NR composites and NR nanocomposites containing (b) StNPs, (c) StAcNPs and (d) StINPs at various filler loadings
Dynamic mechanical analysis

Figure 4.6 depicts the dynamic mechanical spectra (logarithm of dynamic storage modulus log(E’) and E” and loss factor (tan δ)) as a function of temperature for the nanocomposites at 1, 5 and 10 Hz. A sharp decrease over 3 decades is observed around -60 °C, corresponding to the primary relaxation process associated with the glass-rubber transition determined by differential scanning calorimetry (DSC) measurements. This modulus drop corresponds to an energy dissipation phenomenon displayed in the concomitant relaxation process where tan δ passes through a maximum. Dynamic mechanical analysis involves weak stresses, the adhesion between the filler and the matrix is not damaged. Under higher stress, as used for tensile tests, the adhesion is involved. Nanocomposites obtained similar tan δ curve as that of Teh et al. [56]. The tan δ curve of nanocomposites showed a broad relaxation process from -80 °C to -10 °C (Figure 4.6). This may be due to the relaxation of rubber fraction confined inside the layers. The reduction in the tan δ maxima suggests a strong adhesion between NR and modified starch nanoparticles. Sliding along the exfoliated interlayer is suppressed. In addition, chain slipping at the outer surfaces of the aggregates is likely also hampered. Therefore the loss maximum is smallest in case of the nanocomposites system with the strongest filler matrix coupling [30]. Mondragon et al. [57] observed that E’ increases with clay content above Tg which shows that the clay content affects the elastic properties associated to the rubber phase (Figure 4.6). Whereas in the present study the values of E’ and E” does not increase with the filler loading above Tg. This indicates that the nanofillers does not affect the elastic properties associated to the rubber phase. The Tg values of DSC somewhat differ from DMA. This may be attributed to the frequency dependence of transition phenomenon. The activation energy (Table-2) for glass transition was calculated from following equation (eq 1) [58].

\[ \ln \frac{\omega_1}{\omega_2} = \frac{E_A}{R} \left( \frac{1}{T_2-1/T_1} \right) \]  

where \( \omega_1 \) and \( \omega_2 \), are the frequencies and \( T_1 \) and \( T_2 \) are the Tg’s obtained at \( \omega_1 \) and \( \omega_2 \), respectively.
Figure 4.5 (a) DSC curves of NR composites at 40 phr and (b) Effect of filler on Tg of NR composites.
4.3.5 Water sorption of composites

Absorption largely depends on the hydrophobic or hydrophilic components embedded in the matrix, which acts as a semipermeable membrane. The fiber/matrix adhesion is an important factor in determining the sorption behavior of a composite [59]. Moreover, fiber architecture has also been found to affect the absorption. Sorption studies were performed in water and nonpolar solvent toluene in order to understand the degree of hydrophobicity. As the bionanofillers used here are polysaccharides the water sorption was expected to be high and proportional to filler loading. However the results of the experiment (Table-3) showed an interesting trend. The maximum water uptake even at 30 % filler loading is 3.46 % which is not significant. Further, the sorption values decreases with filler loading. The low sorption indicates increasing adhesion between the polymer matrix and filler. The interaction leads to the formation of a bound polymer in close proximity to the reinforcing filler, which restricts the solvent uptake. As the amount of
filler loading increases, the amount of the bound polymer is lower and, consequently, the solvent uptake is lower. Also, the high curing temperatures may have introduced certain degree of crosslinking which also decreases the uptake. However the modified fillers led to decreased water sorption and increased toluene sorption of the nanocomposites which is well in agreement with their hydrophobic nature. The lower toluene sorption values of StINPs/NR also favour the greater crosslink density of StINPs/NR filled nanocomposites compared to StAcNPs / NR nanocomposites.

### Table. 1 TG data of bionanocomposites of NR / starch

<table>
<thead>
<tr>
<th>Fillers</th>
<th>Degradation temperature for % wt. loss</th>
<th>Activation energy Ea(KJ/mol)</th>
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<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Waxy starch</td>
<td>128</td>
<td>179</td>
</tr>
<tr>
<td>StNPs</td>
<td>135</td>
<td>198</td>
</tr>
<tr>
<td>StINPs</td>
<td>203</td>
<td>255</td>
</tr>
<tr>
<td>StAcNPs</td>
<td>170</td>
<td>231</td>
</tr>
<tr>
<td>C-black</td>
<td>114</td>
<td>192</td>
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### Table. 2 DMA data for bionanocomposites of NR / starch

