



Development of Nanopolymer composite membranes of Chitosan for reverse osmosis

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ABSTRACT

Modern polymer chemistry is highly progressive in tailoring polymers to specific requirements such as mechanical, thermal and chemical stability, with better performance with wide range of pore size. Composite materials combine and maintain two or more distinct phases to produce a material that has properties far superior than either of the base materials. Nanoparticles made of chitosan, a naturally occurring polymer isolated from crab and shrimp shells, have shown to be promising as carriers of anticancer drugs, antitumor genes, and other novel therapeutic agents. Cross linking agents improve the properties of polymer and their products. Polymer nanocomposites are a class of reinforced polymer with low quantities of nanometric-sized clay particle, which improved their fair resistance, strength and its porosity decreases. Hence, in the present work nanochitosan was prepared using sodium tripolyphosphate and composite of nanochitosan were prepared with methylcellulose in the presence of clay. However, a greater understanding of the nanoscale features of clays, and the ability to disperse the ultrafine layers within other materials has led to increased interest in their application in composite materials; to provide properties to lightweight polymers that would usually only be found in heavier or more expensive materials (such as glass or metals). The formation of the polymer membrane made by the immersion precipitation process depends on a large number of material and process specific parameters such as choice of the polymer (molecular weight, molecular weight distribution), choice of the solvents, choice of the casting solution temperature and the casting atmosphere. The composites were analyzed for their thermal stability, porosity, X-ray diffraction studies, etc. The results show that the addition of clay along with the nanosized chitosan had decreased the transparency of methylcellulose and with decreased pore size suitable for developing as RO membranes.

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Introduction

Because of population growth and other geological factors, demand for freshwater has risen. This demand has made many areas of the world highly water-stressed, and future indicators point to escalating water scarcity throughout the world. To increase the supply of freshwater, purification of nonconventional water sources, such as seawater and produced water from oil and gas production, is of considerable interest due to the usual immediate proximity of such water sources to areas that are highly water-stressed (Crini and Badot, 2007; Mondal, 2008). Mankind is searching for a new, cheap source to convert the impure (i.e.) polluted water into pure water. Moreover, with rapid increase in number of factory with booming increase in population. There is always a demand for fresh water. Hence, it is necessary to utilize the available water most carefully and economically.

Chitin, a polysaccharide found in the exoskeletons of insects and shellfish, and chitin's most important derivative, chitosan, is nearly a "model" biopolymer with its useful physical and chemical properties, high strength, biodegradability, and nontoxicity, natural occurrence,

hydrophilicity, chemical resistance, adequate mechanical strength, good membrane forming properties.

Chitin, and its derivative chitosan found in the exoskeleton of crustaceans, the cuticles of insects, and shells of shellfish, the wastes of the seafood industry the cells walls of fungi, is the most abundant aminopolysaccharide in nature. Their distinct advantages include availability, biocompatibility, non-toxicity, antimicrobial properties, heavy metal ions chelation, gel forming properties, etc. (Chiellini et al., 2002; Hudson and Smith, 1998). Awareness on growing public health and environment with in cooperation of increasing stricter environmental regulations on discharged waste, there is a need for the use of biopolymer from renewable resources as alternatives to synthetic polymers (Hudson and Smith, 1998; Kurita, 2001).

This paper looks at how chitosan materials can be exploited in membrane based processes and if they can held advance their application in RO water treatment process. Here we have taken chitosan in the nanoform because the electrospun nanocomposite fibers have great potential for the applications where both high surface-to-volume ratio and strong mechanical properties of fibers in general improve substantially with decreasing fiber

diameter. There is considerable interest in the development of eletrospun polymer nanofibers.

Polymer and clay nanocomposites comprise of organic and inorganic hybrid polymer matrix which has a few nanometers thick and several hundred nanometers long can be used in RO system.

In this composites contain one of the natural kaolinite. Kaolin also plays an important role in the controlling the crystallinity, concentration of impurities. And also very cheaper compare to the activated carbon.

Methyl cellulose is a chemical compound derived from cellulose. It is white powder in pure state. And it dissolves in cold water, forming a clear viscous gel. Cellulose, the most abundant organic polymer in the earth is the main constituent of wood and is a homo polysaccharide composed of β -1-4 glucopyranose units. Each repeating unit of cellulose contains three hydroxyl (-OH) groups (Howell, 2002; Li et al., 1992).

