Swelling and Mechanical Behavior of Modified Poly(vinyl alcohol)/Laponite Nanocomposite Membranes

Shubhangi H. Nair, Kiran C. Pawar, Jyoti P. Jog, Manohar V. Badiger

Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411008, India

ABSTRACT: Nanocomposite (NC) membranes based on hydrophobically modified PVA and laponite were synthesized with varying laponite content in the feed. The incorporation of laponite in NC membranes was investigated by FTIR spectroscopy and thermogravimetric analysis. The swelling ratio of membranes was determined as a function of temperature and laponite content. Swelling studies of NC membranes exhibited the decrease in swelling with an increase in laponite content in the NC membranes. The swelling ratio of NC membrane with 20% laponite slightly increased with an increase in temperature. Dynamic mechanical analysis showed the systematic increase in storage modulus with laponite content, which indicates the enhancement of mechanical property upon laponite addition. There was also a decrease in the tan δ peak values of NC membranes with an increase in laponite content in NCs. The permeabilities through NC membranes as a function of solute size and laponite content were studied and the results showed molecular screening based on size. The permeability of solute reduced due to the presence of well-dispersed laponite in the NC. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2896–2903, 2007

Key words: nanocomposite hydrogel; membranes; poly(vinyl alcohol); dynamic mechanical analysis; laponite

INTRODUCTION

Hydrogels are hydrophilic three-dimensional polymeric networks, which are insoluble in water due to the presence of chemical or physical crosslinks. Because of their crosslinked structures, which are random in nature, the conventional hydrogels have morphological inhomogeneties and inferior mechanical properties. Therefore, recently, nanocomposite (NC) hydrogels have gained importance due to their enhanced mechanical property. It is well-established that the mechanical and barrier properties of films can be significantly increased by the incorporation of clays.[1] The influence of inorganic clay on the properties of chemically crosslinked hydrogels has been studied earlier.[2–6] Churochkina et al. found that incorporating the clay into poly(acrylamide) gel enhanced the mechanical properties of gel with little influence on swelling.[2] Stimuli-sensitive NC hydrogels based on N-isopropyl acrylamide (NIPAm) and acrylic acid (AA) have also been demonstrated.[3–6] Haraguchi et al.[7–9] reported novel NC hydrogels without an organic crosslinker, where well-dispersed clay acts as a multifunctional crosslinker. There are also a few reports on the NC based on poly(vinyl alcohol) (PVA).[10,11] It is also known that hydrophilic, nonionic polymers such as PVA and PEO easily adsorb onto clay surfaces.[12,13] The adsorption of PVA onto clay surface occurs through strong hydrogen bonding between the hydroxyl groups of PVA and the oxygen atoms of silicate layers.[11,14] Laponite is a synthetic clay, which belongs to a family of phyllosilicates (trimorphic) 2:1 with an empirical formula of $Na^+_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$ having diameter of 300 Å and height about 10 Å.[15] Previously, we have reported on the hydrophobically modified PVA hydrogel membrane with N-tertiary butyl acrylamide (NTBA), which exhibits discontinuous volume transition at low NTBA content.[16] Unlike the PNIPAm, the hydrophobically modified PVA has an excellent film-forming property and this property prompted us to study the NC hydrogel membranes based on modified PVA.

Furthermore, this work was undertaken with a view to improve the mechanical strength of PVA-g-polyNTBA membranes by incorporating clay (laponite) and to study the influence of clay on the swelling and permeation properties of the resulting NC membranes. NC hydrogel membranes were synthesized by varying laponite content and the incorporation of laponite in the membranes was evaluated by FTIR studies and thermogravimetric analysis (TGA). The swelling properties of membranes were studied as a function of temperature and laponite content. The permeability characteristic of the membrane was correlated to the laponite content.

WILEY InterScience®
DISCOVER SOMETHING GREAT

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) (degree of hydrolysis $\sim$ 86–89%) was purchased from the S.D. Fine Chemicals, India. N-tertiary butyl acrylamide (NTBA) (97%) was obtained from Aldrich Chemicals, USA. Potassium persulfate (KPS) was procured from Loba Chemicals, India. Laponite RD was purchased from Laporte. Theophylline and hemoglobin (Hb) were obtained from Aldrich Chemicals, USA; while vitamin B_{12} was purchased from S. D. Fine Chemicals, India. These chemicals were pure and analytical grade and were used as such.