<table>
<thead>
<tr>
<th>Fillers</th>
<th>Tg °C</th>
<th>Activation Energy Ea (KJ/mol)</th>
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<tr>
<td>StNPs</td>
<td>-55</td>
<td>312.61</td>
</tr>
<tr>
<td>StINPs</td>
<td>-50</td>
<td>369.81</td>
</tr>
<tr>
<td>StAcNPs</td>
<td>-48</td>
<td>324.75</td>
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Table 3 Water and toluene sorption of bionanocomposites of NR / starch

<table>
<thead>
<tr>
<th>Fillers</th>
<th>% mole Uptake</th>
<th>Water</th>
<th>Toluene</th>
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<tr>
<td></td>
<td></td>
<td>10 phr</td>
<td>20 phr</td>
</tr>
<tr>
<td>StINPs</td>
<td></td>
<td>0.98</td>
<td>0.37</td>
</tr>
<tr>
<td>StAcNPs</td>
<td></td>
<td>1.13</td>
<td>0.51</td>
</tr>
<tr>
<td>StNPs</td>
<td></td>
<td>3.10</td>
<td>2.87</td>
</tr>
<tr>
<td>Starch</td>
<td></td>
<td>3.46</td>
<td>2.81</td>
</tr>
<tr>
<td>C-black</td>
<td></td>
<td>1.15</td>
<td>0.71</td>
</tr>
</tbody>
</table>

4.4 Conclusions

Unmodified as well as modified starch nanoparticles were incorporated up to 40 phr in natural rubber matrix successfully. All the bionanocomposites showed superior strength and elongation than conventional Carbon Black/NR composites at all loadings. The modified starch nanoparticles showed better compatibility with NR matrix as per the morphology and XRD studies of bionanocomposites which revealed the uniform morphology and nearly exfoliated structure. Isocyanate modified starch nanoparticles imparted highest strength, increased the Tg and decreased solvent sorption probably due to formation of additional crosslinks during vulcanization process. Despite the polysaccharide origin the starchy fillers did not deteriorate the thermal stability of the nanocomposites. The broad tan δ peak suggested high degree of compatibility of reinforcing fillers with NR matrix with potential application over a wide temperature range. The study opens up a new and green alternative for reinforcement of rubbers.

In the past, cellulose nanocrystals were used up to 30 phr to form nanocomposites with polymers. Starch derivatives are found to induce excellent reinforcement in natural rubber up to 40 phr filler loading (chapter 4A). Hence here the development of nanocomposites highly filled (> 50 phr) with cellulosic fillers has been attempted.
Cellulose-natural rubber bionanocomposites

4.5 Experimental

4.5.1 Materials
Cellulose and cellulose acetate were purchased from Sigma Aldrich, Bombay.

4.5.2 Preparation of bionanocomposites
The bionanocomposites of NR were prepared on two roll mixing mill (as shown in scheme 4.2). Four sets of biocomposites were prepared using upto 60 phr each of cellulose (Cel), cellulose nanoparticles (CelNPs), cellulose acetate (CelAc), cellulose acetate nanoparticles (CelAcNPs) as reinforcing fillers in NR. The procedure and ratio of other ingredients were as mentioned in Chapter 2 (table.2.1.1).

Scheme 4.1 Preparation of bionanocomposites of NR / cellulose
4.6 Results and Discussions

4.6.1 Mechanical Properties

Figure. 4.7 Mechanical properties of NR composites
**Hardness**
The results of hardness of the various nanocomposites are expressed in Figure 4.7. It is observed that in all the nanocomposites the hardness increases with increase in concentration of fillers. The results showed that up to 30 phr all the four fillers showed superior hardness than C-black. After this the hardness increases but is less than that of C-black CelAcNPs imparted best hardness properties followed by, CelAc, CelNPs and Cel.

**Tensile strength and % elongation**
The mechanical properties of the composites were evaluated in terms of tensile strength and % elongation as seen in Figure 4.7. The values for ultimate tensile strength and % elongation for unfilled rubber are 0.58 MPa and 41 % respectively. At 10 phr cellulose fillers impart very high tensile strength and elongation properties compared to C-black. As the filler loading increases there is a steep rise in mechanical properties of C-black composites. This increase is gradual in case of cellulose composites except for those containing CelAcNPs. Among all the fillers CelAcNPs exhibit best reinforcing ability upto 50 phr preserving the elastic behavior of nanocomposites. At still higher loading the performance of C-black was observed to be much superior to the cellulose fillers. The results of mechanical properties also indicate that the combined effect of size reduction and organic modification drastically improves the filler matrix adhesion and hence the performance of cellulose fillers.

