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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF SIBI BENTONITE CLAY-GRAFT-POLY (ACRYLAMIDE/CO-ACRYLIC ACID) SUPERABSORBENT COMPOSITE AND ITS ABSORBENCY STUDY OF WATER

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Abstract

This research paper presents the novelty of a new Na-Bentonite-graft-acrylamide/acrylic acid superabsorbent composite material that has high water absorbency and whose graft ratios were established by graft-copolymerizing acrylamide, acrylic acid, and Sibi Bentonite together in an aqueous solution. Fourier Transform Infra-Red Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and a Thermogravimetric Analyzer (TGA) were employed to determine the shape, thermal stability, graft copolymerization reaction process, and the effects of Na-Bentonite content, initiator concentration, and grafting ratio on the water absorbency of these composite materials. According to the findings, clay concentration increased while water absorbency showed a decrease. FTIR analysis confirmed the presence of acrylamide/acrylic acid on the backbone of clay. TGA data indicated an increase in thermal stability of the sample with the addition of Sibi Bentonite to the polymer network. The SEM results showed the grafting of acrylamide and acrylic acid onto clay. The cross-linking agent Sibi Bentonite in the form of ultrafine mineral powder is crucial in the development of the superabsorbent composite's network structure.

Keywords: Sibi Bentonite, superabsorbent polymer, graft copolymerization, water absorbency, swelling.

1 Introduction

Loosely crosslinked polymeric networks, known as superabsorbents, are capable of absorbing and holding onto aqueous fluids at levels surpassing several hundred times their own weight. Under specific loads, the absorbed water remains bound within the sample without release. Numerous attempts have been made to modify these materials, focusing on enhancing their swelling capacity, controlling the rate of swelling, and fortifying hydrogel strength (Lim *et al.*, 2002; Vazquez *et al.*, 2008; Wu & Liu, 2007; Zhang *et al.*, 2006; Zhang *et al.*, 2007). These superabsorbent materials have attracted significant attention and find widespread applications across various industries, including agriculture (Vazquez *et al.*, 2008), horticulture (Hooper *et al.*, 1990; Shiga *et al.*, 1992, 1993; Wu *et al.*, 2003), hygiene, food, cosmetics (Kikuchi & Okano, 2002; Po, 1994), and medical delivery systems (Felhi *et al.*, 2008; Pourjavadi *et al.*, 2006). The inception of superabsorbent polymers dates back to 1961, when the Department of Agriculture in the United States first prepared these innovative materials (Costa *et al.*, 2008).

Most superabsorbent polymers are made using acrylic acid as a key component. However, acrylic polymers typically exhibit limited gel strength. These polymers have undergone extensive modifications to improve their gel strength, absorption capacity, and absorption rate. Moreover, pure superabsorbent polymers are also quite expensive to purchase. Recently, there has been a growing focus on the inclusion of inorganic materials, such as clay, as they have the potential to reduce manufacturing costs while improving the characteristics of superabsorbent materials (Andrejkovičová *et al.*, 2008; Ni *et al.*, 2008; Patent, 1961; Tiwari *et al.*, 2008; Xu *et al.*, 2007). The incorporation of clay not only decreased manufacturing costs but also enhanced the mechanical, thermal, and swelling characteristics of superabsorbent materials. This has led to the rapid development of these novel materials for specialized applications (Gao *et al.*, 2001; Lagaly *et al.*, 1999; Mostafa, 1995). There is a recent rise in interest in smectite-reinforced polymers because of the exceptional optical, thermal, and mechanical qualities of these heterostructure materials, increasing their technological value (Li & Wang, 2005; Lin *et al.*, 2000; Zheng *et al.*, 2007). Lin *et al.* (2001) reported the creation of superabsorbent nano-composites through the graft-copolymerization of mica or montmorillonite with partly neutralized acrylic acid, resulting in significantly lower manufacturing costs and improved water-absorbing qualities (Santiago *et al.*, 2007).

