



NANO CLAY POLYMER COMPOSITE: SYNTHESIS, CHARACTERIZATION, PROPERTIES AND APPLICATION IN RAINFED AGRICULTURE

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ABSTRACT

This article represents the different unique properties of nano clay polymer composite (NCPC) along with their different types, preparation technique, spectral signatures and morphological characters and its possible use for promotion of rainfed agriculture. Water retention capacities of polymer composite and its control release have the main significant role in rainfed agriculture. NCPC, has potential agro-biotechnological applications for increase in input use efficiency especially fertilizer and water under abiotic stress condition. The slow release pattern of nutrients are potentially helpful to control the deficiency of major nutrient elements in soils like N,P,K etc in the eastern part of India, where mostly rain fed agriculture dominates in rabi season. Another aspect of this article is the encapsulation of different bioagents like *Trichoderma harzianum*, *Pseudomonas fluorescens* loaded through NCPC can control fungal-nematode disease complex that occurs in several pulses due to moisture and nutrient deficiency causing low level of productivity in rainfed rabi cropping. The rice fallows occupy nearly 12 million hectares in India and represent an enormous underutilized resource. The NCPC loaded with biological control agents like *Trichoderma harzianum* coupled with nutrient elements can go a long way for promotion of a second crop after rice in rainfed ecosystem.

KEY WORDS: Cross linker, slow release, Nano clay polymer composite, rainfed agriculture

INTRODUCTION

Nanoparticles (NPs) having at least one dimension in the order of 100 nm or less (Auffan *et al.*, 2009), or as a colloidal particulate systems with size ranging between 10 and 1000 nm (Nakache *et al.*, 1999). Nano clay polymers have potential application in agriculture in terms of nutrition as well as protection due to their size, high surface-to-volume ratio and unique properties. The world demand for fertilizer was forecast to increase day by day. Therefore, there is an urgent need to tackle the excessive usage of bio and synthetic fertilizers and pesticides by a) finding alternatives to current fertilizer deployment, b) locally detecting presence of pests, as well as pesticides and nutrient levels in soil and c) developing methods for either agrochemical removal or degradation to promote soil health and quality. Polymers display controlled release of nutrients and serves as carriers for nutrients as well as pesticide ingredients, fluorescence (QDs) or photo catalytic degradation (metal oxide NPs) that has biotechnological applications in sensor development, agrochemical degradation and soil remediation. Potential applications of nano clay polymer composite in agriculture are: delivery of pesticides encapsulated in nanomaterials for controlled release; stabilization of biopesticides with nanomaterials; slow release of nanomaterial assisted fertilizers, and micronutrients for efficient use; and field applications of agrochemicals, nanomaterials assisted delivery of genetic material for crop improvement. Nanosensors for plant pathogen detection and NPs for soil conservation or remediation are other areas in agriculture that can benefit from nanotechnology. Cost-effectiveness

of such biocontrol preparations can be achieved by immobilization of enzyme/inhibitors on nanostructures, providing large surface areas, to increase the effective concentration of the preparation. Because of their excellent characteristics, superabsorbent are widely used in health, agriculture and horticulture applications (Sakiyama *et al.*, 1993; Yoshida *et al.*, 1989; Shiga *et al.*, 1993; Shiga *et al.*, 1992). Recently, the use of superabsorbent polymers as water managing materials for the renewal of arid and desert environment has attracted great attention, and encouraging results have been observed as they can reduce irrigation water consumption, improve fertilizer retention in soil, lower the death rate of plants, and increase plant growth (Nge *et al.*, 2004; Lokhande and Varadara, 1992).

Types of Nano composites

1. **Intercalated Nano Composites:** The intercalated nanocomposites result from the penetration of polymers chains into the interlayer region of the clay, resulting in an ordered multiple layer structure with alternating polymer/inorganic layers at a repeated distance of a few nanometers (Weiss *et al.*, 2006).
2. **Exfoliated Nano composites:** The exfoliated nanocomposites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix. Exfoliated nanocomposites have been reported to exhibit the best properties due to the optimal interaction between clay and polymer.