Molecular weight of PVA was determined by measuring intrinsic viscosity of PVA in dimethyl sulfoxide (DMSO). Mark-Houwink's equation was used to determine the molecular weight at 30°C. $[\eta] = KM_n^{\alpha}$, where $K = 1.58 \times 10^{-4}$ dL g^{-1} and $\alpha = 0.84$.[17] The molecular weight was found to be 60,000 g/mol.

Synthesis of PVA-g-polyNTBA2 graft copolymer

PVA-g-polyNTBA2, henceforth, abbreviated as PVAN2, where 2 mol % of NTBA was used for the synthesis of graft copolymer. Synthesis of graft copolymer was carried out using KPS as an initiator. Procedure of synthesis of graft copolymer was reported earlier.[16] Briefly, NTBA monomer, initiator, and PVA were dissolved in DMSO. Nitrogen was purged in the solution to remove the dissolved oxygen. The graft polymerization reaction was carried out at 42°C for 22 h. The graft copolymer was precipitated in acetone.

Synthesis of nanocomposite hydrogel membranes

PVAN2/DMSO 4% (wt/vol), 20 cm^3 of solution was mixed with aqueous suspension of laponite and stirred properly. The composition of laponite and polymer is given in Table I. The NC hydrogel membranes were made by pouring the solution into a flat petri dish (4.8 cm diameter), and allowing the solvent to evaporate at 60°C for 7 days.

The membranes were annealed at 120/140°C for 6 h before they were used for swelling studies.

Characterization

Fourier transform infrared analysis

FTIR analysis was done using a Shimadzu FTIR-8300 spectrometer at a resolution of 4 cm^{-1}. Thin films of PVAN2 polymer and nanocomposites (NCs) were made by evaporating solvent at 60°C and used for FTIR analysis. FTIR spectrum of laponite (as a reference) was also recorded using nujol as a medium.

TABLE I
Stiochiometry of Nanocomposite Membranes

Laponite (wt %)	PVAN2 (g)	Laponite (g)	Water (mL)
2.5	0.8	0.02	2.0
5.0	0.8	0.04	2.0
10.0	0.8	0.08	4.0
20.0	0.8	0.16	4.0

Swelling ratio of membranes

The dried, preweighed membranes were kept in water in a constant temperature bath for different temperatures in the range of 10–60°C for 24 h and reweighed after wiping the surface gently. Since membrane thickness is very small, 24 h equilibrium time was found to be sufficient.

The swelling ratio (q) of membrane was calculated using the following equation:

$$q = \frac{W_2}{W_1} \qquad (1)$$

where, W_2 and W_1 are wet and dry weights of the membrane, respectively.

Differential scanning calorimetry

Perkin Elmer DSC-7 was used for studying the melting and crystallization behavior of the polymeric membranes. The temperature and energy scales were calibrated with the standard procedures. The melting studies were performed in the temperature range of 50–240°C at the heating rate of 10°C/min under N_2 atmosphere.

Thermogravimetric analysis

TGA of PVAN2 and NC membranes was carried out by using Perkin Elmer TGA-7. The samples were heated from 50 to 700°C at the heating rate of 10°C/min under N_2 atmosphere.

Dynamic mechanical analysis

The dynamic mechanical properties of PVAN2 and NC membranes were studied with a Rheometrics DMTA IIIE dynamic mechanical analyzer. The samples were analyzed in the tensile mode. The temperature sweep was carried out from 30 to 180°C and the sample was heated at the rate of 5°C/min. The frequency was 10 rad/s and the strain was 0.1%.

Permeation studies

Permeation experiments were carried out using a two-chamber (donor and receptor) diffusion cell with a chamber volume of 70 cm^3. Preswollen mem-
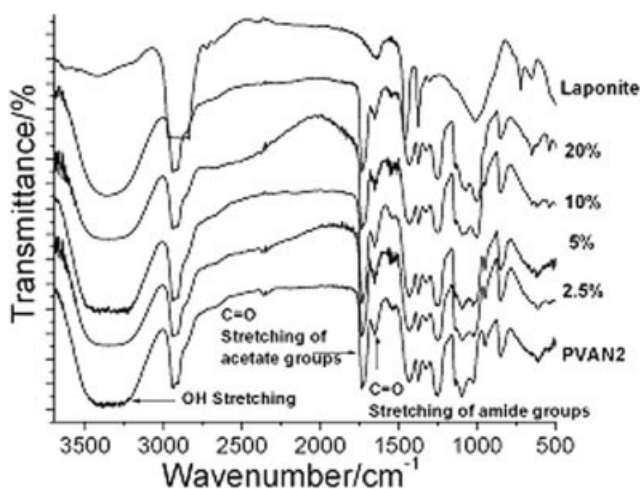
Figure 1 FTIR spectrum of the PVAN2 copolymer membrane and nanocomposite membranes with different loadings of laponite (scale range: 3700–500 cm^{-1}).

