

PREPARATION AND CHARACTERIZATION OF CO-POLYMER (ACRYLIC ACID AND ACRYLAMIDE) AS SUPER ABSORBENT COMPOSITES GRAFTED WITH THAR CLAY

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ABSTRACT: *Thar clay grafting acrylic acid/ acrylamide super absorbent composites with high absorbing water/graft ratio were synthesized by the co-polymerization reaction between Acrylic acid(AA), Acrylamide(AM), and their clay in aqueous solution. The grafting copolymerization reaction mechanics, thermal stability, and morphologies of the composting were determined by FTIR, X-Ray Diffraction, and scanning electron microscope and thermogravimetric analyzer. The contents of clay, initiator concentration on the grafts proportions, and on the water absorption were determined. Water absorbency showed decreased tendency when escalating the contents of clay up to 30%, and after reducing abruptly after rising contents of clay. FT-IR spectroscopic results confirmed the occurrence of Acrylamide/ Acrylic acid in the backbones of clay. Thermogravimetric analysis shows the prologue of the clays to the networks of polymers resulting in rising in the stability of thermal variation. The SEM microstructures also proved grafting of Acrylic/ Acrylamide Acid onto the backbones of clay. Moreover, the results of superabsorbent composites are showing the greater water absorbent and the ultra-fine mineral powder in the formed clay acting as the cross-linkage agent playing a significant role in making the network structures of the superabsorbents composites.*

Keywords; Superabsorbent polymers, graft copolymerization, clay, water-absorbent

1. INTRODUCTION

The superabsorbents are insecurely cross-linked polymer network that may absorb and retain the soluble liquids up to a hundred times with their self-weight. Various steps have been taken to alter their detection abilities, rate of swelling, and strength of hydrogel [1-5]. Due to higher performance characteristics, superabsorbents adopted largely in horticulture, agriculture, hygiene, cosmetics, and delivery of drugs [6-14]. The superabsorbents polymer initially introduced by the agriculture department of America in 1961 [15]. Various steps have been taken to increase the strength of the gel, absorption rate, and capacity. Freshly, the contribution of inorganic materials like clay has been studied for possible decrease in the cost of production and improvement of super absorbent characteristics [16-20]. The addition of these clays does not just decrease the yielding cost it rather accelerates the generation of the latest material for their best application [21-23]. Newly, the reinforced polymers with a smaller quantity of Smectites have drawn interest due to exhibiting notable thermal, mechanical, optical, and various other characteristics [24-26]. Wu *et al.* Organized the super absorbent nanocomposites with a water-absorbent of eleven

hundred times by the grafting of copolymerization in mica and neutral Acrylic Acid and this greatly decreases the yielding cost and improves the water-absorbent characteristics [27-28].

Elsewhere, a comprehensive increase in the characteristics of absorbents and low cost production has been extensively studied [29-33].

In this work, the Co-polymer's characterization of AA&AM as super composites grafted with *Thar* clay has been accomplished.

2. MATERIALS AND METHODS

2.1 Materials

The AA(Acrylic acid) of the analytic grade was from the Tianjin Dengfeng chemicals company China and Acrylamide of reagent grade have the purity ninety-nine percent was bought from Aldrich Company limited China and the N-N-Methylenabisacrylamide use as crossed linking, potassium persulfate, and Sodium Sulfate was obtained by the same company. The nano clay material was obtained from *Thar*, Sindh, Pakistan and the composition of chemicals of *Thar* clay is given in table and fig. 1 show the XRD spectra:.