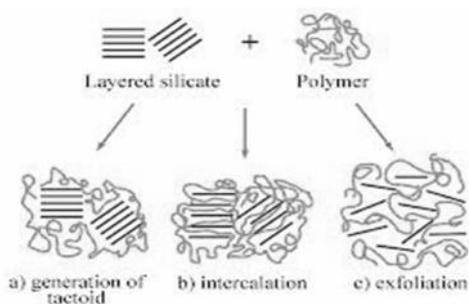


FIGURE 1: Different Types of Nano Clay polymer Composite

Types of modified clays: According to Basak *et al.*, (2012) the modified clays may be of following type:

Pillared layered clay: These constitute a novel class of materials by propping apart the lamellae of 2:1 clays with modified nano sized pillars of organic cations. Charge balancing cations are exchanged with polymeric hydroxyl cations.

Organo clays: These are created by replacing the native exchangeable inorganic cations by organic cations. They become organophilic.

Nanocomposites: When clay materials showed a change in composition and structure over a nanoscale. They clay nanolayer must be exfoliated in the polymer matrix.

The other minor category are acid and salt induced modifications for improving catalytic activities, and the other is thermally and mechanically induced modifications leading to a large change in mineralogical and chemical composition.

Preparation of Nano clay Polymer Composite

Urea and diammonium phosphate (DAP) granule fertilizer; Acrylic acid (AA), acryl amide (Am), N, N'-methylene bisacrylamide, and ammonium per sulfate. All of the chemicals were available from commercial sources. According to Liang and Liu, (2007) standard procedure of preparation of NCPC is as follows: Typically, AA and Am were dissolved in distilled water and then neutralized with ammonia (neutralization degree = 60%) in a three-necked flask equipped with a condenser, a thermometer, and an N₂ gas added to the reaction mixture. The flask was placed on a magnetic stirrer with a heating control. Clay was then added and dispersed in the partially neutralized monomer solution. Under an N atmosphere, the cross linker, N, N'-methylene bisacrylamide was added to the AA/Am/ clay mixture solution, and the mixed solution was stirred on the magnetic stirrer at room temperature for 30 min. Then, the temperature was increased slowly to 70°C with vigorous stirring after the radical initiator; ammonium per sulfate was introduced into the mixed solution. After completion of the polymerization reaction, the resulting product was washed several times with distilled water and then dried at 100°C to a constant weight. Lastly, drying and screening of samples were done.

Preparation of Nano clay Polymer Composite Encapsulated Urea fertilizer with Superabsorbent and moisture preservation:

According to Guo *et al.* (2005) Urea formaldehyde fertilizer was made from the 37 % formaldehyde solution and urea granules. Before adding the cross-linker and ammonium persulfate, dried granules along with certain

amount of tetrachloride, polyethylene glycol octyl phenyl ether Span-80 were added and the temperature rose to 65°C. Then cross linker and ammonium persulfate added to get the desired superabsorbent. According to Sarkar *et al.* (2012) the loading of DAP and urea were carried out by the immersion of reweighed dry gels into the aqueous solution of each fertilizer for 20 h to reach swelling equilibrium. Thereafter, the swollen gels were dried at 60°C for 6 days. Finally, the dried products were screened.

Water absorbency

According to Guo *et al.* (2005) most important property of Slow Release Membrane-Encapsulated Urea Fertilizer with Superabsorbent and Moisture Preservation is the water retention capacity within soil. They showed that the water transpiration of soil with SMUSMP 35.5% and 73% on 12th and 21st day whereas soil without SMUSMP was 51% and 95% respectively, which was 15.5% and 22% higher than former. According to Jatav *et al.* (2013) the water desorption rate of soil with NCPC was lower compared to the soil without it and soil with FYM. The water release ratio of soil without NCPC reached 62.3 and 90.2 wt% on the 15th and 30h days, respectively and soil with FYM reached 59.6 and 82.6 wt% on the 15th and 30th days, while that of the soil with NCPC was 55.7 and 78.6 wt%, respectively. The time needed for 50.0 wt% water evaporation was 12.2 and 13.5 days for the soil without NCPC and with FYM respectively, while it was 14.6 days for the soil with NCPC. The soil moisture desorption curve indicated that after 20 days, the volumetric water content of the soil without application of NCPC was 9.8 % and with FYM was 11.4 %, while that of the soil with NCPC was 21.4 %. Gao *et al.* (2001) developed a novel moisture sensor based on superabsorbent poly (acrylamide)-montmorillonite composite hydrogels. The time dependence of water vapor absorption by superabsorbent polymer clay composite showed good results over the others. According to Wu *et al.* (2000) the Q_{H_2O} varies according to time and reached highest to 4000 g H₂O within 60 minutes for Starch-graft-polyacrylamide/ kaolinite composite.