branes were mounted between two halves of the donor and receptor cell, which were further clamped together and sealed tightly with the rubber packing. The effective membrane area in the cell was 1.76 cm^2. The solution was at the donor side of the cell and the receptor had only water. A fixed volume (1.0 mL) of the sample was taken out at various time intervals from the receptor cell and the solute concentration was measured using an UV spectrophotometer at appropriate wavelengths. The solutes chosen for the permeation studies were theophylline (MW = 180), vitamin B$_{12}$ (MW = 1355), Hb (MW = 64–67,000). The concentrations of these solutes were determined by UV spectrophotometer at wavelengths of 271 nm for theophylline, 405 nm for Hb, and 361 nm for vitamin B$_{12}$. Membranes, which were annealed at 150 and 160°C for 6 h, have been chosen for the permeation studies.

RESULTS AND DISCUSSION

Synthesis of NC membranes

Although, PVAN2 is made partially hydrophobic, the clay can still be homogenized with PVAN2 without the need for organic modifications. We have varied the clay content from 2 to 20% and the membranes were casted. These NC membranes showed superior mechanical properties due to the fine scales of clay dispersed in the polymer matrix. PVA has a strong tendency to form hydrogen bonding within itself as well as with other species containing highly electronegative groups. Laponite has electronegative oxygen and hydroxyl groups, which can assist the adsorption of PVA onto laponite surface. The adsorption of PVAN2 onto surfaces of laponite is presumed to occur through hydrogen bonding. Apart from hydrogen

bonding, van der Waals forces between polymer segments and clay surface would also play an important role in the overall adsorption process.

Characterization

FTIR analysis

Figure 1 shows the FTIR spectra of PVAN2 copolymer membrane, laponite, and NC membranes with varying laponite concentrations. The broad band observed at 3350 cm^{-1} in the IR spectra, is due to the —OH stretching of PVA and laponite as well as the —NH stretching vibration of the NTBA in the graft copolymer. The backbone aliphatic C—H stretching vibrations give rise to sharp bands at 2940 and 2910 cm^{-1}. The sharp bands at 1735 and 1654 cm^{-1} correspond to the C=O stretching of the acetate and amide groups of PVAN2, respectively. Laponite spectrum shows characteristic bands at 1013 and 654 cm^{-1}, which correspond to Si—O—Si stretching frequencies (Fig. 2). It can be readily seen from Figure 2 that, the intensity of the Si—O—Si stretching band increases with respect to increase in laponite content in NC gels, which qualitatively indicates the increase in laponite concentration from 2.5 to 20% in the NC membranes. Furthermore, the NC membranes show slight shift in Si—O—Si stretching frequency to lower value when compared with laponite. This shift can be attributed to the interactions between PVAN2 polymer and the clay through Si—OH groups.

Thermogravimetric analysis

Figure 3 shows the TG curves of PVAN2, laponite, and NC membranes with laponite content of 2.5, 5, 10, and 20%. Laponite shows the loss of weight near
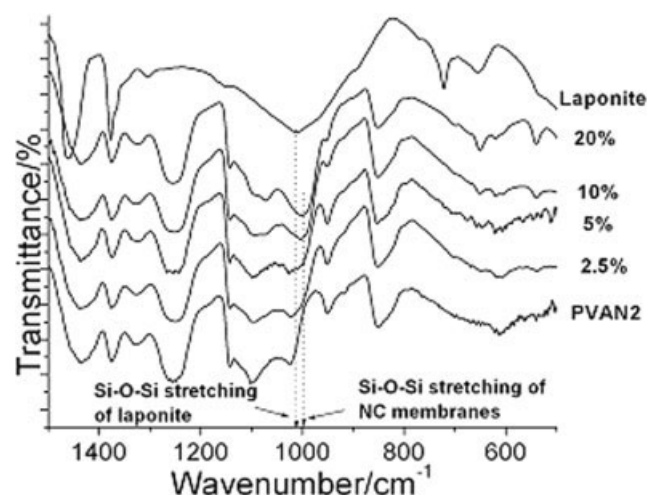

