Synergistic Blends of Natural Polymers, Pectin and Sodium Alginate

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ABSTRACT: A wide range of Pectin and Sodium Alginate blends have been investigated by casting films from aqueous solution. Blends showed synergy both in mechanical properties and water vapor permeation rate. Previously observed synergism in gels at low pH is also maintained in cast films of blends having up to 40% Pectin. Films were made water-insoluble by post-treatment with $CaCl_2$, which develops physical crosslinks among the molecules of both polymers. After $CaCl_2$ treatment, mechanical properties are drastically changed due to development of physically crosslinked tie points in the molecular network structure. The modulus and tensile strength of the resulting network structure are dependent on the nature of the polymers. Even in water insoluble films, synergism in mechanical and water barrier properties is retained in films having up to 20% Pectin content. Structural reorganization before and after $CaCl_2$ treatment was investigated by X-ray and dynamic mechanical analysis. The synergism observed in mechanical properties of the films before and after $CaCl_2$ treatment is attributed to reduction in molecular mobility and change in molecular network structure. Structural reorganization in $CaCl_2$-treated films, and thereby film properties, is dependent on the compositions of the blends; blended films show sharp glassy-rubbery transition in the storage modulus—temperature plot, which is not the case in untreated films. Film flexibility increases with increasing Pectin content in the blends. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2324–2336, 2011

**Key words:** polysaccharides; barrier; polymer blends; biomaterials; coatings

INTRODUCTION

There is increasing interest in using natural polymers to develop edible as well as biodegradable packaging films.[1–7] Polysaccharides such as sodium alginate (NaAlg) and pectin are widely used in food (gelling and thickening agents, imitation cherries, and other soft fruits), pharmaceutical (controlled release of drug, water-absorbent fibers, and gels for wound dressing), and industrial applications (water-soluble pouches, bags for washing linens, and non-woven fabric). However, films made out of these polysaccharides have low water barrier at high humidity. They are also less flexible than synthetic commercial packaging films used to enhance the shelf life of food products.[8,9]

Alginate is a salt of alginic acid, an unbranched binary copolymer of β-D-mannuronic acid (M) and α-L-guluronic acid (G) with various M/G ratios. It has two hydroxyl groups and one carboxyl group in every repeat unit that has α and β configurations. These groups create strong inter- and intramolecular hydrogen bonds. Alginate is almost amorphous and has a very weak melting peak at 220°C.[10] The reported T_g is in the range of 96–119°C.[11] T_g increases with G content, whereas gelling properties are related to M/G composition and the sequential organization of M and G along the chain. Sodium alginate–calcium films with higher concentration of M have low water solubility and high water barrier properties.

Pectin is a complex polysaccharide consisting mainly of esterified D-galacturonic acid residues in an ά-(1–4) chain interrupted by short Rhamnose inserts which disrupt the chain-helix configuration. It also carries other neutral sugars as side chains. These side chains give the molecule the appearance of having smooth (no side chain) and "Hairy" (side-chain) regions. The galacturonate residue is methyl esterified to different extents. X-ray and electron microscopic studies revealed that Pectin is crystalline and the crystallinity in citrus Pectin is about 6%.[12] Naturally occurring Pectin contains fibrillar crystals.[13–16] From various studies[13,16] in solid and in solution, it has been concluded that Pectin is a collection of aggregated rigid rods forming a gel network. Pectin molecules both in solution and solid states have extended chain conformations. The decomposition temperature of Pectin is in the range of 190–200°C and it has no T_g.[16,17]