TABLE 1: Chemical composition of Thar clay of material used in the experiment

S no	Clay Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁺	Organic Carbon
1	Thar Clay (wt%)	47.21	28.03	5.06	3.91	8.11	0.62	3.26	4.01	0.10

**Fig.1 Photograph of Superabsorbent composite**

2 Preparation of super absorbent composites

The groups of specimens with various quantities of clay were prepared by adopting a formal procedure. The clay sample of 36 grams was dispersed in 40ml of distilled water and temperatures raised to 45°C, using water baths. The mixtures were stimulated for forty-five minutes and then the mixed solution of one gram of Acrylic Acid dissolved in 5ml distill water, followed by neutralization with sodium hydroxide solution with 1.5 percent of weight, 1.5 percent by weight sodium hydroxide solution, 1.5 percent of monomers of N. N- Methylenebisacrylamide,

two milliliters of Acrylamide monomers and 1.5 percent weight of water solutions of Potassium Per Sulfate, Sodium Sulfite was gradually poured in the flasks. The solutions were stirred for thirty minutes, maintaining the flow of nitrogen to ensure the achievement of grafting copolymerization. The reaction products, filtered, and washed with distill water and dried in the oven at the temperature of 60°C until the weight of the item was constant. The parameters of the reactions are shown in table 2:

Table 2: Reaction properties of grafting co-polymerization of materials of clay and AM/ AA

Serial No	Materials	Proportion weight by weight
1	Weight of clay of Thar (%)	30 - 50 %
2	Monomers, Acrylamide: Acrylic Acid weight % Cross-linking concentrations	2: 1, 1: 1, 1: 2
3	N N–Methylene bisacrylamide weight ratio Initiators concentrations weight ratio	0.5 – 1.5
4	Sodium Sulfite, Potassium Persulfate weight ratio	1 – 2
5	Temperature of polymerization (°C)	25 – 45
6	Temperature drying (°C)	60

2.3 Analysis of FT- IR

The Fourier transformation infrared spectrum of the superabsorbent composites was recorded on an FT-IR (Thermo Nicolet Avatar 320 spectrophotometer USA) using the ATR technique. The percentage of the total synthetic polymer formed and grafted to clay is called the grafting ratio, determined by the FT-IR technique.

2.4: X-ray Diffraction Analysis

The x-ray diffraction power analysis of the samples was conducted by adopting x-ray diffractometer powders with copper anodes (D5000 Siemens) which runs at forty-kilo volt and twenty milliamper and scans from two to ninety-degree centigrade at 0.005 per minute.

2.5. Morphological analysis

The surface morphology of the superabsorbent composites was investigated by a scanning electron microscopy on (FEI/EO, a type QUANTA Holland) at an accelerating voltage of 10 kV. The samples were coated with a thin layer of gold before the SEM examination.

2.6: Analysis by Thermal

The thermal stability of specimens was analyzed on the thermogravimetric analyzer with temperatures ranging from thirty to nine hundred and fifty degrees centigrade per minute inverse at the scanner rates of ten degrees centigrade per minute inverse by the usage of dried Nitrogen purges at the flowing rates of eighty milliliters per minute inverse.

2.7 Water Absorbency Measurement

The measuring of swelling of the superabsorbents composites was conducted out in the distilled water at the temperature of the ambient. The powder composites of four-gram were immersed in the distilled water about two hundred milliliters for twenty-four hours to reaching the

swell equilibriums that result in the absorptions of the water insides the networks of the composites and forming of the swell specimen. The raw water was disinterested by filtration by a hundred mesh screens. The absorbent of water (QH₂O) of the superabsorbent composites was conducted by the weigh the swelling specimens [21] and the specimens of QH₂O were conducted out by the following formula:

