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## Green Nanocomposites from Renewable Resources: Effect of Plasticizer on the Structure and Material Properties of Clay-filled Starch

Nanocomposites of starch were prepared via different addition sequences of plasticizer and clay by the solution method. The extent of dispersion of the filler was evaluated by wide angle X-ray diffractometry (WAXD) in the resulting composites. Thermal stability, mechanical properties and water absorption studies were conducted to measure the material properties whereas FT-IR spectroscopy was used to study the microdomain structure of composites. The sequence of addition of components (starch /plasticizer (glycerol) / clay) had a significant effect on the nature of composites formed and accordingly properties were altered. Glycerol and starch both have the tendency to penetrate into the silicate layers but penetration of glycerol is favored owing to its smaller molecule size. The filler dispersion becomes highly heterogeneous and the product becomes more brittle when starch was plasticized before filling with clay due to the formation of a bulky structure resulting from electrostatic attractions between starch and plasticizer. It was concluded that best mechanical properties can be obtained if plasticizer is added after mixing of clay in the starch matrix.

**Keywords:** Nanocomposites; Clay-filled starch; WAXD; Effect of plasticizer

### 1 Introduction

In order to develop an environmentally friendly material, many efforts have been made to solve problems generated by plastic waste, particularly by one-time-use disposable commodity material [1, 2]. Most of the research attention is focused on the replacement of petro-based commodity plastics in a cost-effective manner by biodegradable material with competitive mechanical properties. Biopolymers have been considered as most promising materials for this purpose as they exist abundantly and may form a cost-effective end product [3, 4], whereas compatibility with thermoplastics is a serious issue that may be solved by modification in both matrices [5–7]. In the family of biopolymers, starch has been considered as most promising candidate for the development of such materials. By destroying the crystalline structure of starch under pressure and heat in the presence of plasticizers (e.g., water, glycerol and other polyols), it is possible to convert it into thermoplastic starch (where starch content is as high as 95%), which could be processed alone or with a particular synthetic polymer [4, 8, 9] but the moisture sensitivity limits its applications for many purposes. Although moisture resistance can be improved by adding

poly(ethylene-co-vinyl alcohols) and acetylation [10, 11] or by cross-linking [12, 13], starch still has not come to real practical use as traditional plastics. In earlier studies an increased biodegradability of starch-polycaprolactone blends was found with the compatibilization and it was demonstrated that the compatibilization not only increased mechanical properties but also the accessibility of the comparatively less active matrix to microbes [14]. In all the starch-based systems, the mobility of polymer chains determines the generation of chain to chain interactions and entanglement, the processing parameters and composition, and is believed to influence the mechanical properties, but the direct relation to the structure and properties of the resulting products are very complex and little known. Moreover, the total goal in the area of starch thermoplastic composites is to enhance processibility, compatibility and water resistance in a very cost-effective manner, because these factors decide the fate of products as possible substitutes for petro-based traditional packaging materials.

Recently a new class of hybrid materials of polymers and layered silicates has emerged. This class has improved material properties due to the high aspect ratio and easy phase-to-phase energy transfer, even at very low filler concentration, if the filler is uniformly and completely dispersed in the host matrix [15, 16]. Starch has been filled with layered silicates and an improvement in