Amourphase iron oxides, chlorite, calcite, feldspar, quartz, aluminium silicates are all present in Sibi clay, sourced initially from the Koh-e-Sulaiman Mountain. The presence of aluminium silicate in the clay suggests potential advantages for enhanced water absorption properties. The process of copolymerization (graft) between Sibi clay and acrylamide-coacrylic acid (poly) is anticipated to increase the variety and quantity of hydrophilic groups, thereby influencing the network structure of the resulting superabsorbent materials (Omidian *et al.*, 1998; Santiago *et al.*, 2007).

Consequently, these modifications contribute to an overall improvement in the absorbent qualities of the superabsorbent composite materials while concurrently reducing manufacturing costs (Chen *et al.*, 2005; Lee & Chen, 2005; Li *et al.*, 2005; Ramazani-Harandi *et al.*, 2006; Wang *et al.*, 2007). This study delineates the synthesis of a novel superabsorbent composite material crafted from Sibi clay and poly (acrylamide/acrylic acid), characterized by a high grafting ratio and impressive water absorption capabilities.

2 Materials and methods

2.1 Materials

The analytical grade acrylic acid (AA), reagent-grade acrylamide (AM), and N,N.'-methylenebisacrylamide (MBA) employed as crosslinkers, sodium sulfite (SS), and potassium persulfate (KPS) were procured from Aldrich Co. Limited, Germany. All other chemicals were also of reagent grade. Table 1 displays the chemical composition of Sibi clay, while Figure 1 depicts its XRD spectrum.

Table 1. Chemical composition of Sibi clay.

Clay materials	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**NaO**	**K_2O**	**H_2O**	**Organic carbon**
Sibi clay (wt%)	47.21	28.03	5.06	3.91	8.11	0.62	3.26	4.01	0.10

2.2 Preparation of superabsorbent composite materials

These techniques were used to make a variety of samples using varied clay concentrations. Five grams (5 g) of clay powder was added to distilled water (40 ml) in a 250 ml flask and thoroughly stirred. The mixture was continually agitated for 45 min at 45°C. Subsequently, a solution comprising 1.5 wt% NaOH solution, 1.5 wt% N, MBA monomer, 2.0 mol of acrylamide monomer, 1.5 wt% potassium persulfate, sodium sulfite water solution, and acrylic acid (1g) was added to the flask. This experimental procedure was conducted under an atmosphere of nitrogen. The resulting product underwent precipitation, filtering, washing of the filtrate with distilled water, and finally drying in an oven at 60°C (Table 2).

Table 2. Reaction parameters of graft copolymerization of clay material and acryl amid acrylic acid.

Materials	Ratio
Sibi clay (wt%)	30% ~50%
Monomer, AM: AA (wt%) ratio Crosslinker concentration	2:1, 1:1, 1:2
N,N’-Methylenebis acryl amid (wt%) Initiator concentration (wt %)	0.5 ~1.5
Potassium persulfate, sodium sulfate (wt%)	1~ 2
Polymerization temperature (C°)	25-45
Drying temperature (C°)	60

2.3 FT-IR analysis

Fourier transform Infrared spectra of the superabsorbent composites were recorded using a FT-IR (Thermo Nicolet Avatar 320 spectrophotometer, USA) employing an ATR technique. The grafting ratio, representing the percentage of the total synthetic polymer formed and grafted to clay, was determined using the FT-IR technique.

2.4 XRD analysis

The composite material samples were prepared in powder form, and their XRD spectra were obtained using an X-ray diffractometer with Cu anod SEIMENS D50000 operating at 40 kV and 20 mA with scattering measurements conducted in the range of 2 to 90°

2.5 Morphological analysis

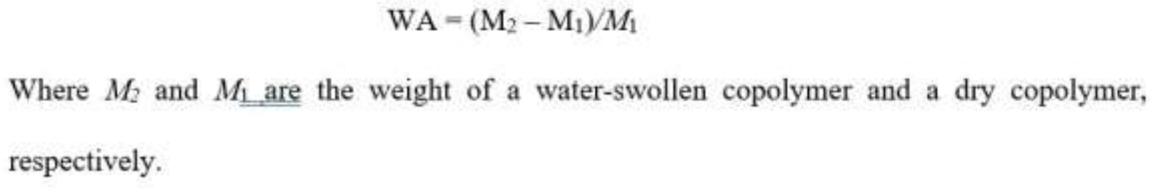
The surface morphology of the superabsorbent composite material sample was studied using a SEM at a 10 kV accelerating voltage using a FEI/EO of the Quanta Holland type. Prior to their placement in the SEM, the samples were coated with a thin layer of gold film.