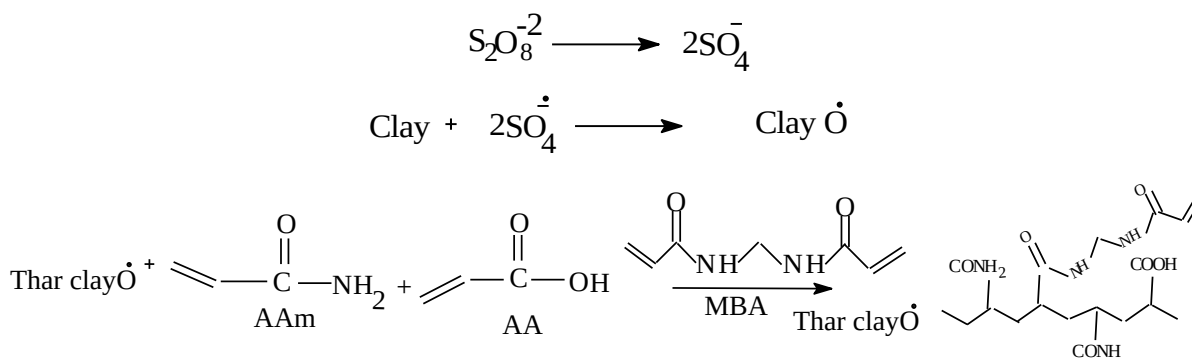
$$WA = (M_2 - M_1) / M_1$$

3. RESULT AND DISCUSSIONS

Thar clay in a homogeneous medium using Potassium persulfate (KPS) and sodium sulfite as a redox initiator and (N,N'-methylenebisacrylamide) MBA as a crosslinking agent under an inert atmosphere, was employed. The effects of the crosslinking concentration and the monomer ratios, (two important variables) on the swelling capacity of the composite were investigated. The reaction mechanism of copolymerization of AA and AAm onto *Thar* clay in the presence of an MBA is shown in Scheme 1.

3.1. Initiator Decomposing

Under the heat for generating the radicals of Sulfate anion, the Persulfate initiators are decomposed. The abstract radical's hydroxyl groups of hydrogen groups of clays of *thar* substrates to forming activating radicals on the substrates. Further that Persulfate redox systems are resulting in activating centers on the substrates to initiating radical polymerizations of acrylamide and acrylic acid leading to the grafting copolymers. Further, the crossed linking agents like MBA occurs in the system, the copolymers comprising the cross-link structures.



Scheme 1

3.2 Diffraction Analysis with X- rays

The clays of *Thar* and the composites were determined by the x ray powder diffractions and the powder patterns of the clays of *Thar* and composites are revealed in fig. 1 (a and b). The spacing of layered is determined by this equation $2d\sin\theta = n\lambda$. The X-ray Diffraction patterns are revealed in fig. 1 (a) of the clay of *Thar* show the parameters at peak 12.3°, 21.9°, 26.3°, 29.3°, 36.3°, 45.3°, 50.3° 2θ. Whereas the relation to x-ray patterns of the three clays composting

are shown in fig. 1 (b) and resulting and indicating that the 12.63°, 24.31°, 29.51°, 31.43°, 34.53°, 35.9°, 37.24°, 42.62° 2θ. The interlinked *Thar* clays patterns showing that the latest peak appeared at the 24.31°, 34.53° 2θ. This results in indicating that the solution of Hydrochloride for Acrylamide reagents may enter the Inter layering and rising the spaces and the similar period the monomers may polymerize under silicates and aluminum layering and enlarges the spaces more.