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mechanical and barrier properties was observed [17–20]. Nanocomposites of starch containing cellulose whiskers have been reported with improved properties in comparison with neat starch [21, 22]. During synthesis of nanocomposites, polymer chains from the bulk try to penetrate inside the silicate layers and, depending on penetration extent, an intercalated or exfoliated structure is formed. If polymer chains are not able to penetrate effectively, microcomposites formation takes place. There are a number of parameters that decide this degree of diffusion, viz. modification of clay, polar-polar interactions, molecular weight of polymer, packing density inside the gallery, concentration of filler, etc. [15, 23, 24]. The preparation of nanocomposites is still a trial and error effort, ranging broadly from a lower to higher filler concentration by varying the different parameters as mentioned above. Optimization of parameters is generally done by examination of several formulations. In the present study, we found out that apart from these deciding parameters of composite structure, the sequence of mixing can also affect the nature of the resulting product, whether it will be a nano-level or micro-level distribution, at least in starch clay nanocomposites prepared by the solution method. To the best of our knowledge there is no report on the study of different interactions among the components in starch nanocomposites. Since both components (starch and plasticizer) of the composite (starch / clay / plasticizer) must show the tendency toward accommodation inside the gallery space of filler, due to the presence of polar-polar interactions with clay, the study of interactions may insure the preparation of tailored nanocomposites of starch. In the present attempt we studied the behavior of starch / plasticizer (glycerol) with clay to investigate the cause of intercalation and to study, which molecule enters the clay gallery with what preference. Mechanical properties, thermogravimetric analysis, and moisture sensitivity of the composites were studied. WAXD results were used to evaluate the interaction extent between filler and starch / glycerol and different structural representations were made on the basis of these results.

## 2 Materials and Methods

### 2.1 Materials

Native corn starch with 15% moisture content was obtained from S.D. Fine-Chem. Ltd. (Mumbai, India). Clay, sodium montmorillonite (Cloisite Na<sup>+</sup>) was from Southern Clay Products, Inc. Gonzales, TX, USA, having a cation exchange capacity (CEC) of 92 meq / 100 g clay. Glycerol was used as plasticizer and supplied by S.D. Fine-Chem. Ltd. (India).

### 2.2 Preparation of nanocomposites

The clay was dispersed in water at  $35 \pm 5^\circ\text{C}$  for 48 h. Weight of clay and starch was taken after drying at  $110^\circ\text{C}$ . Plasticizer concentration was 20% (w/w) and clay concentration was constant at 5% (w/w) in all the compositions. Starch / clay / glycerol (75 / 5 / 20) were mixed in the following ways: i) Starch was gelatinized with water followed by plasticization and then clay slurry was added. This mixture was heated for 30 min to boiling and the obtained composite samples were designated as STN1, ii) The clay slurry was mixed with starch in water and heated to boiling for 30 min with constant vigorous stirring, followed by the addition of plasticizer. These samples were named as STN2, iii) Starch, clay slurry and glycerol were mixed together and heated for 30 min to boiling and were designated as STN3 and iv) glycerol was mixed with clay slurry and stirred for 5 h at room temperature followed by addition of starch. This mixture was heated to boiling for 30 min and samples were named STN4. The glycerol-clay mixture was also obtained under the same conditions (ST-GLC) to study the migration of glycerol into clay layers. Commonly, after completion of all procedures, the solutions were poured in petri-dishes and evaporation was carried out in a vacuum oven at  $50\text{--}60^\circ\text{C}$ . The films of  $\sim 150\text{--}200\ \mu\text{m}$  thickness were obtained and samples were equilibrated according to ASTM E 104–02 [standard practice for maintaining constant Relative Humidity (RH) by means of aqueous solutions] at defined RH and temperature.