Figure 2 FTIR spectra of PVAN2 and nanocomposite membranes with different loading of laponite (scale range: 1500–500 cm^{-1}).
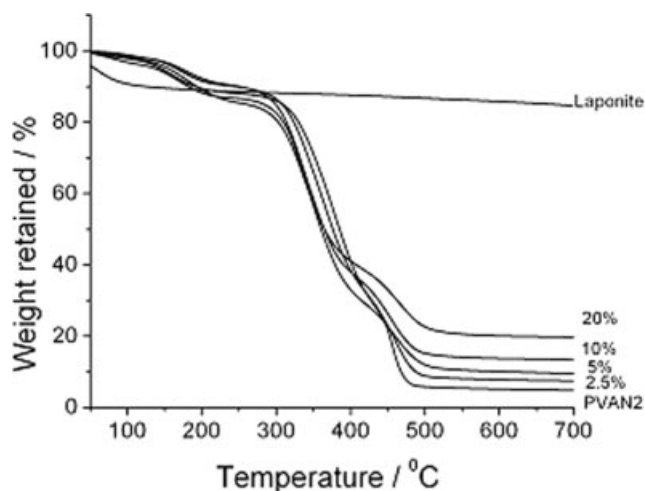
Figure 3 TGA curves of PVAN2, laponite, and nanocomposite membranes.

TABLE II
Thermal Analysis of PVAN2 and Nanocomposite Membranes with 5 and 20% Laponite

Membrane	$T_m/°C$	$T_c/°C$	ΔH_f (J/g)
PVAN2	174	122	95.647
5%	173	135	94.37
20%	168	–	79.88

of PVA in polymer NCs by the introduction of organophilic montmorillonite.

Swelling behavior

PVAN2 graft copolymer membrane with 2 mol % of NTBA is partially hydrophobic and partly dissolves in water. Therefore, all the membranes were annealed to prevent the dissolution of membranes.

The influence of laponite content on the swelling behavior of the membranes at 30°C is shown in Figure 4. It can be seen from the figure that the swelling ratios of the NC membranes gradually decrease with an increase in the laponite content of the membranes. The decrease in swelling ratio with increasing laponite content can be attributed to the increase in physical crosslinking in which the clay can act as a physical crosslinker and prevents the dissolution of polymer in water due to the noncovalent interactions between polymer and clay. Similar observation was made by Haraguchi et al.[7] in both NCs and conventional hydrogels. Xia et al.[4] reported the decrease in swelling with an increase in clay content in poly(N-isopropylacrylamide)/Na-MLS NC gels. Laing et al.[3] have reported a thermoresponsive polymer–clay NC with enhanced temperature response based

100°C, which is mainly from the evaporation of water from the layers. It can be seen from the figure that the degradation temperature decreases in NC membranes and such decrease was also observed for polystyrene/organically modified montmorillonite NCs.[18] The decrease in degradation temperature suggests that the presence of laponite may facilitate the degradation of PVAN2 copolymer membrane. The weight ratio of clay incorporated in the NC membranes were evaluated by TG measurements. The NC membranes exhibit plateau after 500°C due to the presence of an inorganic residue. Therefore, the inorganic contents in the NC membranes could be obtained from the weight percentage of the residue at 600°C. It was found that the weight ratio of laponite in the NC membranes obtained from the plateau corresponds to the initial feed composition.

Differential scanning calorimetry

DSC results of PVAN2 copolymer membrane and the NC membranes are shown in Table II. The data revealed that with an increase in laponite content in the NC membranes, the value of heat of fusion (ΔH_f) as well as melting transition of the membranes decreased. The decreased value of T_m is due to the formation of crystals with lower thermal stability. Since the degree of crystallinity is the measure of ratio of heat of fusion of polymer to the heat of fusion of 100% crystalline polymer, the decrease in ΔH_f value indicates the decreased degree of crystallinity of the NC membranes. Our results are in line with Ogata et al.[19] reported that the well-dispersed montmorillonite in PVA-montmorillonite composites showed reduction in heat of fusion and crystallinity with increase in montmorillonite content. Yu et al.[20] also indicated the suppression in crystalline behavior
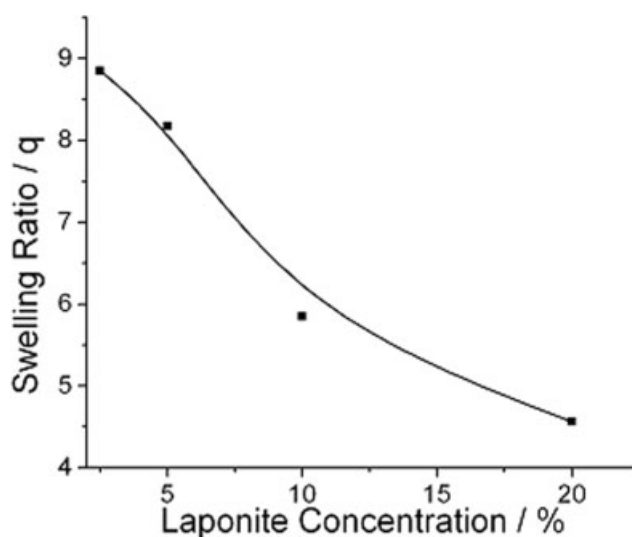