Chitosan, a derivative of the naturally abundant biopolymer chitin, is fully stable in methyl cellulose and hence can be selected for its dehydration, keeping in minds its highly hydrophilic nature and good mechanical strength. The promising potential of chitosan as a pervoporate membrane has already been exploited for dehydration of alcohols such as ethanol and isopropanol. This polymer has recently been used to form selective and permeable blend membranes with poly (vinyl alcohol), sodium alginate, etc. However, unfortunately polymeric membranes behaved unsuitable in terms of selectivity and flux in general for water-organic mixtures (selectivity and flux of about 10 and 0.01 kg/m²h, respectively) (Ravindra et al., 1999a,b, 1998; Shiguang et al., 2001).

There has been an increasing interest towards zeolite membranes due to their strong potential in separation of liquid mixtures by pervoporation. Polymer-clay suspensions and composites have considerable commercial and technological importance (Chang et al., 1991). As a result of the current climate stressing the development of advanced materials, there are also recent reports of *in situ* intercalative polymerization processes (Messersmith and Giannelis, 1993) and of unique structural and electrical properties of polymer-clay composites. Nevertheless, this support is expensive and makes the membranes uneconomical. It is thus important to study the possibility of obtaining membranes with cheep supports. Considering its abundant resource, its low cost and its easy processing into a support with a regular structure by sintering; kaolin is a good candidate for the zeolite membrane. Dehydration of organic solvents is presently the major market of pervoporation. Zeolite NaA membrane were reported to be excellent materials for solvent dehydration by pervoporation. But under slightly harsh conditions and under hydrothermal stresses, zeolite NaA membranes turned out to be unstable due to hydrolysis. There are only a few attempts to develop hydrophilic highly siliceous zeolite membranes of different Si/Al ratios with improved hydrothermal stabilities (Lizhi et al., 2005; Mikihiro et al., 2001, 1998; Takao et al., 2003; Travis et al., 2004).

Cross linking agents improve the properties of polymer such as the stiffness, surface hardness, resistance to temperature and resistance to solvent attack (Mark, 1942) their products. Polymer nanocomposites are a class of reinforced polymer with low quantities of nanometric-sized clay particle, which improved their fair resistance, strength and its porosity deceases. Hence in the present work nanochitosan was prepared using

polyphosphoric acid and composite of nanochitosan were prepared with methylcellulose in the presence of clay.

The purpose of this paper is to discuss some general aspects of clay chemistry, particularly its interaction with different natural polymers such as nanochitosan and methylcellulose.

Materials and methods

Composites of nanochitosan (CS), methylcellulose (MC) and kaolin clay (KC) were prepared by sol-gel method. Binary composites of nanochitosan and methylcellulose CS+MC, 1:1; nanochitosan and clay CS+KC, 2:1 were prepared first and then ternary composite CS+MC+KC, 2:2:1 was prepared and characterized by FTIR, DSC and XRD studies.

Results And Discussion

TGA

The profile of thermograms for composite materials could represent a combination of the individual profile of each component. TG curves from this analysis provide information on changes in the mass of a sample during heating or cooling process. The DTG curve, i.e., the first derivative of the sample mass changes as a function of temperature, gives the rate of the mass changes (Sames and Lenzing, 1998; Suh et al., 1996).

As the temperature increases, the sample might experience a mass gain due to oxidation, but more often than not the TG curve shows a weight loss indicative of drying at $T \leq 50^\circ\text{C}$ or of thermal decomposition at $T \sim 250^\circ\text{C}$. The maximum rate of the weight changes is recorded as a peak in the curve. The TGA curve of binary composite of nanochitosan with methyl cellulose, nanochitosan with clay and ternary composite of nanochitosan with methylcellulose and clay shows the gravimetric loss and its first derivative recorded during thermal analysis. The weight loss of the composite nonwoven depicted by TG curve is a monotonous decreasing function of temperature (Fan and Maier, 2006; Ribeiro et al., 2001).

The changes in the mass could be divided into three distinct regions. The first region, starting from room temperature up to 250°C , the weight loss is due to water vaporization. The weight changes were not significant and the composite was thermally stable. The second narrow regions from 250 to 320°C for nanochitosan with clay and $250\text{--}280^\circ\text{C}$ for nanochitosan with methylcellulose. The composite nonwoven experienced a great weight loss because of the thermal decomposition, whereas, the thermal decomposition of ternary composite is from 250 to 400°C is shown in the Fig. 1 indicating the addition of clay in the binary composite of nanochitosan with methylcellulose increases the thermal decomposition temperature of the composite. About 60% of the sample decomposed into volatiles. In the third region, the temperature range of 400 - 600°C , the composite remnant continued to decompose slowly with 10% of the weight loss (Seavey et al., 2001; Seavey and Glasser, 2001).