### 2.3 Characterization and measurements

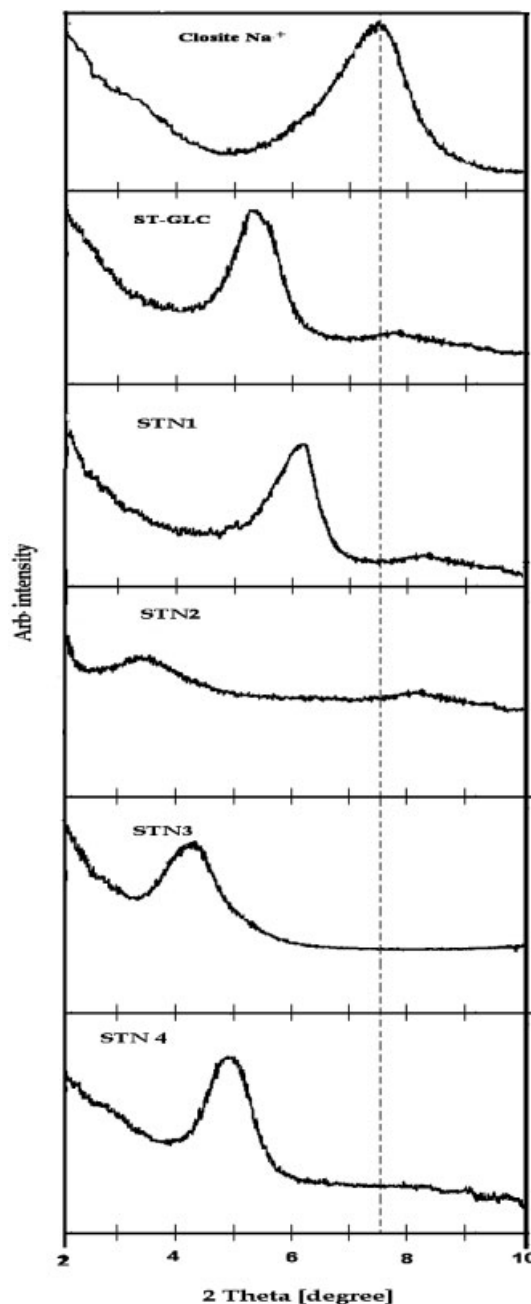
The pattern of X-ray diffraction of the samples was obtained by a Rigaku (Tokyo, Japan) diffractometer with Cu-K<sub>α</sub> radiation at 50 kV in the scan range of  $2\theta$  from  $2\text{--}10^\circ$  at a scan rate of  $1^\circ/\text{min}$ . The  $d$ -spacing was calculated by Bragg's equation where  $\lambda$  was 0.154 nm. Thermogravimetric analysis was performed under nitrogen flow at a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of  $25\text{--}500^\circ\text{C}$  in the Perkin Elmer TGA-7 instrument (Norwalk, CT, USA) after maintaining the samples for two weeks at  $25 \pm 2^\circ\text{C}$ . Mechanical properties of five samples for each composition, were determined by using an Instron machine (Canton, MA, USA) at  $27^\circ\text{C}$  and 5% humidity with cross-head speed of 1.5 mm/min, after conditioning for three weeks at 57% RH. The samples were dried until constant weight in an oven to remove the moisture before water absorption testing by gravimetric methods and this weight was taken as initial weight ( $W_i$ ). The samples were kept at 98% RH for 50 h and increase in weight was taken as final weight ( $W_f$ ). The percentage of water absorption

was calculated by the formula,  $(W_f - W_i) / (W_i) \times 100$ . An FT-IR (Fourier Transform Infrared 16 PC Spectrometer, Norwalk, CT, USA) was also used to characterize the composite samples, interest was focused mainly on the changes in  $\text{CH}_2$  stretching and bending bands.