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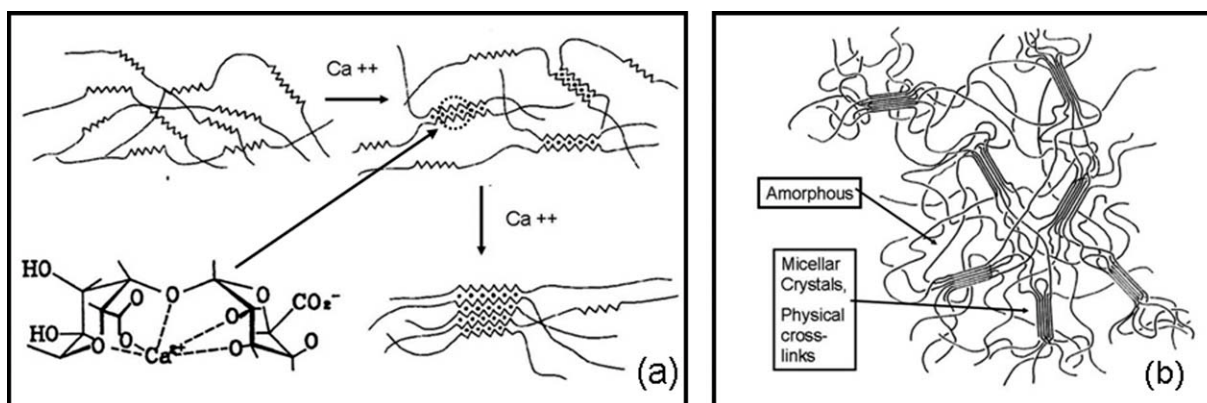
Figure 1 a: Schematic representation of the "Egg-Box Model" which describes the interaction of calcium ions with carboxyl acid groups of Pectin and Alginate. The insert depicts chelate formation with Ca^{2+} ions. b: Schematic representation of the "Fringed Micellar" structure of semicrystalline polymers.

Rheological studies on Pectin, NaAlg, and blends of these polymers have been conducted under a variety of pH values, temperatures, and different water activities.[18] NaAlg and Pectin blends form synergistic mixed gels at low pH which are structurally different from the pure components.[18–20] The gel characteristics are highly dependent on the nature of the Alginate and pectin samples and pH values. The strongest gels form from a mixture of high-methoxy Pectin and high G-content Alginate suggesting the formation of hydrogen bonds between the methoxyl groups of Pectin and the hydroxyl groups of guluronic acid.[21] It is observed that gel formation is hindered at pH above 4.0.[18] The microstructure of Pectin gel, as well as gels of Pectin/NaAlg blends, has been investigated using transmission electron microscopy.[19,22] Pectin forms an open molecular network structure where the pore size is dependent on the methoxy content.[23] The ratio between the Alginate and Pectin also influences the microstructure. The proposed network structure to explain gel formation is discussed below.

There have been numerous attempts to make water-insoluble NaAlg and Pectin films or strong gels using a variety of divalent cations including calcium.[9,24–27] The interaction of calcium ions with the carboxyl acid groups of NaAlg and Pectin creates a unique molecular network structure, described by the "Egg-Box" model [Fig. 1(a)]. It is an amorphous molecular network structure consisting of physical tie-points made by association of Ca^{2+} ions with the molecules.[26] These physical tie points are different from chemical crosslinks as they are formed by aggregation of many Ca^{2+}.[24] This "Egg-Box" model resembles the "Fringed-Micellar" model [Fig. 1(b)] that describes the morphology of synthetic semicrystalline polymers crystallized under high super cooling.[21,28] Molecular chains pass through several crystalline (Micellar) and amorphous zones forming an interconnected molecular network structure. The

structure resembles chemically crosslinked polymers. The major difference being that the amorphous tie point (ATP) formed by Ca^{2+} is similar to "Micellar" of "Fringed-Micellar" model but the Micellar formed by Ca^{2+} is amorphous in nature. Pectin forms a crystalline network structure which resembles the "Fringed-Micellar" structure. On $CaCl_2$ treatment it transforms to the molecular network structure described by the "Egg-Box" model. Various molecular network structures of gel formed in aqueous solution are summarized by Miles.[21]

The study was undertaken to design an edible, high water-barrier film whose properties are similar to nonedible cellophane film and is useful for increasing the shelf life of food products containing various food components (sandwiches, pizza, etc.) that have different water activities. In this study, it is intended to, (1) understand whether the synergistic gel network effect observed in the NaAlg/Pectin blend can be retained in cast films; (2) find out the effect of Ca^{2+} on the modification of network structure at various blend compositions; (3) investigate the role of microstructural reorganization in influencing mechanical and water-barrier properties, and (4) find out if the crystalline nature of Pectin, monitored by X-Ray, can help us in understanding the nature of the resulting blends, composition ranges of compatible and noncompatible blends, the types of molecular network structure present in the blends, extent of diffusion of Ca^{2+} in films, cause of increasing or decreasing physical crosslinking, occurrence of skin-core effect, etc.