The mass loss profile for composite materials is usually the sum of the individual profiles of each component under the same experimental conditions (Shodai et al., 1994). As shown in the spectra the ternary composite has a better thermal stability than the binary composites. It had also noticed that the binary composite of nanochitosan with clay, nanochitosan with methylcellulose nonwoven decomposed earlier than the ternary composite of nanochitosan with methylcellulose in the presence of clay. Hence the prepared ternary composite is thermally stable.

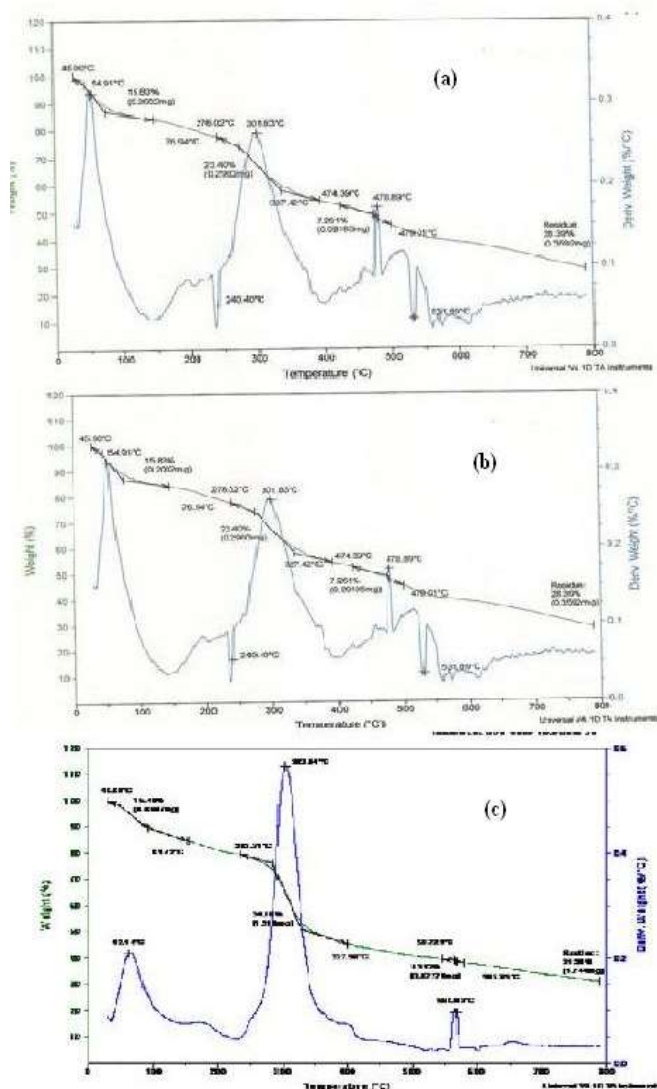


Fig. 1. TG curves of CS+KC (a), CS+MC (b) and CS+MC+KC (c).

Surface morphology

AFM and SEM is a modern tool for a special view for surface morphology of materials (Henrich and Cox 1994). AFM provides a number of advantages over conventional microscopy techniques. AFM requires no specific sample preparation procedure, can be operated in ambient condition and provides information about the sample surface. There are several scanning modes of AFM, such as contact mode and tapping mode. Tapping mode is generally used to visualize the surface structure of biological samples.

Atomic force and scanning electron microscopy

AFM height image Fig. 2(a) and phase image Fig. 2(b) showing aggregates of ternary composites. The contrast covers height variation in the range of 0-40 μ m (a) and phase variations in the 0-360 $^{\circ}$ degree range in (b) (Nobuhiko and Ryoji 2003). Scanning electron microscopy of ternary composites of chitosan without cross linking agent Fig. 2(c) And with cross linking agent Fig. 2(d) shows the surface morphology (Martio et al., 1988). From the SEM and AFM images of the ternary composites shows smooth surface. so it is concluded that the prepared ternary composites act as a membranes.