### 3 Results and Discussion

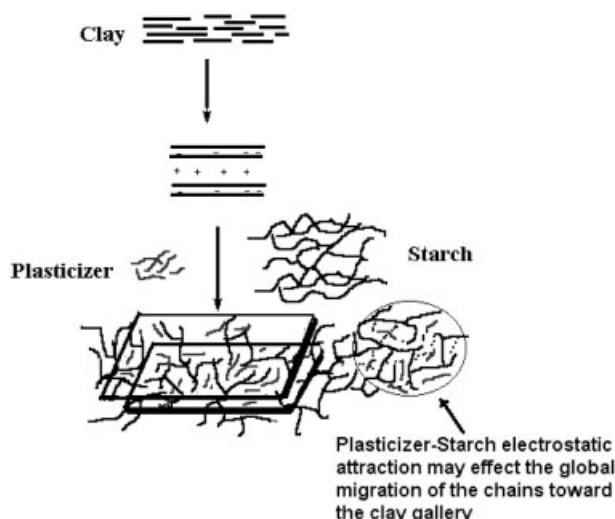
#### 3.1 Structure of nanocomposites

The dispersion extent of silicate layers has typically been elucidated by WAXD, which allow a direct evidence of polymer chain confinement into the silicate gallery. The X-ray diffraction pattern of all samples is shown in Fig. 1. The presence of narrow peaks for all samples except STN2 is an evidence of the ordering in clay layers and confirming the finite diffusion of polymer chains with a repeat distance of few nanometers. The highest increase in  $d$ -spacing was observed for STN2 specimens ( $2\theta = 3.32^\circ$ ,  $d$ -spacing = 2.68 nm) and the lowest for STN1 ( $2\theta = 6.37^\circ$ ,  $d$ -spacing = 1.38 nm) whereas STN3 shows a significant shift of theta towards lower values with an intermediate gallery height ( $2\theta = 4.58^\circ$ ,  $d$ -spacing = 1.93 nm). All the observations indicate the presence of some interactions, deciding the starch chain diffusion in the clay gallery, as all components had the same concentration in the composites. The small increase in STN1 may be explained on the basis of electrostatic attraction between plasticizer and starch, which results in large structures by developing hydrogen bridges, thus negatively affecting the global mobility (Fig. 2). Another cause must be the decrease in polar-polar attraction between the hydrophilic clay and starch as in this case starch is also attracted by the plasticizer or in other words a counterbalance of driving forces (polar-polar attraction of clay and starch is partly balanced by electrostatic hydrogen bonding between starch and plasticizer) takes place which consequently decreases the attractive force between clay and starch. This argument becomes more explanatory by obtaining the WAXD patterns of clay and starch mixture where  $d$ -spacing was higher than STN1 (for ST-GLC,  $2\theta = 5.43^\circ$ ,  $d$ -spacing = 1.62 nm and for STN1,  $2\theta = 6.37^\circ$ ,  $d$ -spacing = 1.38 nm), and this fact gave the credit to conclude that plasticizer also face the difficulties in moving towards the gallery due to the H-bonding with starch and could not intercalate as freely as in absence of starch. Further, when the composites were prepared without earlier plasticization (STN2), the characteristic peak was highly diminished giving the indication of high extent of intercalation i.e. the extensive diffusion of polymer chains inside galleries of clay, which results in high dispersion of filler throughout the matrix. These results confirm the presence of attraction forces in all the



**Fig. 1.** XRD pattern of all composites and clay including glycerol-clay composition.

systems, those are decisive factors for the effectiveness of dispersion in the overall polymer matrix. The gallery height was not increased in the case of STN2 after plasticization, suggesting that plasticizer can be accommodated among the starch chains which may not lead to any further increase in gallery height. In the case of STN3, increase in  $d$ -spacing was less than for STN2 but significantly higher than in the case of STN4, which may be attributed to the diffusion of starch chains inside the filler.



**Fig. 2.** Representation of interactions between plasticizer and starch during migration towards clay galleries.

Here, if we suppose that complete diffusion of plasticizer had taken place in this sample, then also the increase in gallery height is more than in ST-GLC, which confirmed the migration of starch chains. Since complete diffusion of plasticizer is not possible due to presence of interactions between plasticizer and starch, it was concluded that both components in the STN3 samples have moved faster towards the gallery than in STN1 and slower than in STN2. In a previous study, the non-escaping of small molecules in thermoplastic starch-clay nanocomposites, prepared by melt intercalation method inside the gallery was argued to be due to the absence of significant increase in gallery height. In the present system we observed a clear migration of plasticizer inside unmodified clay layers. Moreover, the possibility of better dispersion of clay in the starch matrix decreases if glycerol and starch will be allowed to diffuse together inside the layers of silicates.