**4.6.2 X-ray diffraction pattern**
The XRD of nanocomposites at 60 phr loading (Figure 4.8) showed no diffraction peak corresponding to pure NR unlike other reports [60,61]. This is due to higher filler loading. On the other hand, for high filler loadings Dufresne et al. have observed that the processing by casting and evaporation at 40 °C did not affect the crystallinity of starch in nanocomposite [62]. While the vulcanization process in the present case may have led to change in the structure of the nanocrystals from crystalline to amorphous. This accounts
for the absence of peaks corresponding to modified and unmodified cellulose in XRD of present nanocomposites.

**Figure. 4.8 XRD spectra of cellulose based composites at 60 phr loading.**

### 4.6.3 Morphology studies

The results of the mechanical properties can be explained on the basis of morphology. The SE micrographs of fractured samples of composites at 40 phr loading are shown in Figure.4.9. SEM image of Cel/NR composite showed the presence of particles on the surface which may have leached out during fracture (Figure.4.9(a)). The CelAc/NR composite revealed somewhat homogeneous surface characteristics indicating filler-matrix compatibility (Figure.4.9(b)). CB/NR composite shows two-phase morphology and the presence of holes formed during fracture as evident from Figure.4.9(c). Against this, the nanofillers are more evenly distributed in the polymer matrix (Figure.4.9(d) and (e)). In case of unmodified CelNPs/NR nanocomposite the reduction in size compensates for the hydrophilic nature (Figure.4.9(d)). Among all CelAcNPs/NR nanocomposite appears to show almost single phase morphology which does not reveal any particles on the surface (Figure. 4.9(e)). This probably means the filler particles are deeply embedded.
in the matrix. The decrease in mechanical properties of CelAcNPs/NR nanocomposite at 60 phr may be due to formation of aggregates of excessive filler resulting in improper distribution. This is evident from the micrograph in Figure.4.9(f) which shows the occurrence of holes similar to those seen in CB/NR composite at 40 phr.

![Fig. 4.9 SE Micrographs of NR composites at 40 phr loading of (a) Cel (b) CelAc (c) C-black (d) CelAcNPs (e) CelNPs and (f) CelAcNPs at 60 phr](image)

**4.6.4 Thermal analysis**

**Thermal gravimetric analyzer**

The TG data of all the composites at 60 phr loading showed an initial mass loss from temperature 150-250 °C attributed to elimination of volatile components such as water [63] (Figure.4.10(a)). The degradation temperatures of biocomposites are in close
proximity with those of C-black composites. This may be because high vulcanization temperatures may have resulted in some extent of crosslinking within the polysaccharide network. The results also show that modified cellulose imparts better thermal stability to the composites compared to native cellulose. As already seen in the mechanical properties due to combined effect of size reduction and organic modification, the decomposition temperatures of CelAcNPs/NR nanocomposite are even higher than those of C-black/NR composite (Table-4). This is due to increase in onset temperature as compared to other composites which leads to increase in thermal stability. Also the thermal stability of increases as the amount of CelAcNPs increases (Figure.4.10(b)). This is due to the improved reinforcement imparted by CelAcNPs to hydrophobic NR matrix.

**Differential scanning calorimetry**

DSC analysis of NR composites at 60 phr filler loading show that the biocomposites have Tg comparable with that of C-black/NR composite (Table-4). This means that cellulosic fillers does not have affect the Tg of NR (Figure.4.11(a)) The Tg also goes on increasing with the filler loading as expected (Figure.4.11(b)). The Tg of CelAcNPs/NR nanocomposite is highest due to its hydrophobic nature and small size which imparts rigidity and strength to the network.

<table>
<thead>
<tr>
<th>Fillers</th>
<th>Degradation temperature for % wt. loss</th>
<th>Tg ºC at 40 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Cel</td>
<td>137</td>
<td>191</td>
</tr>
<tr>
<td>CelNPs</td>
<td>161</td>
<td>202</td>
</tr>
<tr>
<td>CelAc</td>
<td>145</td>
<td>198</td>
</tr>
<tr>
<td>CelAcNPs</td>
<td>187</td>
<td>222</td>
</tr>
<tr>
<td>C-black</td>
<td>114</td>
<td>192</td>
</tr>
</tbody>
</table>
Figure. 4.10 TG curves of (a) NR composites and (b) NR nanocomposites containing CelAcNPs at various filler loadings
Figure 4.11 (a) DSC curves and (b) effect of filler on Tg of NR composites
Dynamic mechanical analyzer