Effect of cross linker on water absorbency

Wu *et al.* (2000) showed that Q_{H_2O} sharply increases with decreasing the amount of cross linker in the range of 0.3% to 0.02%. Beyond a cross linker amount of 0.02%, Q_{H_2O} cannot be measured. Clearly, a higher concentration of cross linker produces a larger number of growing polymer chains, which are in turn involved in generating an additional network. Therefore, Q_{H_2O} decreases with an increase in the cross linker concentration because the network space gets diminished, and less water enters the composite. When the concentration of the cross linker is smaller than *e.g.* 0.02%, the copolymerization reaction between starch molecules and acryl amide monomer does not occur effectively. In this case, the cross linked network of superabsorbent cannot form, since starch and acryl amide exist as monomer or low-molecular weight polymers. Singh *et al.* (2010) also proved that increase in cross linker in the concentration of 0.06-0.12 wt %, the swelling of the clay also increased, but beyond this concentration swelling decreased. Guo *et al.* (2005) when cross linker was below 0.06%, water absorbency increased with increase in cross linker level up to 75 g/g, then decreased gradually.

Effect of Neutralization degree on Water absorbency

Guo *et al.* (2005) showed that up to 90% neutralization degree the water absorbency increased after that it gradually decreased. Liu *et al.* (2006) they exhibited that at 80% neutralization degree with 7% MMT clay with 0.15% showed the optimum water absorbency than acrylic acid monomer. Zhang *et al.* (2005) also reported that compared with the sepiolite-free hydro gel, sepiolite contributed to liquid absorbency, and at its weight content of 15.0%, Q_w (distilled water absorbency) and Q_p (physiological saline water absorbency) were enhanced as high as 11.6% and 14.5%, respectively. Under experimental conditions, a cross linked sepiolite/poly (AA-co-AM) hydro gel composite with the water absorbency of 830 gH₂O/g and the physiological saline absorbency of 98 gH₂O/g was synthesized, which has a composition of 0.02 wt % of MBA, 0.41 wt % of KPS (potassium persulfate), 16.2 wt % of sepiolite, a neutralization degree of 85%, and a reaction temperature of 65-80°C. This excellent water absorbency and low cost may be considered as a good candidate for large scale production of superabsorbent hydro gel especially useful in agricultural and horticultural applications.

Effect on water releasing capacity of the soil

According to Jatav *et al.* (2013) the water desorption rate of soil with NCPC was lower compared to the soil. With increase of clay loading in NCPC water desorption rate is decreases. Thus, NCPC had good water-retention capacity in soil, and that with NCPC use water can be saved and managed so that they can be effectively used for the growth of plants. These results showed that the NCPC had excellent water absorbency, water-retention, and moisture preservation capacity. The reason was that the superabsorbent polymer NCPC could absorb and store a large quantity of the water in soil, and allow the water absorbed in it to be slowly released with the decrease of the soil moisture. The swollen NCPC was just like an additional nutrient reservoir for the plant-soil system. Consequently, it prolonged irrigation cycles, reduced irrigation frequencies, and strengthened the ability of plants to tolerate drought stress.