When another set of the composites (STN4) were prepared by the mixing of starch in the mixture of clay and glycerol, which had already been stirred at room temperature for 5 h, followed by heating the whole solution at boiling point for 30 min, a WAXD pattern showing a greater gallery height than ST-GLC and STN1 but less than STN2 and STN3 was found (STN4,  $2\theta = 4.96^\circ$ ,  $d$ -spacing = 1.78 nm). These results were surprising, because glycerol was supposed to increase the gallery height and act as surfactant, which would have been facilitated penetration of starch chains. Further, in this composition starch diffusion should be higher, because starch chains encounter two attractions: one with clay and the other one with the plasticizer inside the clay. The explanation for this behavior may be as follows;

1. There was enough plasticizer outside the clay stacks after a optimum migration inside the layers as only glycerol can not cause the formation of nanometer thick silicates layers. The not migrated plasticizer can form hydrogen bond bridges with the starch molecules resulting in slow diffusion as in STN1. Further, the unplasticized starch chains may require an additional force to replace the plasticizer on the surface of the filler. Thus, the number of contacts decrease by presence of starch on the gallery surface.
2. The tetrahedral sites in the layers, containing  $\text{Si}^{4+}$  (a Lewis acid site), might be helping in intercalation, for oxygen-containing functional groups (O-H) in starch as in the case of STN2 are now engaged with OH of glycerol and unavailable during penetration of starch chains as the diffusion starts after surrounding the filler particles. Again the concentration of glycerol inside the gallery may increase the packing density, which will disfavor the penetration of polymer chains.
3. Another most probable explanation may be, as soon as starch chains meet glycerol present in the gallery, close packing starts, which may generate a solid-like structure after a definite penetration of starch chains. At this stage of penetration, other chains diffusion becomes difficult, resulting in a microcomposite.

The migration of plasticizer inside the clay galleries was studied by FT-IR spectroscopy which gives more realistic information about the different interactions at molecular level. IR bands between  $2800\text{--}3000\text{ cm}^{-1}$  are related to the stretching of  $\text{CH}_2$ , and bands around  $2920$  and  $2850\text{ cm}^{-1}$  are generated due to the asymmetric and symmetric stretching of methylene, respectively. Peaks at  $1472\text{--}1466\text{ cm}^{-1}$  arises due to the scissoring vibrations of  $\text{CH}_2$ . These scissoring bands show variations with interchain interactions, packing arrangement and ordering of methylene chains [25]. Fig. 3 shows FT-IR spectra of glycerol, obtained at room temperature, with different components. The shifting of the band at  $2925$  to  $2920\text{ cm}^{-1}$  after clay mixing suggests an increase in packing density, thus the surface area per guest (starch) chains decreased. There was no change in this band for STN4 specimen, which was attributed for the close packing in the silicate layers. The increase in packing density or decrease in chain motion of glycerol after mixing with clay was further confirmed from the rising of  $\text{CH}_2$  bending at  $1472\text{ cm}^{-1}$ . Thus the migration of glycerol into silicate layers increases in the absence of starch thus resulting in an increase in packing density, which inhibits the further penetration of starch chains.

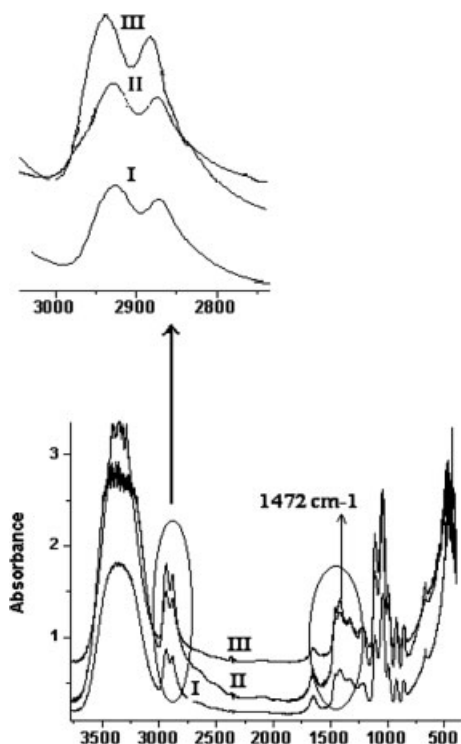


Fig. 3. FT-IR spectra of glycerol-clay mixture (I), STN4 (II) and glycerol (III).