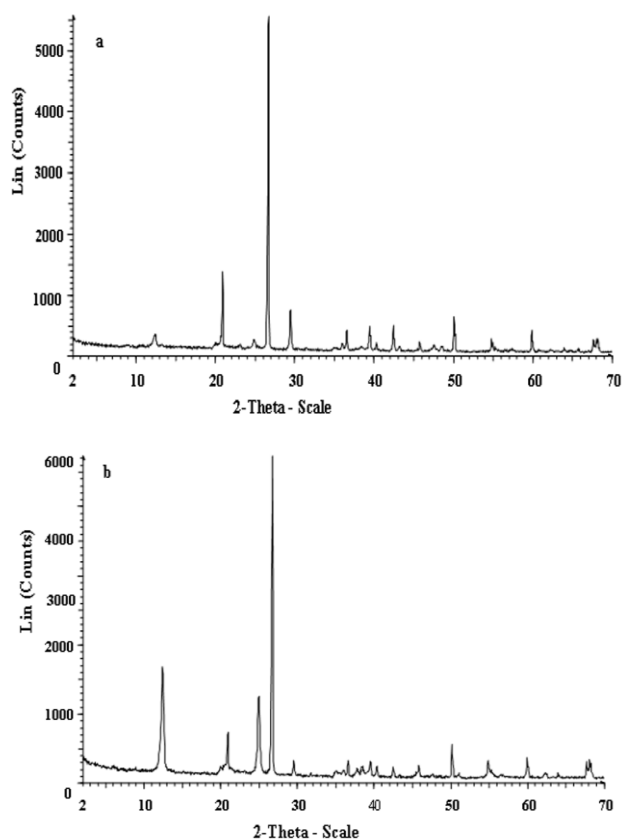
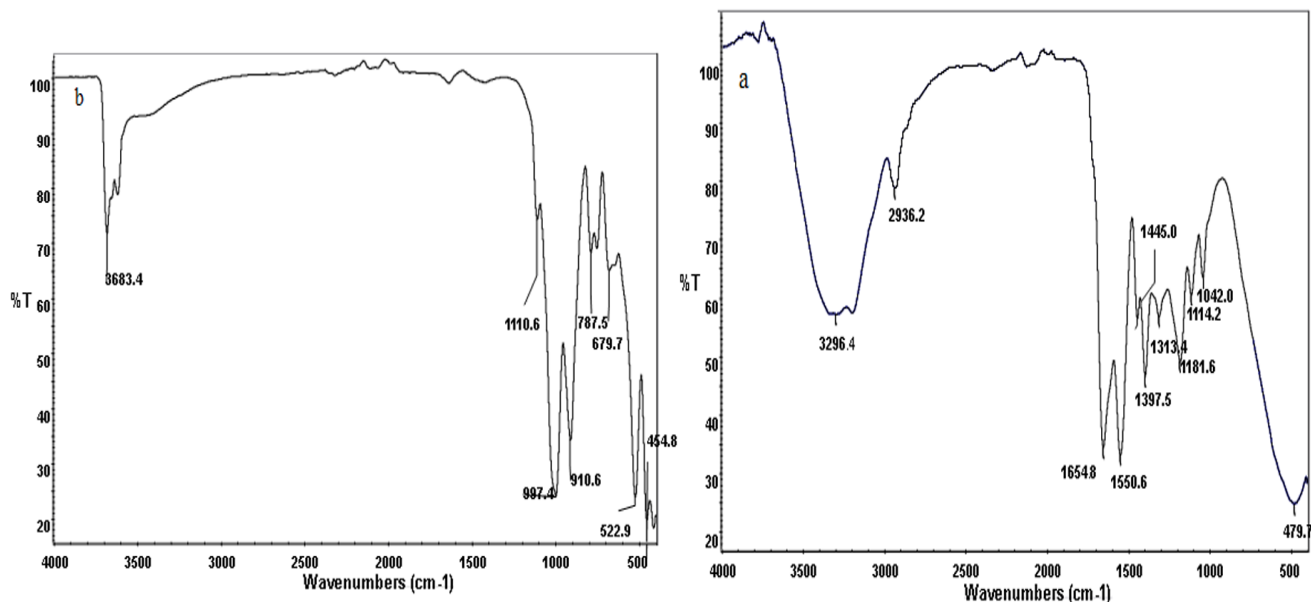


Fig. 1: Powder patterns of XRD for a) clay of thar b) composites of clay thar



3.3 Analysis of FT IR

The analysis of FT- IR of poly AA- co- AM is explained in fig. 2 (a) and could shown which appearing of absorptions band at 3335, 1655 and 1115 cm⁻¹ attributing to amino, amide groups, and bands of hydroxide giving the clear evidence for the reactions in AM and AA.