Slow release behavior of nutrients

One of the most important characteristics was its slow release property. Wu *et al.* (2008) reported that the N, P, and K in untreated NPK fertilizers had released out more than 80% and 87% within 2 and 5 days, respectively, while the release rate of the untreated NPK fertilizer mixed with superabsorbent polymers decreased compared with the untreated NPK fertilizers. These results indicated that the slow-release proper ties of Double coated slow release fertilizer superabsorbent and water retention (DSFSW) conformed to the standard of slow-release water-soluble NPK compound fertilizer is easily dissolved in water, so it will quickly dissolve in the soil solution after being added to the soil, and the nutrient will be quickly exhausted. While the PAA superabsorbent can absorb a lot of water in soil, the NPK compound fertilizer dissolved in soil solution can be absorbed into it and on its surface. The absorbed NPK compound fertilizer can be released or desorbed slowly through the exchange of free water or minerals between soil solution and PAA. Therefore, the mixture of PAA and NPK compound fertilizer had a slower release rate than untreated NPK compound fertilizer. Sarkar *et al.* (2012) also proved that release pattern among the Clay 1 *i.e.*, polymer synthesized from kaolinitic clay, Clay 2, *i.e.*, Polymer synthesized from micaceous clay, Clay 3 *i.e.*, polymer synthesized from montmorillonite was different. Within 48 hour percentage of nutrient released was around 70% in polymer clay 3 to 90% in polymer/ clay 1 composite. There was no difference in nutrient release rate in presence of amorphous aluminosilicate. Guo *et al.* (2005) also studied the slow release of nitrogen through urea. More than 85% nitrogen was released from uncoated urea by the second day and 90% by the fifth day. The release rate of the fertilizer mixed with superabsorbent polymers was much lower than uncoated fertilizer. Nitrogen in SMUSMP released 10%, 15%, and 61% on second, fifth and thirtieth days respectively, with lower than 15% on second day and not above 75% on thirtieth day. Thus, NCPC loaded with different fertilizer like N, P and K showed the slow release due to intercalation of clay surrounding the polymer composite. This property has the great potential especially for promotion of rainfed cropping.