2.6 Thermal analysis

The thermal stability of samples was investigated using a thermogravimetric analyzer, a Mettler Toledo TGA/SDTA 851e thermal analyzer, operating at atmospheric pressure.

2.7 Measurement of Water Absorbency

The measurement of swelling for samples of superabsorbent composite materials was conducted using distilled water at room temperature. In order to attain equilibrium for swelling, powdered composite (1g) was submerged in distilled water (200 ml) and left for a minimum of 24 hours. The water was absorbed into the network of the composite material, resulting in the formation of swollen samples. A 100-mesh screen was used to filter out the excess water. The water absorbency (QH_2O) was estimated by weighing the swollen samples of the prepared superabsorbent composite materials, following the method described by Xie *et al.* (2012). The following formula was used for the computation of the water absorbency (WA), i.e., (QH_2O) in the samples:



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

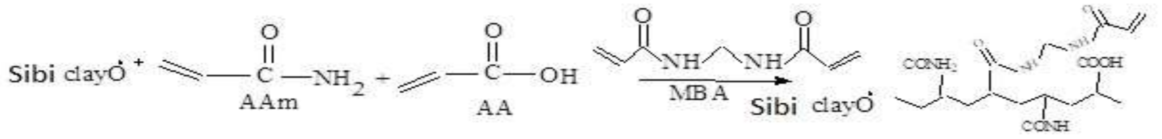
Where M_2 and M_1 are the weight of a water-swollen copolymer and a dry copolymer, respectively.

3. Results and Discussion

The KPS and SS were used as redox initiators. In an inert environment, the crosslinking agent was an MBA. Acrylic acid and acryliamide were concurrently glued to Sibi clay. The ability of composite material to expand depends on two crucial variables, i.e., the concentration of the crosslinkers and the ratio of monomers employed. The reaction process is illustrated in Scheme 1.

$$S_2O_8^{-2} \longrightarrow 2SO_4^{\overset{\bullet}{-}}$$

$$\text{Clay} + 2SO_4^{\overset{\bullet}{-}} \longrightarrow \text{Clay }\dot{O}$$



Scheme-1

3.1. Initiator decomposition

The persulfate-active redox system led to the formation of active centres on the substrate. They act as initiators for the radical polymerization of acrylic acid and acrylamide, resulting in the formation of graft copolymers. The graft copolymers are formed due to the covalent bonding of the active centres in the presence of a crosslinking agent, i.e., MBA.

3.2. XRD analysis

The Sibi clay and the resulting composite materials were also examined using XRD. Figure 1(a and b) shows the powder patterns of the Sibi clay and its composite. The spacing between two layers, 'd', is calculated using Bragg's equation: $2d \sin \theta = n\lambda$

where θ is the angle of diffraction and λ represents the wavelength of the incident X-ray. The XRD pattern for Sibi clay, Figure 1(b), has distinctive peaks at 12.3°, 21.9°, 26.3°, 29.3°, 36.3°, 45.3°, and 50.3°. The XRD pattern of the Sibi clay composite material is shown in Figure 1(a). The XRD pattern of the composite material exhibits additional peaks at 12.63°, 24.31°, 29.51°, 31.43°, 34.53°, 35.9°, 37.24°, and 42.62°. According to the intercalated Sibi clay pattern, a new peak may be seen at 24.31° and 34.53°. The data suggests that the acrylamide reagent HCl solution may have penetrated in between the layers of the composite material and is the cause of an expansion in the spacing between its two successive layers, i.e., 'd'. The formation of monomer and its polymerization may take place simultaneously and increase the gap 'd' between the layers of aluminium and silicate.