The spectrum of FT-IR of thar clay and corresponding super absorbents composites incorporated with various weight percents are revealed in figure 2 (b and c) and the absorbing banding in the ranges of 3683 to 3510.6 cm⁻¹ are attributed to the stretch of hydroxide group of clays of thar and parameters peaks at 1110 cm⁻¹ were because of the outer of planes Si- O stretch modes of the thar clays. The bands were attributes at 997 cm⁻¹ to in planes of silicon monoxide stretch for layers of silicates, but the bands at 997 cm⁻¹, 522 cm⁻¹, and 472 cm⁻¹ relating to hydroxide and M-O and Al- O- Si bends [34].

The AA/AM grafts and FTIR medium grafts on the thar clay are shown in fig. 2 (c) and also it could be revealed in fig. 2, where latest banding of absorptions appears at 3336, 1656, 1547.9 and 1385 cm⁻¹ indicating the NH bend of the Amides, -CONH₂ stretch of the Acrylamide unites, c-n stretch and n-h bends for the groups of Amides. The strongest bands at 1652 cm⁻¹ attributes to the stretch's vibrations of carbon are equal to oxygen at 1547.9 cm⁻¹ relating to carbon dioxide. Depending upon the earlier discussions which grafting copolymerization in -OH group on Thar clay and monomers present in the reactions.

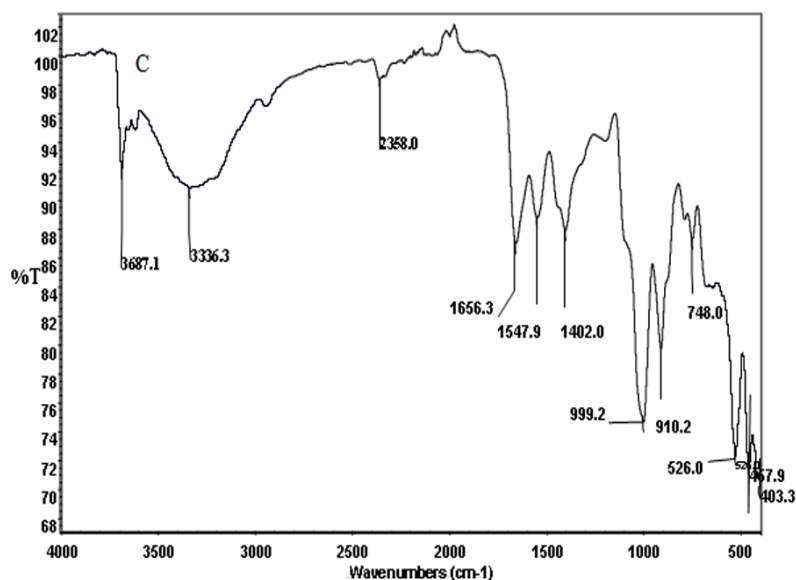


Fig. 2: Spectra of Infrared (a) Poly AA- co- AM (b) Clay of thar (c) clay of thar super absorbent composites

3.4 Effects of contents of clay on absorbent of water

Influence on the contents of clay on absorbents of water is shown in the table-3 for the clay grafts Acrylic Acid and Acrylamide superabsorbent composites and it is worth mentioning that the number of powders of clay is the significant factor affecting water absorbent capacity of the grafts of clay with these acids. The reduced composites raise the quantity of clay from five-thirty percent of the weight, [25].

In this experimental work, the AA&AM and a group of hydroxide on the surface of the clays reduce the absorbents of water on the supersorbents of water on the supersorbents composites with the thirty percent by weight.

Captivatingly, the reduction of tendencies of water-absorbent with rising contents of clay can attribute to the given facts. The interactions in Acrylic Acid and Acrylamide and the clay slowly concentrated with raising the contents of clay. Therefore, greater physical and chemical cross-linking were made in the networks of polymers which rises the cross-linking densities of the polymers and the elasticities of the reduction of chains of polymers that reduces the absorbents of water of the composites of superabsorbents. Further, the superabsorbent composites' hydrophilicity is the lesser with the greater contents of clay which restricted the swelling. These results are similar to the experiments of Wu et al. [27].