Characterization of NCPC FTIR Analysis

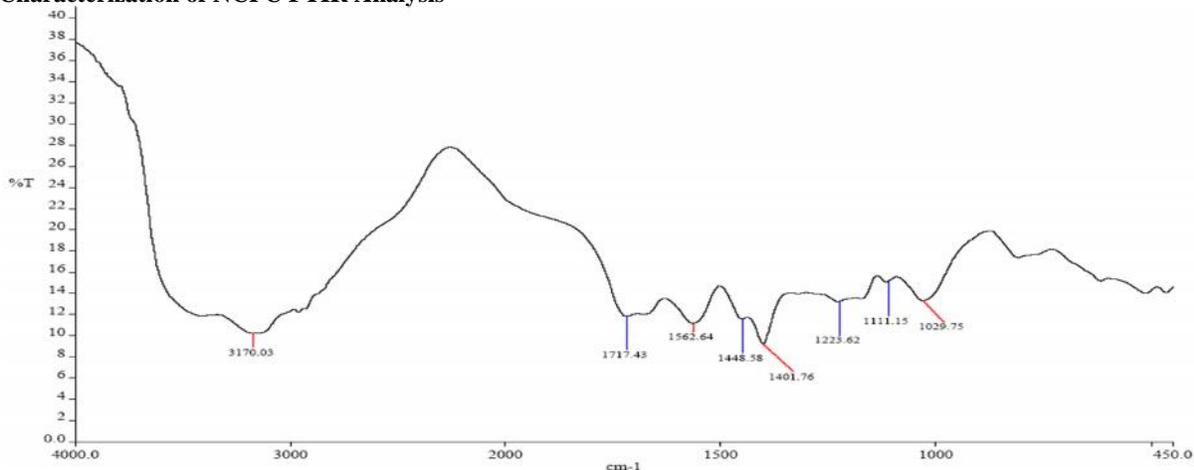


FIGURE 2: FTIR Analysis of NCPC

According to Sarkar *et al.* (2012) the FTIR spectra showed that the absorption bands of -OH stretching of various clays in the range 3400–3700 cm^{-1} disappeared, and the absorption bands at about 1030 cm^{-1} , ascribed to the Si-O stretching of clays, were weakened after the incorporation of various clays into the polymer network. It was suggested that graft copolymerization between the -OH groups on kaolin and the monomers took place during the polymerization reaction. Lin *et al.* reported that AA could graft onto mica and form a poly (acrylic acid)/mica superabsorbent composite. The -OH group of kaolinite could react with acrylamide, and kaolinite particles could chemically bond with the polymer chains to form a starch-graft-acryl amide/kaolinite composite. Thus, the disappeared and weakened absorption bands may have been due to the same reason, and the clays reacted with monomer unit during the polymerization process. The absorption band at 1690 cm^{-1} , ascribed to the $-\text{CONH}_2$ of the pure polymer, shifted to 1704, and 1717 cm^{-1} . In the spectra of polymer/clay3 (A), and polymer/clay3 (B), respectively; this indicated that the interaction between the clays and polymer had some influence on the chemical environment of $-\text{CONH}_2$ and/or $-\text{COO}^-$ and might have had some influence on the physicochemical properties of the corresponding super-absorbent composites. Liu *et al.*, (2006) investigated the structure, spectral signature and micrographs of the superabsorbent with Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. The results showed that the acrylic acid monomer was successfully intercalated into the montmorillonite layers and banded together with them. The montmorillonite layers were exfoliated and basically dispersed in the composite on a nanoscale after the polymerization. Due to proper ratio of carboxyl and a carboxyl ate group plays the major role for water absorbency and charge density. Carboxyl group has the affinity to absorb water and carboxyl ate group has the infiltration pressure which varies on neutralization degree from 45-80% after which water absorbency decreased due to imbalanced ratio. Higher neutralization degree repulsed the carboxyl ate groups. The above said composition also

proved that well dispersion of Na-MMT throughout the polymer. Zhang *et al.* (2005) the FTIR spectra of sepiolite, sepiolite/poly (AA-co-AM) composite, and sepiolite-free poly (AA-co-AM) showed strong absorption peaks, of asymmetric and symmetric R-COONa groups, appear at 1560 and 1410 cm^{-1} , respectively. The characteristic absorption peak of CONH_2 appears at the band of 1672 cm^{-1} . The peak at 1675 cm^{-1} is attributed to C=O stretching and the absorption band at 1020 cm^{-1} shows the existence of Si-O group. The disappearance of absorption bands at 877 and 3689 cm^{-1} corresponding to the Si-O-H groups showed the esterization of carboxylic acid with silanol and the grafting of AA and/or AM on the sepiolite surface occurred. The grafting mechanism was presumed that the hydroxyl groups in sepiolite may react with AA, and then radical polymerization take place. Another possible mechanism is that the hydroxyl groups may react with radical and liberate free radicals on the sepiolite structure and that the graft polymerization will take place on these free radicals, giving AA-AM branches on the sepiolite backbone.

XRD Analysis

X-ray Diffractograms of Hydra gel, Nanoclay and Nanoclaycomposite

According to Sarkar *et al.* (2012) the reactions between the clay and polymer were also investigated by XRD. The XRD patterns of various clays and their corresponding superabsorbent composites incorporated with 10 wt % clay and a physical mixture of clay with pure polymer (10 wt %) are shown in Figures for clays. The XRD pattern of clay 3 showed a strong peak at $2\theta = 7.0$, which corresponded to a basal spacing of 12.6 \AA of the sodium-saturated smectite, which was also found when clay 3 was mixed physically with the polymers. After the reaction this peak disappeared in the polymer/clay 3 composites. After clay 3 (the smectite-dominated clay) was incorporated into the polymeric network, the typical diffraction peak of the smectite clay disappeared; this indicated the intercalation of the polymer into the stacked silicate galleries of the clay and the exfoliation of the clay.