## 3.2 Effect of filler dispersion on the material properties

### 3.2.1 Mechanical properties

The mechanical properties of the composites are listed in Tab. 1. The modulus of composites increased significantly for all candidates as compared with the unfilled matrix, irrespective of the preparation fashion. The highest enhancement in STN2 and lowest in STN1 suggests that the stiffness increases with the gallery height of silicate layers in the matrix. Such kind of improvements are well known in intercalated / exfoliated nanocomposites for other polymers also and attributed to the higher reinforcing effect of layered fillers [24]. A significant increase of strain in STN2 as compared with the other samples indicates that the extent of plasticization is sufficient enough, which allows segmental mobility of starch chains. Thus, when glycerol was mixed after starch diffusion inside the clay gallery, it can migrate throughout the system owing to its smaller size and retaining the plasticizer efficiency. In the case of STN1, reduction in strain is attributed to the presence of large stacks of filler inside the matrix consisting of agglomerates of layered silicates, that are surrounded by polymer chains. STN3 showed intermediate results but the maximum strain was less than that of unfilled starch, which is an indication of decreased plas-

ticization efficiency. The specimen of STN4 exhibited results close to STN3 but are not significantly different, which gives the information that most of the glycerol resides inside the gallery space and is not available for electrostatic bonding with starch leading a restricted motion of chains.

Tab. 1. Mechanical properties of starch-clay composites at 5% filler concentration.

Sample	Young's modulus [MPa]	Maximum strain [%]
Plasticized starch	790	10
STN1	820	6
STN2	825	12
STN3	824	9
STN4	821	7

### 3.2.2 Moisture resistance

Moisture sensitivity of starch-based material is a key challenge towards the substitution of traditional plastics for commodity, most precisely, for packaging applications. The water uptake of composites during the exposure at R.H. 98% was evaluated for 50 h (see Fig. 4). The increased permeability of starch films after plasticization for water, gas and solute has been reported [26]. Plasticized starch films showed the highest moisture sensitivity in comparison to other samples. Plasticization increased the hydrophilicity of the starch matrix around 1.5 times, which is attributed to the increase in chain mobility at room temperature by breaking the attraction forces in the host matrix and a consequent increase in concentration of exposed moisture-sensitive hydroxyl groups, facilitating diffusion of water molecules throughout the polymer matrix. After mixing with clay, an overall decrease in hydrophilicity, regardless of the clay concentration in the systems, must be attested to the presence of barriers in the form of torturous paths of clay, which generate difficulties in diffusion through the matrix. The STN1 specimens showed a little lower moisture sensitivity than plasticized starch, which was due to the hurdles in the way of moisture because of clay presence. The concomitant increase in water resistance in the case of STN2 must be attributed to the excellent dispersion of fillers which could result in a higher engagement of OH groups with layers, making them less available for moisture absorption. Secondly, the number of barriers also increased in this composition. Since the plasticizer was added after clay dispersion in the matrix, the plasticizer also moved towards the gallery, i.e., there were two attraction forces working together to pull the plasticizer inside the gallery, clay-