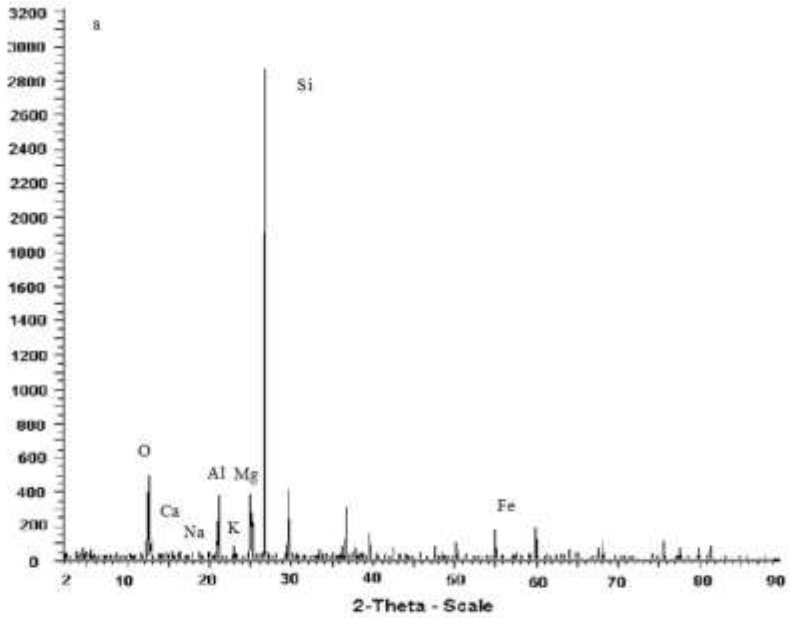


Fig.1.（a）XRD pattern of composite material

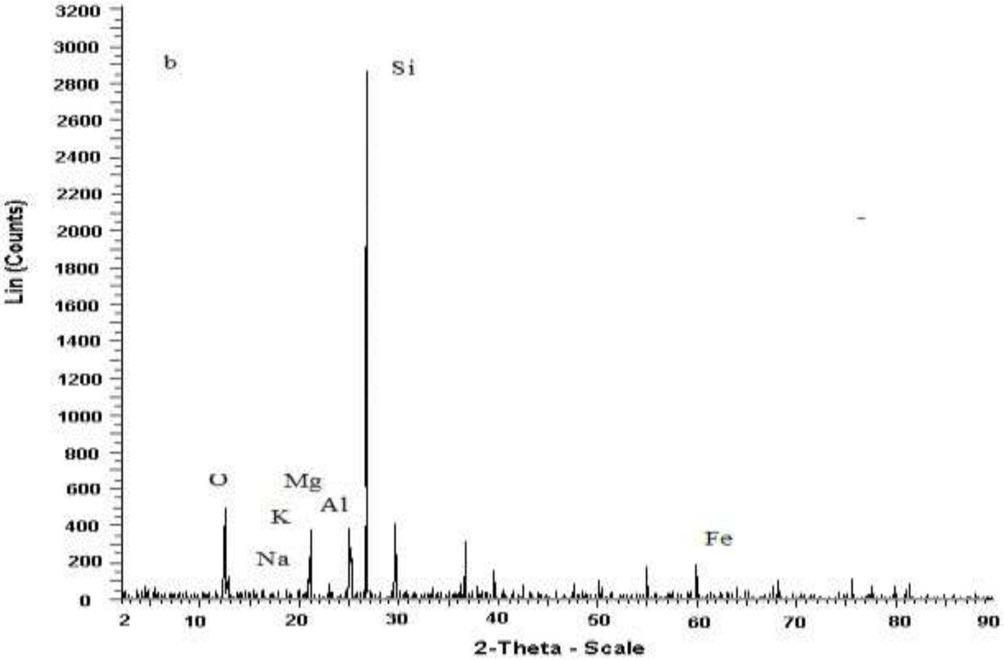


Figure 1.（b）XRD pattern of Sibi clay.