Figure 4.12 shows the dynamic mechanical spectra (logarithm of dynamic storage modulus $\log(E')$, $E''$ and loss factor (tan $\delta$)) of CelAcNPs/NR nanocomposite at 60 phr loading, as a function of temperature at 1 Hz. A sharp decrease is observed around -62 °C, corresponding to the primary relaxation process associated with the glass-rubber transition determined by differential scanning calorimetry (DSC) measurements. In this temperature range the loss angle passes through a maximum (Figure 4.12). A low temperature, i.e., below $T_g$, the reinforcing effect of cellulosic nanoparticles was low justifying the normalization of the modulus. Above $T_g$, a much more significant reinforcing effect of nanoparticles was observed. Dynamic mechanical analysis involves weak stresses, the adhesion between the filler and the matrix is not damaged. Under higher stress, as used for tensile tests, the adhesion is involved. The values of $E'$ and $E''$ does not increase with the filler loading above $T_g$ (Figure 4.12). This indicates that cellulose acetate nanoparticles do not affect the elastic properties associated to the rubber phase. The tan $\delta$ curve of CelAcNPs/NR nanocomposite shows a broad relaxation process from -90 °C to 25 °C. This may be due to the relaxation of rubber fraction confined inside the layers [6].

4.6.5 Water sorption

The filler/matrix adhesion along with the components embedded in the matrix is important factor in determining the sorption behavior of composite. In cellulosic composites, the water sorption was expected to increase with the amount of filler. However, the results demonstrated in Table-5 showed that water uptake decreases with the amount of filler. Adsorption of macromolecular chains at the filler/matrix interface through interactions between cellulose nanoparticles and NR could reduce swelling. Indeed, the formation of a three-dimensional network has already been reported for polysaccharide nanoparticles [6]. It may result from hydrogen bonding forces between unreacted hydroxyl groups of nanoparticles during the vulcanisation. At higher loadings, nanoparticles connect to form an infinite percolating network, which could be a barrier limiting the diffusion of toluene within the material. A fraction of the matrix material
thus becomes inaccessible for swelling (entrapped NR fraction). This indicates that the interaction between polymer matrix and filler leads to the formation of a bound polymer in close proximity to the reinforcing filler, which restricts the solvent uptake. However, this hypothesis needs deeper analysis.

Figure. 4.12 Effect of CelAcNPs on (a) mechanical loss factor tan δ, (b) logarithm of storage modulus $E'$ and (c) loss modulus $E''$
Table 5 Water and toluene sorption of NR composites containing various fillers

<table>
<thead>
<tr>
<th>Fillers</th>
<th>% mole uptake</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>Tolene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 phr</td>
<td>40 phr</td>
<td>60 phr</td>
<td>20 phr</td>
<td>40 phr</td>
<td>60 phr</td>
</tr>
<tr>
<td>Cel</td>
<td>2.81</td>
<td>1.94</td>
<td>1.07</td>
<td>2.77</td>
<td>2.19</td>
<td>1.76</td>
</tr>
<tr>
<td>CelNPs</td>
<td>1.05</td>
<td>0.56</td>
<td>0.25</td>
<td>2.56</td>
<td>2.11</td>
<td>1.67</td>
</tr>
<tr>
<td>CelAc</td>
<td>1.37</td>
<td>0.88</td>
<td>0.31</td>
<td>2.86</td>
<td>2.33</td>
<td>1.87</td>
</tr>
<tr>
<td>CelAcNPs</td>
<td>0.87</td>
<td>0.31</td>
<td>0.17</td>
<td>2.85</td>
<td>2.22</td>
<td>1.81</td>
</tr>
<tr>
<td>C-black</td>
<td>0.71</td>
<td>0.42</td>
<td>0.22</td>
<td>2.38</td>
<td>1.61</td>
<td>1.12</td>
</tr>
</tbody>
</table>

4.7 Conclusions

The study led to the conclusion that filler–matrix adhesion dominates the performance of fillers. Cellulose acetate nanoparticles with the special advantage of nanosize as well as hydrophobicity exhibited the best mechanical strength, optimum being at 40 phr. Similar to carbon black composites the water sorption of the biocomposites was found to decrease linearly independent of the nature of the filler. Further, the polysaccharides did not lead to significant thermal degradation of the composite while acetylation improved the thermal stability. It can be concluded that the cellulose acetate nanoparticles can be potential green reinforcing agents even at higher loadings.
4.8 References