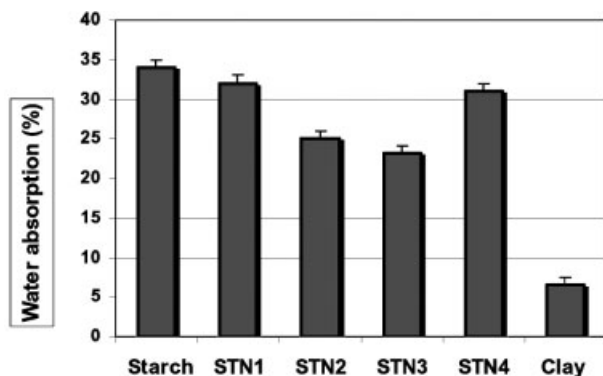


Fig. 4. Water absorption at 98% RH and 25 ± 2°C for 50 h.

plasticizer and plasticizer-starch attractions. This conclusion was strongly supported by increase in elongation at break of this system. Thus, water sensitivity can be altered more effectively by the dispersion extent of clay than by the presence of moisture-sensitive groups, as the concentration of these functional groups in STN3 was higher than in STN2. Water absorption by STN4 is higher and almost equal to STN1. Thus, for higher water resistance clay must have an optimum ordered structure that could develop an effective and sufficiently enough diffusion paths.

### 3.2.3 Thermal properties

In general, thermal stability of polymers increases after filling with inorganic fillers [29]. The results of thermogravimetric analysis are depicted in Fig. 5. A three-step process was clearly observed in the composites. All specimens showed highest weight loss at 296°C. The I, II and III step were attributed to the water loss, starch plus glycerol decomposition and final decomposition of remaining starch during oxidation. In comparison to starch the percentage mass loss was decreased in the second step and increased in the third for all composites, suggesting that the decomposition temperature of glycerol and starch has shifted to higher temperature, i.e. the thermal stability of starch and glycerol increased after clay filling. This must be a result of protection of starch and glycerol by the silicate layers. Furthermore, STN2 presented the highest thermal stability in comparison of all specimens, which is attributed to the higher dispersion of filler in the matrix. The concentration of exposed hydroxyl groups was least in the STN2, as has been discussed earlier, which may be another cause of thermal stability. Significant difference was not found in the thermal stability of STN1, STN3 and STN4 but it was better than that of the unfilled plasticized starch matrix. The decrease in plasti-

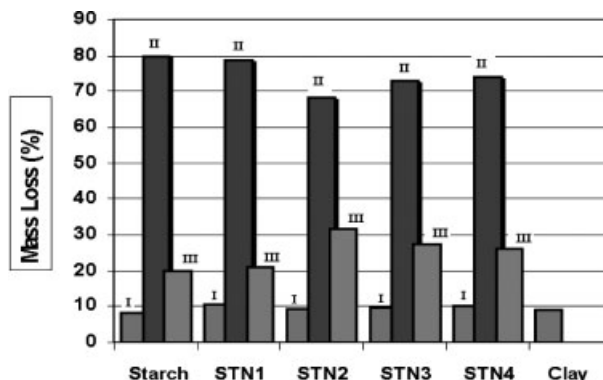


Fig. 5. Mass loss (%) during thermogravimetric analysis of samples at the rate of 10°C/min. (I step corresponds to the weight loss of water, II step is the weight loss relative to total mass of samples, III step is the weight loss relative to mass of plasticizer and starch in the sample).

cization extent after removal of water is expected, at least at those polymer segments that could not be reached effectively by glycerol, because it was not perfectly homogenized in these systems (STN1, STN3 and STN4). Since water content was higher in STN1, this effect (decrease in plasticization efficiency) was obviously more pronounced. As soon as water evaporates, the starch chains may tend to reorganize and the low degree of ordering tends to convert to a higher degree. The overall phenomenon may result in the re-association of starch chains after formation of entanglement or juncture points and again the chances of helical structure formation increases. This reorganizing may decrease the thermal decomposition temperature of the matrix. Thus, there may be three factors determining the behavior of clay-filled starch at thermal treatment, i) exposure of hydroxyl groups ii) clay dispersion extent in the host matrix and iii) re-association of starch chains. All factors can be written in the following order of effectiveness of samples during thermal treatment;

Clay dispersion > Hydroxyl groups exposure > Re-association of matrix chains.