Figure 4 Influence of laponite concentration on the swelling ratio of membranes at 30°C (membranes, annealed at 140°C for 6 h prior to swelling).
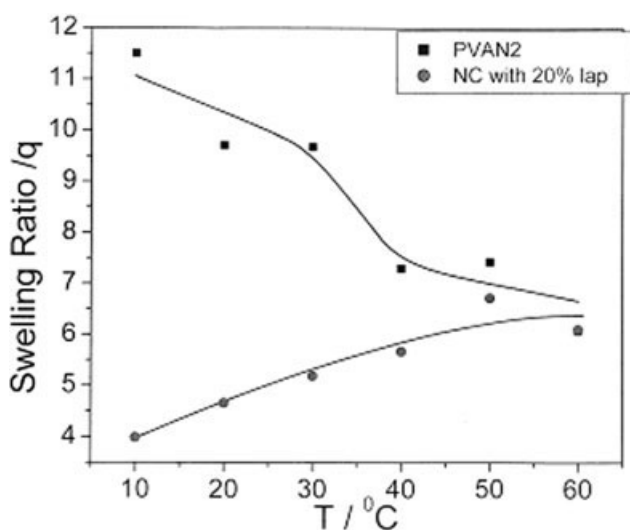
Figure 5 Temperature-dependent swelling of PVAN2 and 20% nanocomposite membrane annealed at 120°C for 6 h.

on organically modified clay-PNIPAm. Surprisingly, in their study, the swelling ratios of NC gels increased with an increase in the clay content and the kinetics of swelling was faster when compared with the normal clay-PNIPAm NC gels. The most efficient thermal transition claimed and the increase in swelling ratios in their studies was attributed to the presence of coupling agent, which interfaces the clay and polymer. However, we find that their explanation on the above effect is not convincing. We believe that, since the clay acts as a physical crosslinker, the swelling ratio is expected to decrease with an increase in clay content.

Figure 5 shows the temperature-dependent (10–60°C) swelling ratios (q) of PVAN2 membrane and NC membrane with 20% laponite content, annealed at 120°C for 6 h. The swelling ratios were measured in water. It can be readily seen from the figure that, PVAN2 membrane exhibits higher swelling ratios in the lower temperature range of 10–30°C and decrease in swelling ratio with increasing temperature. The higher swelling ratios of the membranes at low temperature can be attributed to the strong H-bonding interactions between polymer and water. The hydroxyl groups of PVA form strong H-bonds with water molecules, which enhance the interaction between PVA and water. However, upon increasing the temperature, the H-bonding between polymer and water breaks and inter/intramolecular hydrophobic associations due to the presence of hydrophobic, N-tertiary butyl groups dominate resulting into the collapse of polymer chains. The collapse of the polymer chains lead to the decrease in the swelling ratio. However, the swelling behavior of 20% NC membrane with respect to temperature is totally different. The swelling ratios of NC hydrogels are low

when compared with PVAN2 at all the measured temperatures. This can be because of the presence of laponite, which acts as a crosslinker. However, it is intriguing to note that, at the constant laponite loading of 20%, the swelling ratio in the NC gels slightly increase with temperature. This could be attributed to the fact that, the laponite being hydrophilic in nature inhibits the hydrophobic associations of PVAN2 chains resulting in slight increase in swelling ratios. Therefore, the temperature-dependent swelling of NC gels is a complex phenomenon, which involves the interactions between polymer–clay–water and interplay between these dictates the swelling ratios.

Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) gives information about the variation of storage modulus ($E^{|}$), loss modulus ($E^{||}$), and tan δ with temperature at a fixed frequency. The DMA of PVAN2 and all the NC hydrogel membranes were carried out in the temperature range of 30–180°C. Figure 6 shows the variation of storage modulus ($E^{|}$) with temperature for annealed and unannealed PVAN2 composite membranes. It can be seen that annealing results in a significant increase in the storage modulus over the entire temperature range. The observed increased in $E^{|}$ could be attributed to the presence of secondary interactions such as van der Waals forces that favor further adsorption of PVAN2 onto laponite by bridging clay surface and polymer into close contact.