The absorption parameters of the poly Acrylamide- co- Acrylic Acid were to determine for comparisons which are shown in table 3 and the absorbent of water in these both composites was greater than the Thar clay of super absorbent composites in distill water at maximum reactive conditions.

TABLE- 3: Effects of the number of clays on the absorption of water of super absorbent

S no	The weight percent of clay contents	Absorbents of water (gm/gm) Q_{eq}
Clay of Tthar		
1	5	986.2
2	10	870.1
3	20	669.3
4	30	575.8
5	35	450
6	40	335.6
Poly (AM/ co- AA)		
6		1119.5

3.5 .Thermal stability

The thermogravimetric analysis curve of the clays grafting Acrylamide/ Acrylic Acid super absorbent compositing incorporates with different amounts of clays were depicts and compares in figure 3 (sample 1, 2, 3, 4 and 5) and it is obvious from the outcomes which the thermally decomposes shifts to the higher temperatures regions significantly where the contents of thar clay rise and mostly these super absorbents composite exhibit the three stagings thermally decomposition. The initial step is in the limit of seventy to one hundred and eighty-degree centigrade is because of lesser moist founds in the specimen and following the initial step the quickest weights losing in the temperatures of two hundred and ninety to four hundred and ninety-degree centigrade is attributed to the thermally decomposing of amide sides group of Acrylamide/ Acrylic Acid and crossed linkers on the networks[35-36]. The slowly losing weigh of Kaolinite/ PAM compositing at six hundred and eighty to seven hundred degrees centigrade is recommended because of the thermally decomposing of the Poly Acrylamide chain backbone. The 3rd step is in the limits of six hundred and eighty

to seven hundred and fifty centigrade is suggested because of the thermally decomposing of the inorganic Poly Acrylamide clay chain backbone. It could conclude from the said information which observes from the thermogravimetric analysis curve which clay microparticles in networks may act as the heating barriers enhancing the all thermally stability of the systems.

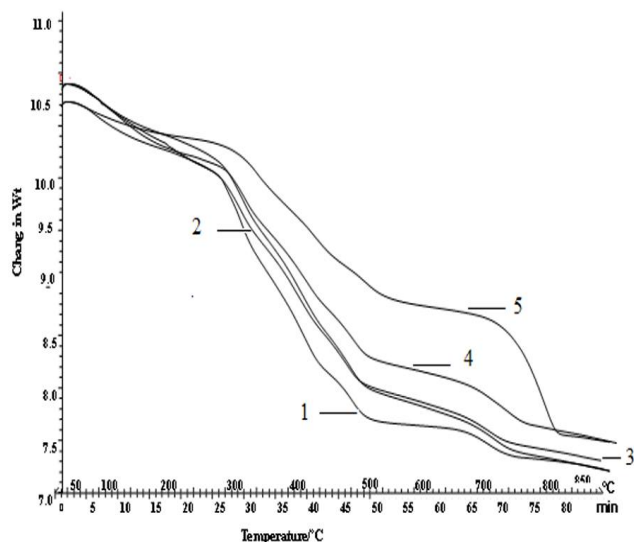


Fig.3.Effect of the quantity of clay on the thermal stability of the superabsorbent composite (1: 0.00 wt% clay, 2: 5 wt% clay, 3: 10 wt% clay, 4: 20wt% clay, 5: 30 wt% clay)