3.3. FT-IR analysis

The FTIR results for poly (acrylic acid-co-acrylamide are displayed in Figure 2(a). In Figure 2(b), Sibi clay materials containing various weight percentages of clay are shown. The existence of absorption bands between 3683 cm^{-1} and 3510 cm^{-1} is shown in Figure 2(b).

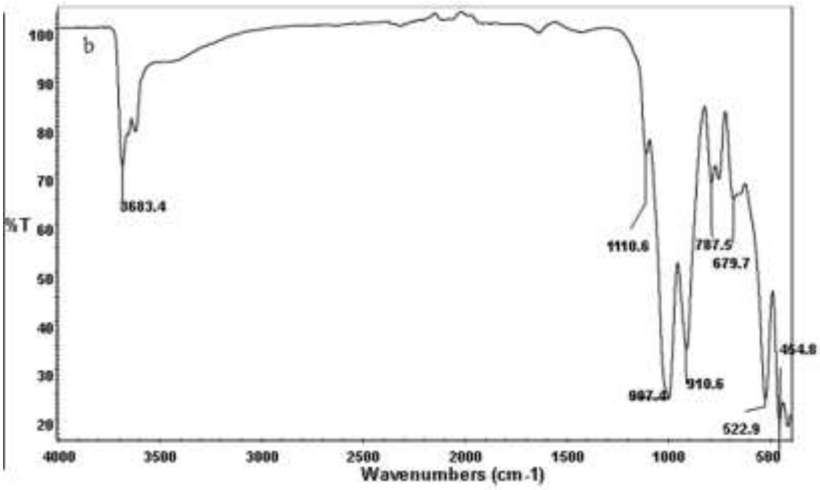


Figure 2. Infrared spectra of **(a)** Poly (acrylic acid-co-acrylamide) **(b)** Sibi clay **(c)** Sibi clay superabsorbent composite.

Figure 2(b). Infrared spectra of Poly (acrylic acid-co-acrylamide).

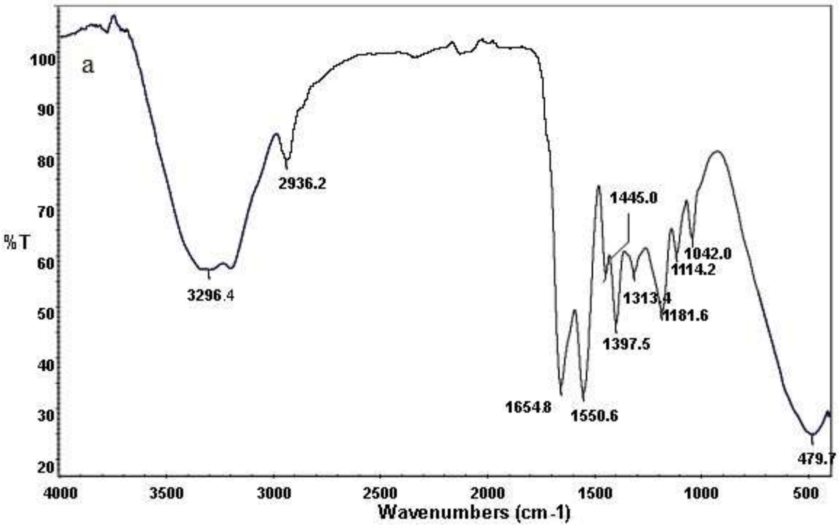


Figure 2. (a) Infrared spectra of Sibi clay.