Figure 7 shows the tan δ curves for PVAN2 and membranes with different laponite contents. The tan δ peak temperature for the polymer PVAN2 and the NC membranes remains almost constant irrespective of laponite content. However, tan δ peak values of
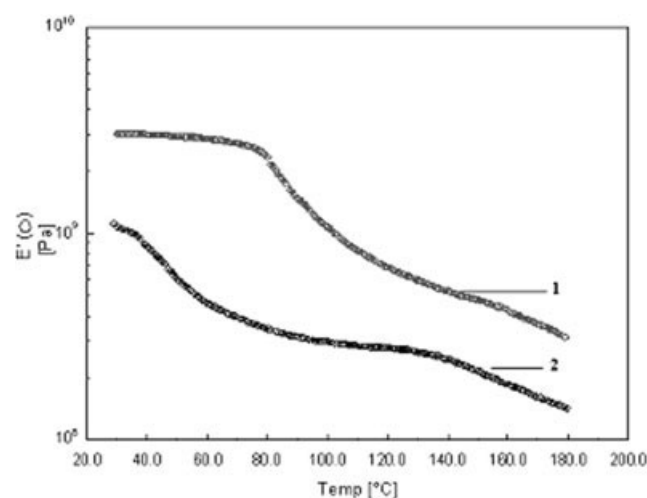

Figure 6 Effect of annealing on the storage modulus, $E^{|}$ as a function of temperature for the sample PVAN2 with 20% laponite; annealed (170°C) (1) and without annealing (2).
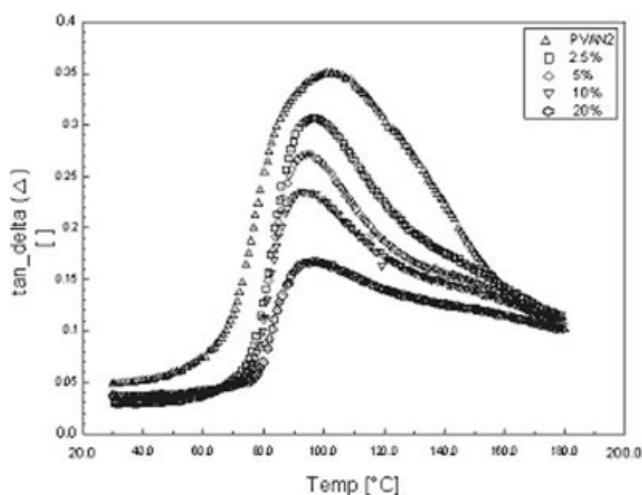
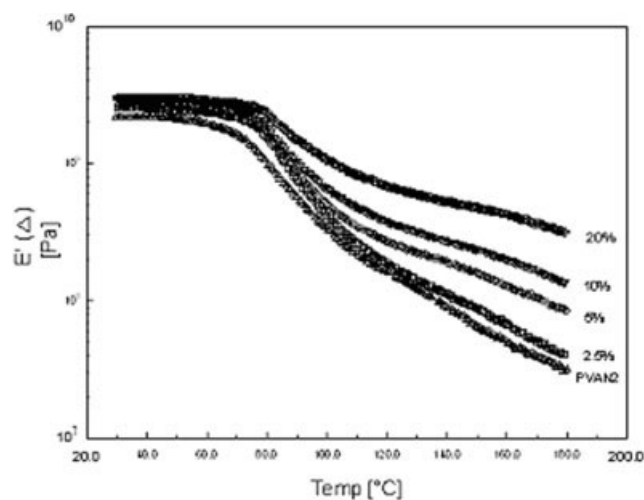**Figure 7** Effect of laponite on the tan δ peak as a function of temperature for annealed membranes (annealed 170°C).

Figure 8 Influence of laponite content on the storage modulus (E^{1}) of annealed PVAN2 and nanocomposite membranes.

NC membranes decrease upon increase in the laponite content. Since tan δ value is directly proportional to the amorphous content of the membrane, its decrease indicates the decrease in the amorphous content of the NC membrane. In an ideal case, this decrease should be balanced by an increase in crystallinity. However, we find that our DSC results indicate the decrease in crystallinity. Therefore, the decrease in tan δ peak values with respect to increase in laponite content can be ascribed to the formation of a rigid amorphous phase (RAP) resulting from the constrained amorphous phase. This suggests that the molecular motions of amorphous chains are restricted due to well-dispersed laponite in the NC membranes. The constrained volume of amorphous phase can arise from the surface interactions of clay and polymer through functional groups. Table III shows the tan δ peak values for NCs and calculated values of the peak normalized with respect to the PVAN2 content. The significant decrease in tan δ values with an increase in laponite content indicates the existence of the RAP. Similar observations were made by Ogata et al.[19] on the PVA/montmorillonite blend system.