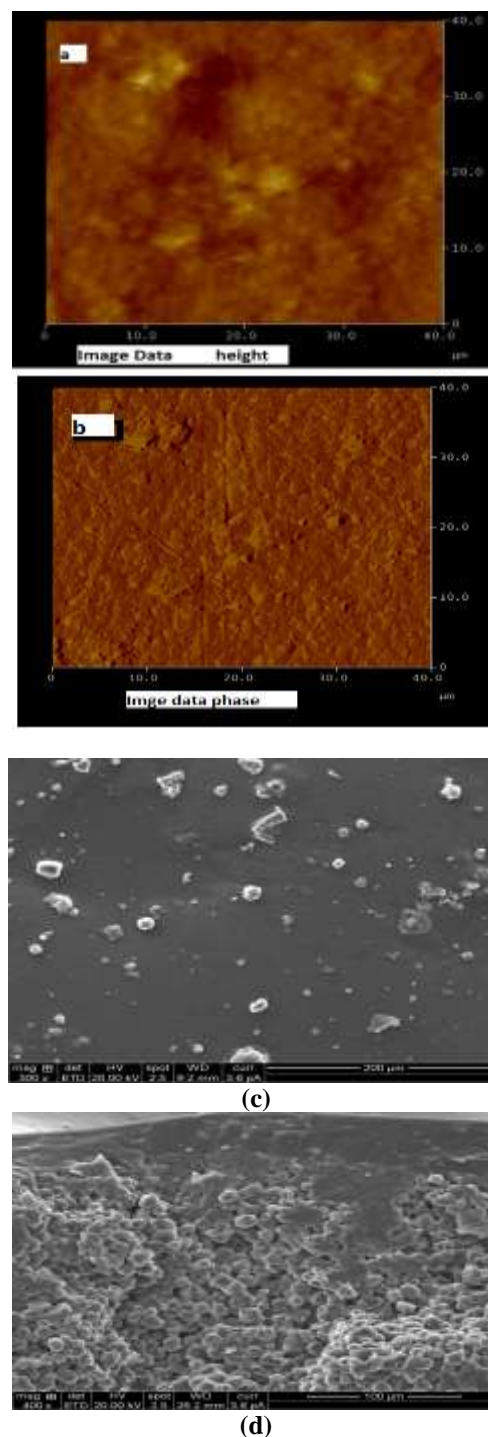


Fig. 2. AFM micrographs of ternary composites height image(a), phase image(b), SEM images of ternary composite without(c) and with(d) cross linking agent.

FTIR

IR spectra of binary and ternary composites of nanochitosan show the typical bands for -OH stretching, NH stretching, C-O-C stretching, -CH stretching, -CH bending and groups corresponding to the inorganic elements such as Si, Mg etc proving the formation of the composite (Fig. 3 (a), (b) and (c)).

In all the binary and ternary composites the peak around 3363 cm^{-1} is due to chitosan band corresponding to nNH from amide II and nNH in addition to the OH band at 3664 cm^{-1} and the different nC-O-C at 1063 cm^{-1} of methylcellulose. The band appears at 1583 cm^{-1} is most probably due to the unprotonated amino group. The broad band ranging from 3100-2900 cm^{-1} is due to presence of CH stretching vibration of methyl group. The

bending vibrations help to tell more about the basic structure. For example a strong methyl band (1470 cm^{-1}) and a weak methyl band (1380 cm^{-1}) plus a band at $725\text{--}720\text{ cm}^{-1}$ in spectra III is indicative of a long chain and linear aliphatic structure and is attributed to a crystallinity and a high degree of regularity for the linear back bone structure (Szymanski and Erickson, 1970; Gans, 1975; Colthrup et al., 1990).

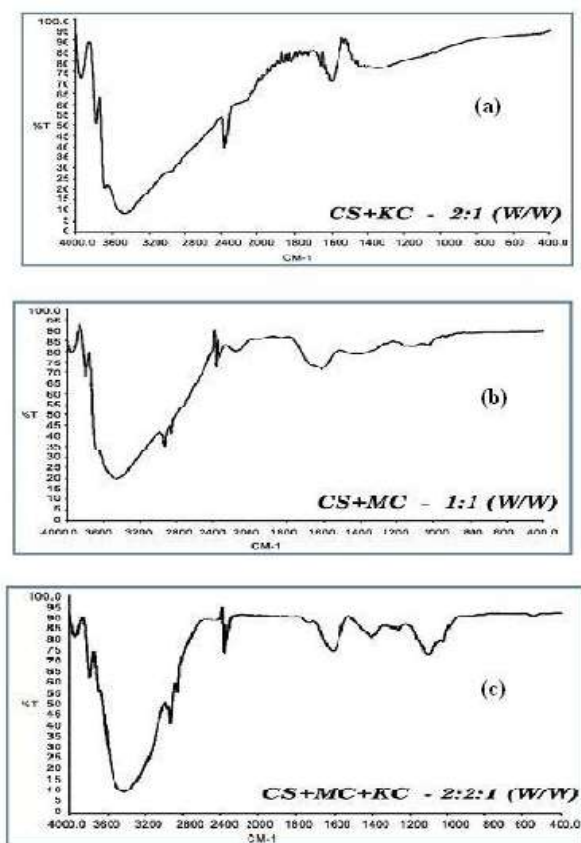


Fig. 3. FTIR of CS+KC (a), CS+MC (b) and CS+MC+KC (c)