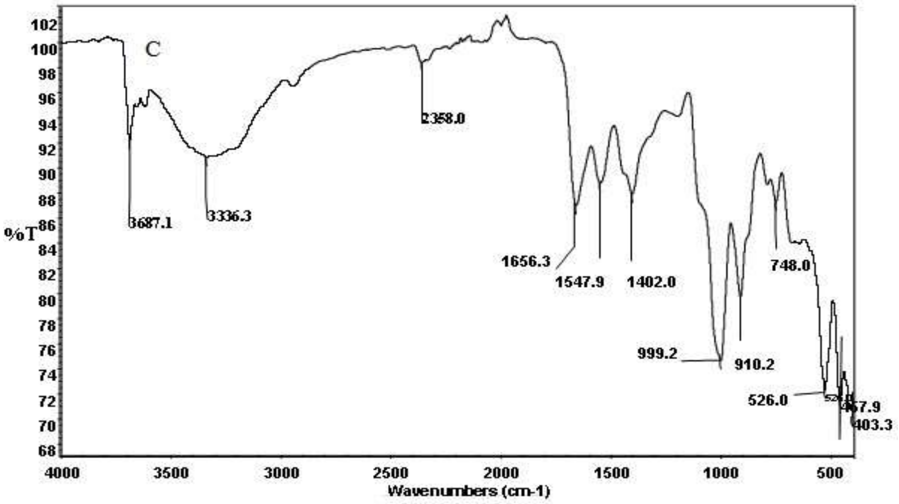


Figure 2. (c) Infrared spectra of the Sibi clay superabsorbent composite contributed to the ⁻OH groups, and the absorption bands located at 1110 cm^{-1} of the Sibi clay is attributed to the Si-O stretching. (Lanthong *et al.*, 2006).

Figure 2(a) shows the spectrum of AA/AM. New absorption bands can be observed at 3296.4 cm^{-1} and 1654.8 cm^{-1} and 1550 cm^{-1} attributed to the N–H stretching of the acrylamide unit, the -CONH2 stretching, the C-N stretching, and the amide group N-H bending, respectively.

In Figure 2(c), additional bands appeared in comparison to Figure 2(b). These new absorption bands are located at 3296.4 cm^{-1}, 1654.8 cm^{-1}, and 1550.6 cm^{-1}. The peaks observed at 320.4 cm^{-1}, 2936.2 cm^{-1}, 1654.8 cm^{-1}, and 1550.6 cm^{-1} are attributed to the N–H stretching of the acrylamide unit, 2926 cm^{-1} was attributed to the –C–H stretching of the acrylate unit, 1654.8 cm^{-1} is attributed to the -CONH$_2$ stretching, and the C-N stretching of the acrylate unit, 1550.6 cm^{-1} is attributed to NH and is related to the carbonyl moiety stretching of the acryl amide. It is suggested that the graft copolymerization between the –OH groups on Sibi clay and the monomers occurred during the reaction.

3.4. Water absorbency as affected by clay content

Table 3 shows how clay concentration affected the superabsorbent clay-graft composite made up of acrylic acid/acrylic acid and the quantity of water it can absorb. It has been shown that the quantity of clay powder has a significant impact on how well the clay graft acrylamide/acrylic acid superabsorbent composite absorbs water.

Table 3. Effect of the concentration of clay on water absorbency of the super absorbent composite materials.

S.No	Clay content (wt %)	Water absorbency (g/g) Qeq
1	5	986.2
2	10	870.1
3	20	668.3
4	30	575.8
5	35	450
~~6~~	~~40~~	~~335.6~~
~~Poly(acrylamide-co-acrylic acid)~~		~~940.6~~

These findings clearly demonstrate that the water absorption in composite material is generally reduced with an increase in clay concentration in the sample. However, water absorbency initially tends to increase and then dramatically drops as the clay percentage in the sample is increased from 5 to 30 weight percent. These findings are in good agreement with earlier results, as reported by Lin *et al.* (2000). We can conclude that more crosslink sites are created with an increase in the concentration of clay in the specimen. This leads to an increase in crosslink density, which lowers the water absorbency in the resulting composite materials. Additionally, the -OH group might react with surface clays with acrylamide and acrylic acid to strengthen the polymeric network, making it more difficult for water to permeate the composite network and, consequently, reducing water absorbency. In our investigation, the same interactive effects among OH groups and AA/AM were determined on Sibi clay powder. The following facts may be responsible for the declining water absorbency trend with rising clay concentrations: With an increase in clay concentration in the composite material, the interaction between clay and AA/AM grew more intense. As a result, the polymeric network developed more physical and chemical cross-links. A decreased hydrophilicity due to a greater clay component is the cause of less swelling. The findings are in line with the experiment conducted by Lin *et al.* (2001). They reported that among the three types of superabsorbent composites, the composite containing kaolinite had the maximum water absorption, followed by that of doped bentonite and doped sericites. Poly (acrylamide-co-acrylic acid) was also examined for its water absorption capabilities for the comparison. In distilled water under ideal reaction conditions, Table 3 shows that poly (acrylamide-co-acrylic acid) had a greater water absorbency than the Sibi clay superabsorbent composite.