Figure 8 shows the temperature-dependent storage modulus (E^{1}) of PVAN2 and all NC membranes,

which were annealed at 170°C for 6 h. It can be readily seen from figure that, the modulus of the membranes increases systematically with an increase in the laponite content. The data from Table IV also shows that, below the glass transition temperature (T_g), the increase in storage modulus is about 37% whereas increase in the modulus above the T_g is about 90%. This result clearly shows that the addition of laponite has a strong effect on the elastic properties of the membranes. The increase in modulus can be attributed to the nanoscale dispersion of laponite leading to the efficient interactions between polymer and clay or creation of three-dimensional network or physical crosslinks in the structure.

Permeation studies

The permeation of solutes through NC membranes depends on the aspect ratio of clay,[21] clay content, and tortuosity path,[22–24] and electrostatic interactions between membrane and solutes when both are charged.[5] Permeability of the membranes is determined by using the following equation,

$$\ln\left(1 - 2\frac{C_t}{C_0}\right) = \frac{-2A}{V}Pt \qquad (2)$$

TABLE III
tan δ and Normalized tan δ Values at Peak Temperature for Membranes

Membrane	tan δ at peak value after annealing	Normalized value of tan δ
PVAN2	0.3499	–
2.5%	0.3075	0.3411
5%	0.2717	0.3324
10%	0.2346	0.3054
20%	0.1668	0.2799

TABLE IV
Storage Modulus (E^{1}) of Annealed Membranes at 30 and 170°C

Membrane	E^{1} (Pa) at 30°C	E^{1} (Pa) at 170°C
PVAN2	2.2036×10^9	3.8423×10^7
2.5%	2.5441×10^9	5.0251×10^7
5%	2.7133×10^9	1.0367×10^8
10%	2.8920×10^9	1.6112×10^8
20%	3.0294×10^9	3.6555×10^8

Figure 9 Size exclusion phenomenon of 20% nanocomposite membrane at 30°C.

Figure 10 Relative permeability of hemoglobin (Hb) through membranes as a function of laponite content at 30°C (membranes annealed at 160°C for 6 h).

where C_t = solute concentration in the receptor cell (mg/mL), C_0 = initial solute concentration in the donor cell (mg/mL), V = volume of each half cell (mL), A = effective permeation area (cm^2), P = permeability coefficient (cm/s), and t = time (h or s).

To determine the permeability coefficient, P, a plot of $-V/2Aln(1 - 2C_t/C_0)$ against t was constructed and a linear fitting was performed. The slope of the linear portion of the graph yields the permeability coefficient, P.

Solute permeation experiments were performed using three representative solutes with different molecular weights and hydrodynamic sizes to understand the effect of solute size on the permeation through NC membrane. Figure 9 shows the permeation of theophylline, vitamin B12, and Hb through a membrane with 20% laponite at 30°C. To enhance the mechanical strength of membrane in water, the membrane was annealed at 150°C for 6 h before taking it for permeation studies. It can be seen from the figure that as the size of solute increases the permeability decreases.

To study the influence of laponite content on the permeation properties of the NC membranes, we studied the permeation of Hb through the PVAN2 membrane and NC membranes with varying laponite concentration. The relative permeability of Hb through the PVAN2 membrane and NC membranes with 10 and 20% laponite is shown in Figure 10. It can be seen from the figure that the permeability of solute through NC membranes reduced when compared with the PVAN2 membrane. This reduction in permeability can be attributed to the well-dispersed laponite in the polymer matrix, which are impermeable to the solute. Solute has to follow a tortuous path in the NC membranes due to the presence of clay, which results into increase in effective path of diffusion and consequently, permeability through NC membranes decreases.
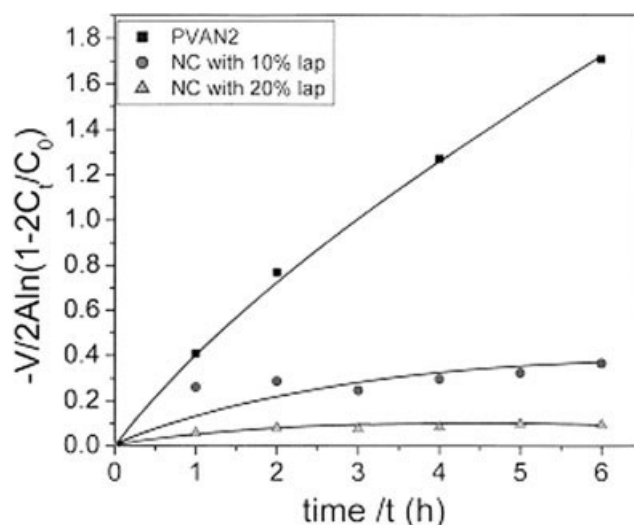
CONCLUSIONS