3.6. Influencing of initiators on the degree of grafts

The influencing of the quantity of the initiators on the degree of grafts of Acrylamide/ Acrylic Acid on the clays is shown in table and fig. 4. It is obvious from the outcomes (greater intensities) which are grafts degrees importantly rising with rising initiators contents up to thirty percent and after reduces constantly with raising the initiator's contents. The increase can be attributed that the Hydroxyl groups found in the clay of *Thar* can react with the Potassium Persulfate and liberates ions on the structures of clay and grafting copolymerization will occur on this given poly AM co- AA branching on the backbones of *Thar* clay. The other cause for the improvements in grafts proportions for the superabsorbents composite owns to introducing the initiators may be attributed to the facts which clays containing a greater number of the cations like sodium ions, calcium ions, grouping functions like Carboxylates[37-38],

TABLE 4: Effects of initiators contents on grafts degree of the superabsorbent composite

Serial no	Initiators weight in percentage	Grafts proportion in percentage
1	1	8.8
2	2	19.8
3	3	29.4
4	4	20

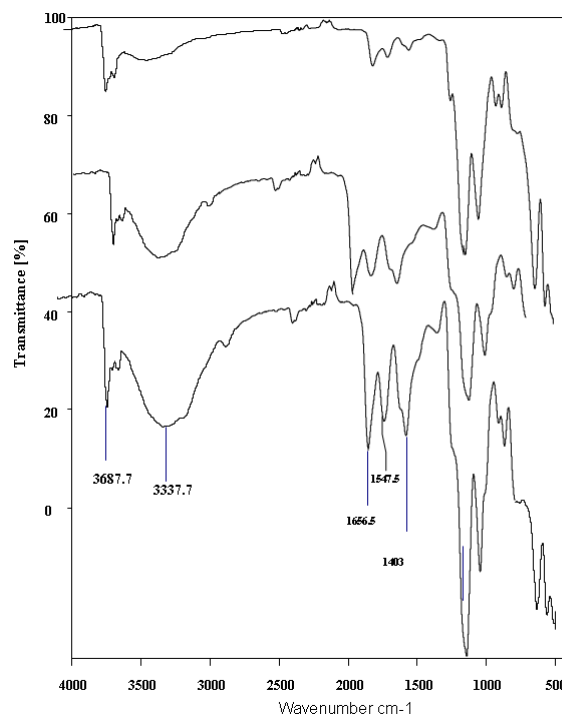


Fig. 4: Effects of initiators contents on grafts degree of the superabsorbent composite

OH and Amino groups. Furthermore, the clay of *Thar* could chemically bond with the improvement of the networks of polymers among the process of polymerizations and suggests that the reactions of chemicals for the grafts are mostly completed.

3.7. Morphological Analysis

The surface morphology of *Thar* clay and its superabsorbent composites are shown in Figure 5(i)(a-c) and snapshots of the super absorbent compositing are given in fig. 5 (ii) respectively. The surfacing morphologies of the ingrafting clays are depicted in fig. 5 (a) that has a totally diverse character than the grafting polymers. The snapshots of the ingraft clay resins showing greater roughly and the shapes of the particles are irregular, but grafts polymers had good network structures and microporous appearing on the micrographs of the clay of *thar* Acrylamide and Acrylic Acid. The scanning electron microscopy micrograph of the cross-linking of *thar* clay Acrylamide/ Acrylic Acid contains thirty percent as depicted in fig. 5 (c) showing losing and greater pouring comparing to clay of *Thar*. The surfacing is suitable for the penetrations of water in the networks of polymer and can be the benefitted to absorbent of water of the corresponding superabsorbent composites. The particle sizes of *thar* clay composites are lesser than the clay of *thar* and may explain the reduction of particle sizes leading to

the rising of the properties of absorption of water due to the particles laid side by side and several spacing would be left in the swelling particles. That spacing would be known interstitial volumes that serving to accommodate more water by the unique capillary actions and if the sizes of the particles are too smaller than the absorption of water was reduced by varying the cross linking densities [27].