3.5. Thermal stability

Figure 3 shows and compares the thermogravimetric analysis (TGA) curves for samples 1, 2, 3, 4, and 5. The findings clearly indicate that an increase in Sibi clay concentration significantly influences thermal decomposition, particularly at elevated temperatures. The reduction in moisture content in composite materials occurred in the first stage, spanning from 70 to 180°C. In the second stage, there is a rapid weight loss observed between 290 and 490°C, attributed to the thermal breakdown of the network's crosslinker and the amide side group of AM/AA.

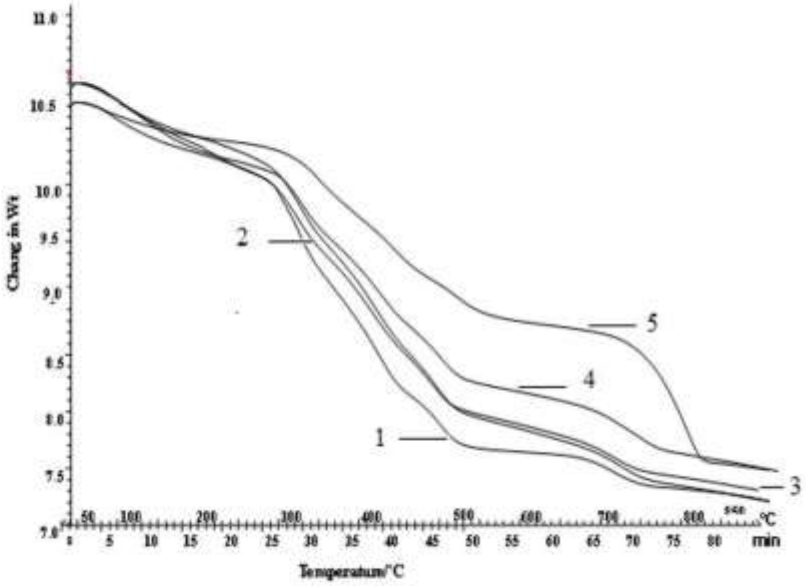


Figure 3. Thermal stability of composites under the influence of clay at varied levels (Samples: 1 with clay content 5%, 2 with clay content 10%, 3 with clay content 20%, 4 with clay content 30%, 5 with clay content 40%, and 6 with clay content 50%).

Similar thermal behaviour for polyacrylamide has also been observed (Lanthong *et al.*, 2006; Patel *et al.*, 2007). The thermal degradation of poly-acrylamide is thought to be the cause of the PAM/kaolinite composites' steady weight losses at 680°C and 700°C. The third stage, which occurs between 680°C and 750°C, is thought to be caused by the thermal breakdown.