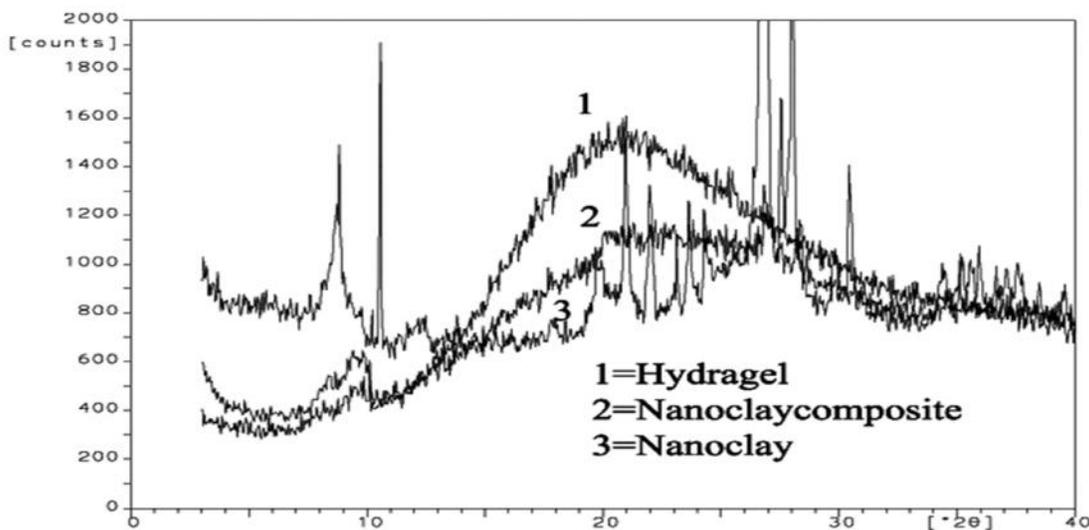


FIGURE 3: Absence or weakening of montmorillonite peak ($6^\circ = 2\theta$) in nanoclaycomposite indicate exfoliation or intercalation of clay during polymerization

In case of the NCPC incorporated with clay, the reaction occurred on the surface of the clays. However, the polymer layer penetrated into silicate layers, and the clay was exfoliated when clay 3 (the smectite-dominated clay) was introduced. The equilibrium water absorbency and nutrient-release rate decreased with the incorporation of clay into the polymer matrix because of the increase in cross-linking points and the decrease in the mesh size of the NCPCs as compared to those in the pure polymer. This cross linking was highest in case of the smectite clay. So, the study suggested that the smectite type of clay should be selected to prepare NCPCs to obtain better slow-release properties. No effect was found with the presence of amorphous aluminosilicate in the clay. According to Singh *et al.* (2010) XRD pattern of clay (1:1), exhibited the scattering due to their c-axis spacing, but significant

distinguishing peak observed in back bone and NCPC because of only intercalation of clay surrounding the polymer.

Scanning Electron Micrograph Analysis

Adzmi *et al.* (2012) also showed that there was a clear distribution of conidia of *Trichoderma harzianum* UPM 40 loaded in Ca –alginate MMT clay. Singh *et al.*, (2010) also described the surface morphology of NCPC. Micrographs of clay exhibited disordered flakes with ragged and some irregular edges. Clay free gel was comparatively smooth. Zhang *et al.* (2005) also exhibited the micrographs of sepiolite was needle shaped where sepiolite free composite was homogeneous. The sepiolite nanocomposite was 85 nm which confirmed that it was a nanocomposite.

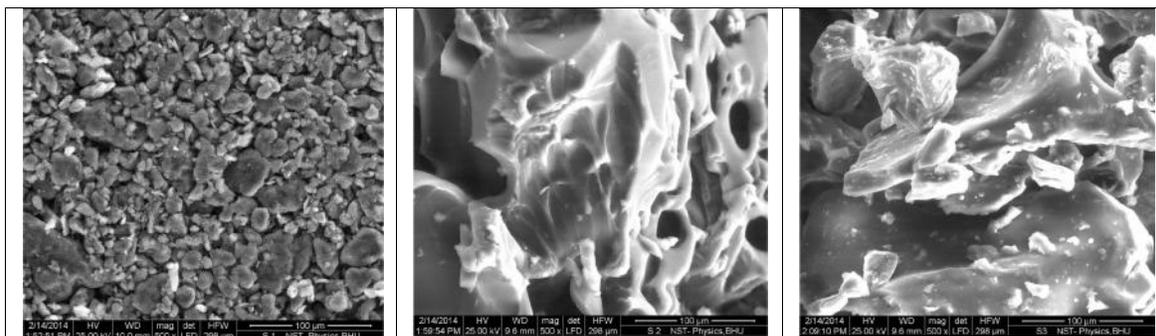


FIGURE 4: Scanning electron microgram of clay (S1), nano polymer composite without clay (S-2) and nano-clay polymer composite (8%) loaded with *Trichoderma harzianum* (S-3)

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