The comparison of the spectrum of ternary composite the peak correspond to -OH stretching, NH stretching, C-O-C stretching, -CH stretching, -CH bending is same as that of the binary composites. It shows all the molecules are retained.

DSC

A Perkin-Elmer model TGA-7 thermogravimetric system with a microprocessor driven temperature control unit and a TA data station was used. The mass of the samples was generally in the range of 2-3 mg. The sample pan was placed in the balance system equipment and the temperature was raised from 25 to $550\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}$ per minute. The mass of the sample pan was continuously recorded as a function of temperature (Zhang and Fang, 2006; Sari and Karaipekli, 2007; Gilman et al., 2000).

The DSC thermogram confirmed the crystalline forms of the composites shown in XRD. Here it is visible that the addition of clay in nanochitosan that the degree of crystallinity of nanochitosan annealed at $224.3\text{ }^{\circ}\text{C}$, where as for nanochitosan with methylcellulose is at $145.4\text{ }^{\circ}\text{C}$ which is less than the nanochitosan with clay.

The glass transition temperature of CS+MC is less ($145.4\text{ }^{\circ}\text{C}$) (Fig. 4(a)), where as it had increased in CS+KC composite ($224.3\text{ }^{\circ}\text{C}$) (Fig. 4(b)). But the values had decreased in ternary composite $116.9\text{ }^{\circ}\text{C}$ (Fig. 4(c)). The decomposition of CS+MS starts at $\sim 150\text{ }^{\circ}\text{C}$, where as it had increased around $230\text{ }^{\circ}\text{C}$ in the

composites with clay showing higher thermal stability of clay containing composites.

Hence the clay containing composites have higher tensile strength and toughness than the other composites. This stability is probably due to the increased hydrogen bonding interaction between nanochitosan clay and methylcellulose. This good thermal behavior has potential for a variety of individual application particularly here in RO process (Zhang et al., 2009; Patakfalvi et al., 2003; Aderemi and Oludipe, 2000; Aderemi et al., 2001).

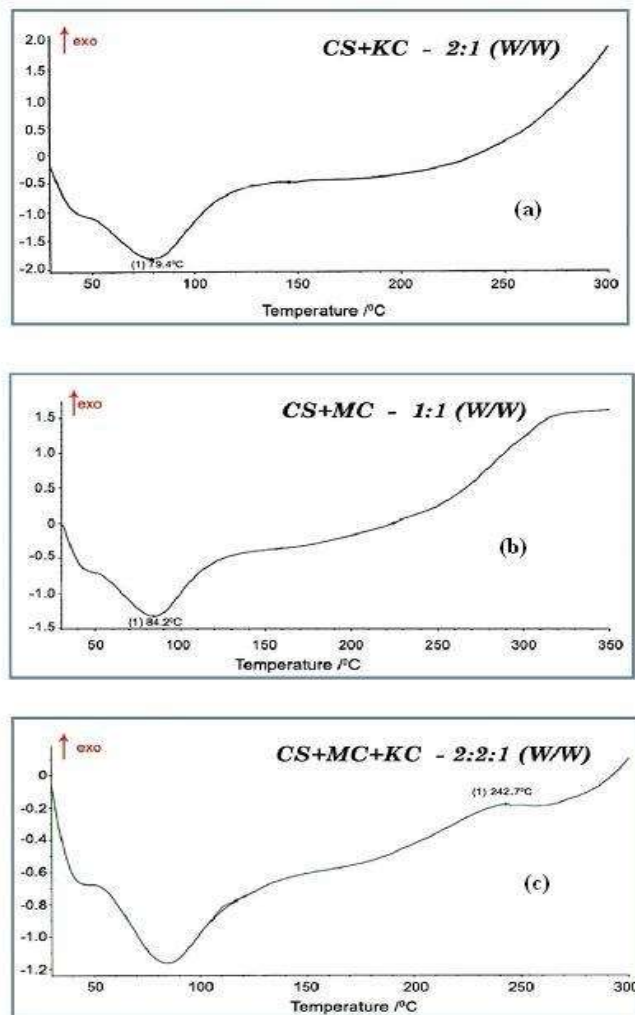


Fig. 4. DSC of CS+KC (a), CS+MC (b) and CS+MC+KC (c)