3.6. Influence of initiator on grafting degree

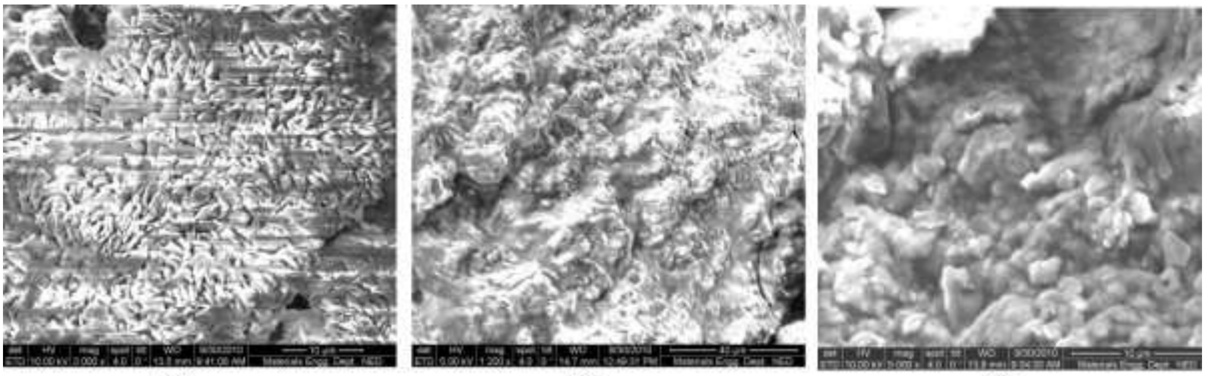
In superabsorbent composite materials, the value of the AM/AA grafting ratio on clay strongly depends on the concentration of initiator (w%) and is given in Table 4. The findings clearly show that the grafting ratio increased dramatically with an increase in initiator concentrations, up to approximately 3%. If the initiator concentration is increased beyond 3%, the then grafting ratio decreases steadily, attaining a value of 20. This decrease in grafting ratio might be caused by a reaction between the potassium persulfate and the hydroxyl group in the Sibi clay. Another factor contributing to the increase in grafting ratio for superabsorbent composites following the addition of an initiator is the clay's high content of cations like Na^+, Ca^{2+}, and Fe^{3+} (Mathakiya *et al.*, 1998; Saeidi *et al.*, 2004).

Table 4. Effect of concentration of initiator on grafting ratio in superabsorbent composite materials.

S. No.	Initiator (wt %)	Grafting ratio (%)
1	1	8.8
2	2	19.8
3	3	29.4
4	4	20

3.7. Morphological analysis

The surface morphology of Sibi clay and superabsorbent composite materials prepared using different Sibi clay concentrations are shown in Figure 4(a-c) and Figure 4(ii), respectively. The behaviour of the morphology of clay without any grafting is entirely different from that of grafted polymers and is shown in Figure 4 (a). The resin containing clay without grafting resin seems quite rough and has irregularly shaped particles in the image. On the other hand, Figure 4(b, c) shows that the grafted polymers have fine network structures and appear microporous in the micrograph of Sibi clay-g-acrylamide/acrylic acid. The crosslinked Sibi clay-g-acrylamide/acrylic acid containing 30 wt% SEM micrograph, on the other hand, displays a looser and more porous texture in comparison to Sibi clay.



(a) (b) (c)

Figure 4. SEM micrographs for dried superabsorbent composite materials. **(a)** Sibi clay without grafting; **(b)** Sibi clay with grafting AA/AM (32 wt% clay); **(c)** Sibi clay with grafting AA/AM (35 wt% clay).

Figure 5. Photograph of superabsorbent composite material.

While in Figure 5, this surface makes it easy for water to penetrate the polymeric network and might help the associated water absorption in the superabsorbent composite material. The Sibi clay composite materials have smaller particles than Sibi clay. Because there may be voids between the swelled particles when they are laid side by side, it can be stated that decreasing the particle size results in an increase in the water absorption characteristics of composite materials. This area, which may hold more water through normal capillary action, is known as the interstitial volume. By altering the crosslinking density, it was possible to reduce the water absorption property when the particle size was too small (Lin *et al.*, 2001).

Conclusion

Sibi clay (acrylic acid-coacrylamide) is a novel poly that was created by grafting acrylamide and acylic acid copolymerization reactions onto Sibi clay.The surface of Sibi clay micropowder exhibits interactions between -COO- and -OH groups, according to FT-IR. There is more and fine dispersion of clay particle in the polymer matrix, according to the SEM data. According to TGA curves, clay has a great influence on thermal stability, and adding clay to the polymer network improves the thermal stability of superabsorbent composite materials.

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Author Contributions

SW performed the experiments, MI Khattak supervised the study, and SW, MIK, and MIK wrote the manuscript. Adnan Afridi aligned the figures and tables.

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