Thermosensitive NC hydrogel membranes based on PVAN2 and water-swellable laponite were synthesized by varying laponite concentration. The incorporation of laponite in NC membranes was demonstrated by FTIR spectroscopy and thermogravimetric analysis. The swelling of NC membranes was very much dependent on the laponite content and the solution temperature. The swelling of NC membranes in water decreased with an increase in the laponite content, and at constant clay content (20%), swelling ratio of membrane increased with an increase in temperature. Dynamic mechanical analysis indicated the enhanced mechanical property with an increase in laponite concentration in NCs. The permeabilities of the membranes were strongly dependent on the solute size as well as the laponite concentration in membrane.

References

1. Alexandre, M.; Dubois, P. Mater Sci Eng R Rep 2000, 28, 1.
2. Churochkina, N. A.; Starodoubtsev, S. G.; Khokhlov, A. R. Polym Gels Networks 1998, 6, 205.
3. Liang, L.; Liu, J.; Gong, X. Langmuir 2000, 16, 9895.
4. Xia, X.; Yih, J.; D'Souza, N. A.; Hu, Z. Polymer 2003, 44, 3389.
5. Lee, W.-F.; Fu, Y.-T. J Appl Polym Sci 2003, 89, 3652.
6. Lee, W.-F.; Chen, Y.-C. J Appl Polym Sci 2004, 91, 2934.
7. Haraguchi, K.; Takehisa, T.; Fan, S. Macromolecules 2002, 35, 10162.
8. Haraguchi, K.; Farnworth, R.; Ohbayashi, A.; Takehisa, T. Macromolecules 2003, 36, 5732.
9. Haraguchi, K.; Takehisa, T. Adv Mater 2002, 14, 1120.
10. Toyoshima, K. In Polyvinyl Alcohol, Properties and Applications; Finch, C. A., (Ed.) Wiley-Interscience: Chichester, UK, 1973; Chapter 13.
11. Xu, J.; Meng, Y. Z.; Li, R. K. Y.; Xu, Y.; Rajulu, A. V. J Polym Sci Part B: Polym Phys 2003, 41, 749.

12. Greenland, D. J. J Colloid Sci 1963, 18, 647.
13. Zebrowski, J.; Prasad, V.; Zhang, W.; Walker, L. M.; Weitz, D. A. Colloids Surf A 2003, 213, 189.
14. Emerson, W. W.; Raupach, M. Aust J Soil Res 1964, 2, 46.
15. Bonn, D.; Kellay, H.; Tanaka, H.; Wegdam, G.; Meunier, J. Langmuir 1999, 15, 7534.
16. Gholap, S. G.; Jog, J. P.; Badiger, M. V. Polymer 2004, 45, 5863.
17. Pritchard, J. G. Poly(vinyl alcohol): Basic Properties and Uses, Polymer Monographs, Vol. 4; Gordon and Breach: New York, 1970.
18. Wang, D.; Zhu, J.; Yao, Q.; Wilkie, C. A. Chem Mater 2002, 14, 3837.
19. Ogata, N.; Kawakage, S.; Ogihara, T. J Appl Polym Sci 1997, 66, 573.
20. Yu, Y.-H.; Lin, C.-Y.; Yeh, J.-M.; Lin, W.-H. Polymer 2003, 44, 3553.
21. Cypes, S. H.; Saltzman, W. M.; Giannelis, E. P. J Controlled Release 2003, 90, 163.
22. Messersmith, P. B.; Giannelis, E. P. J Polym Sci Part A: Polym Chem 1995, 33, 1047.
23. Yeh, J.-M.; Yu, M.-Y.; Liou, S.-J. J Appl Polym Sci 2003, 89, 3632.
24. Xu, R.; Manias, E.; Snyder, A. J.; Runt, J. Macromolecules 2001, 34, 337.