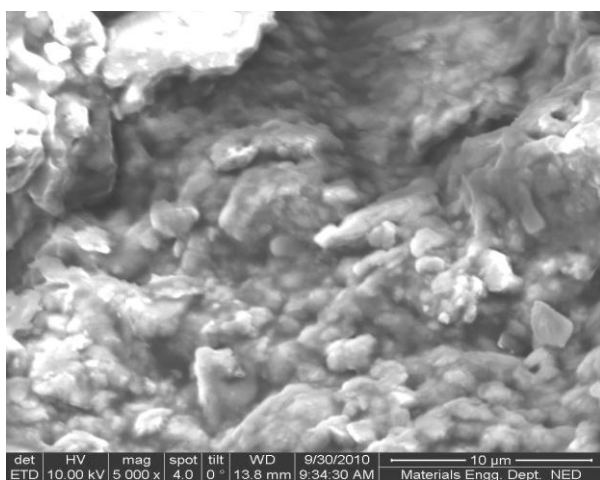
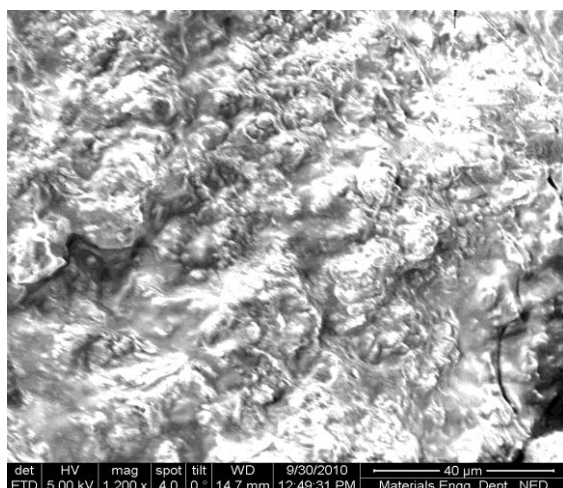
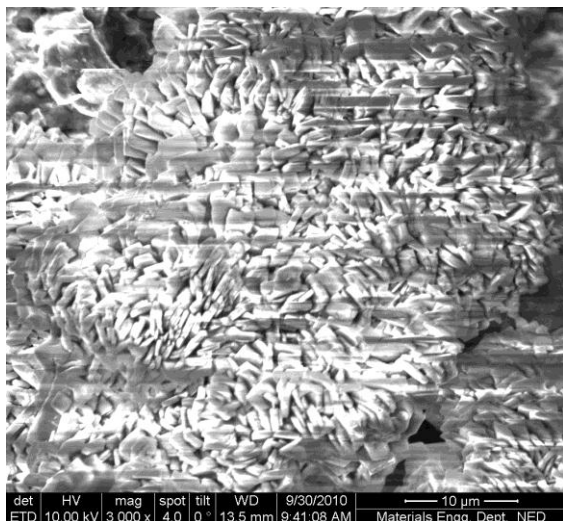


Fig. 5(i): Scanning electron microscopy micrographs for dried superabsorbents (a) ungrafted absorbent resin (b) Thar clay –g – AA/AM (32wt % clay) (c) Thar clay –g – AA/AM 35 wt % clay)



Fig. 5(ii) Photograph of Superabsorbent composite

4. CONCLUSION

The Novel poly AA-co-AM clay of *their* super absorbent composting were synthesized by the grafting co-polymerizations reactions of Acrylic Acid and Acrylamide onto the clay adopting n.n-Metylenebisacrylamide as the crosslinkers, and potassium Persulfate as an initiator in solvent solutions. The equilibrium absorbent of water and grafts proportion for the super absorbent composting was greatly affected by the contents of the clays and the higher absorption of water. The graft's proportion was determined when thirty-five percent of clay by weight was incorporated. The FT- IR indicates the reaction occurring in –COO- groups on the surfacing of the clay of *thar* micro powder. The scanning electron microscopy reveals greater dispersions of particulates in the matrix of polymers. The thermodynamic analysis shows that the clay has significant influences on thermally stable composites for *Thar* clays which in other words, enhances thermal stability of the composites of super absorbent.

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