XRD
The main part of XRD patterns confirms the crystalline character of the investigated sample. In these patterns the most intensive lines are observed at 2θ between 30 ° and 60 ° . The peak around $2\theta \approx 30\text{ }^{\circ}$ and 60 ° represents the most intensive diffraction lines of chitosan and methylcellulose (Fig. 5). These peaks are present in ternary as well. There are two prominent peaks ($14^{\circ}\text{--}21^{\circ}$) and one broad peak (41°) showing higher crystallinity nature of the sample in the XRD of nanochitosan with clay. The crystallinity has reduced forming three less prominent peaks with shifting in 2θ to the extent of $10^{\circ}\text{--}20^{\circ}$ showing the less crystalline nature of composite.

On the formation of the composites with methylcellulose there are three peaks formed at 14° , 21° and 41° showing not much difference with that of nanochitosan. The number of crystalline forms has increased in the composite of CS+MC+KC. Hence the ternary composite of methylcellulose with nanochitosan in the presence of clay decreases the porosity,

which enhances the composite as good membrane of water treatment (Schwieger et al., 1991; Theng, 1979, 1982; Barrer, 1978; Lagaly, 1986; Ege et al., 1985).

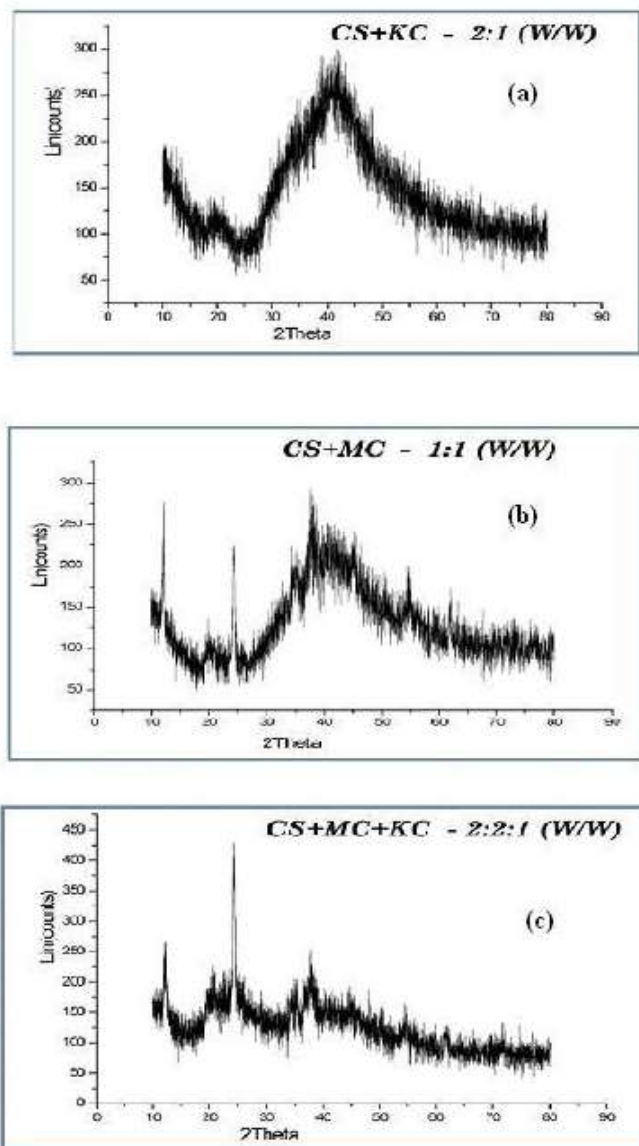


Fig. 5. XRD pattern of CS+KC (a), CS+MC (b) and CS+MC+KC (c).

Conclusion

The experimental results indicate that the composite formed using nanochitosan methylcellulose and kaolin clay have more stability, higher tensile strength, toughness, flexural strength and modulus without sacrificing their impart strength. The permeability studies shows that CS+KC+MC composite has the least permeability when compared to CS+KC and CS+MC under normal condition proving the lesser pore size of the ternary composite prepared. Hence the ternary composite can be used as the good reverse osmosis membrane.

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