All three are present effectively in the STN2 whereas poorly in STN1 and as intermediate in STN3 and STN4.

Finally, all results of this study tend to demonstrate the effect of preparation methods and sequence of addition of components on the composite nature. The possible ways of interaction by which the four types of composites could be obtained are illustrated in Fig. 6. Starch and glycerol tend to migrate to clay galleries as both encounter polar-polar attraction forces with clay. Glycerol is preferred over starch in this competition due to its smaller molecular size. The rate of diffusion of both starch and



STN1



STN2



STN3



STN4

**Fig. 6.** Different structure of composites. Composite formed by the mixing of filler into plasticized starch (STN1), composite structure formed by the mixing of filler into starch followed by plasticization (STN2), composite structure formed

by the together mixing of all components (clay / starch / plasticizer) (STN3) and composite structure formed when starch was mixed into slurry of plasticizer and clay (STN4). The thick bold rods indicate the silicate layers, whereas long and short chains denote starch and plasticizer, respectively.

glycerol inside the layers decreases when mixed together because of mutual attraction forces, which formed a mass-like structure resulting in slow transport around the tectoïdes and consequently delay in migration inside the silicate layers (Fig. 2). If already plasticized starch is mixed with clay, almost a microcomposite is formed and whatever the increase in gallery height observed, is due to the migration of some glycerol inside the layers. The best nanocomposites were formed when first starch-clay was mixed followed by plasticization. In this case, the starch chains were involved in only one dominant polar-polar attraction with clay and confinement occurs without interference. At this moment, the plasticizer molecules encounter double attraction towards the gallery space; first with clay and second due to electrostatic hydrogen bonding formation with starch chains. Since the plasticizer is small in size, it can be accommodated in gaps of starch chains between the silicate spacing. This process leads to an efficient plasticization of the starch matrix retaining the elongation of resulting product. The increase in modulus was not very significant in the composites which may be the indication of insufficient concentration of filler as at the high concentration, modulus can increase by many fold but it is not necessary that the silicate layers are individualized at nano level. The composites cannot be immersed in water due to extreme moisture sensitivity. All the composites were water resistant for at least 50 h and this fact (high water resistance) may be easily eliminated for prolonged exposure because clay will swell and gallery space will increase with time which may result in complete leaching of components.

#### 4 Conclusion

An improvement in all material properties of the composites could be achieved by better dispersion of clay. Better dispersion can be achieved by first mixing of starch and filler followed by plasticization. Thus, the interplanar distance of clay strongly depends on the sequence of mixing. Although an enhancement of mechanical properties takes place in the clay-filled composites, still the water resistance is too poor to use these composites in packaging applications, at least not for liquids. From a moisture sensitivity point of view, well-ordered intercalated structures are also helpful to lower the moisture sensitivity in comparison to a structure consisting of individual nanometer dispersion of layered silicate in a starch matrix. Diffusion of plasticizer inside the clay is easier than diffusion of starch. Starch chains must penetrate through clay galleries first, followed by plasticization in order to maintain the plasticization efficiency. The composites obtained are very far from becoming substitutes for traditional commodity plastics like polyethylene and

polypropylene, mainly because of their extreme moisture sensitivity. The material properties of layered silicate-starch composites may not change very significantly by a small decrease or increase in gallery height of filler. We have successfully prepared nanocomposites with higher moisture resistance by modification of starch and plasticizers, i.e. starch esters and ethers, and also measured the effect of degree of substitution. The results of our ongoing work will be submitted for publication very soon.

## Acknowledgement

Authors are grateful to Dr. S. Sivaram, Director, National Chemical Laboratory, and Pune for fruitful discussions and encouragement. JKP is thankful to Council of Scientific and Industrial Research (CSIR) for providing Senior Research Fellowship (SRF).

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(Received: May 6, 2004)

(Revised: September 10, 2004)

(Accepted: September 13, 2004)