EXPERIMENTAL

Materials

Alginic acid, Sodium salt was received from Aldrich (Viscosity 200000.00–400000.00 cps. M/G ratio = 1.56), whereas Pectin was received from Danisco,

USA. The Grindsted Pectin LC950 has 31–33% degree of esterification (% methoxy content).

Film preparation

A 5% aqueous solution of pure NaAlg, Pectin, and blends of both were prepared by mixing at 70°C for 4–6 h. The films were made on glass plates by drawing down using Paul Gardner Roll bar number 0018 or by pouring solution into specially made 8″ × 8″ Teflon® molds with depth of 0.25″. The solution was incubated at 23°C in a fume hood until dry. The films were treated with a 1M CaCl$_2$ solution for 10 min at 23°C.

Instron (mechanical properties measurement)

For quickly achieving equilibrium at 50% RH, samples were first conditioned for at least 48 h at 23°C at 65% RH. Films were cut into strips measuring 0.25″ wide using a Thwing-Albert cutter. Strips were exposed to 50% RH (to satisfy ASTM requirements) at 23°C for at least 45 min and then tested on a load frame utilizing a 2000 g maximum load cell. Test speed was 0.2″/min with grip separation (gauge length) of 2.0″.

Water vapor transmission rate (WVTR)

Water vapor transmission rate (WVTR) was determined gravimetrically using a modified version of ASTM method E96. Film specimens were mounted on PMMA cups (1.0″ in diameter and 0.375″ deep) filled with distilled water and placed in a desiccator cabinet containing water at 23°C. The cups were weighed at 3 h intervals over a period of 3 days and WVP (g m^{-1} S^{-1} Pa^{-1}) of the film was calculated as follows: WVP = $(wx)/At \times (P_2 - P_1)$, where w is mass permeated or the weight gain of the cup (g), x is the film thickness (mm), A is the area of exposed films (m^2), t is the time of gain (s), and $(P_2 - P_1)$, is driving force which is the vapor pressure differential across the film (Pa).

Modulated DSC

TA Instruments-Q 2000 was used for thermal characterization of the films. All samples were scanned using a heating rate of 5°C per minute. The heating rate used for conventional DSC studies was 10°C per minute.

TGA analysis

TA Instruments Q5000 was used for thermal gravimetric analysis (TGA) with a heating rate of 5°C per minute

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out using a Seiko DMS210 instrument in the temper-

ature range of 0–250°C using a frequency of 1 Hz, a heating rate of 2°C/min, and sample dimensions of 5.67 × 2 mm.

Wide-angle X-ray scattering (WAXS)

Wide-angle X-ray diffraction (WAXD) measurements were made on a PANalytical X'Pert MPD instrument using fixed slits (1/2 degree) with a Cu X-ray tube (1.54 Å wavelength). Samples were mounted on a flat sample holder made of Aluminum for data collection in reflection mode and the scans are represented as intensity (counts) versus the angle 2θ.

Small-angle X-ray scattering (SAXS)

Data was collected on a Small-angle X-ray scattering (SAXS) instrument from Molecular Metrology/Osmic. The instrument uses Osmic Confocal Maxflux Optics with pinhole collimation. Sample to detector distance was 140 cm, calibrated using silver behenate. Cu Kα radiation (1.542 Å) was generated using a Rigaku rotating anode generator operated at 40 kV and 60 mA. Two-dimensional data sets were collected with a Vantec-2000 detector from Bruker X-ray. The 2D image was azimuthally averaged to produce a 1D plot.

RESULTS AND DISCUSSION

Mechanical properties of Na-alginate, pectin, and blended films

The variation in Tensile Modulus (TM), Tensile Strength (TS), and Percentage Elongation (%E) in pure and CaCl$_2$-treated ("TR" in figures) films is shown in Figure 2.

As shown in Figure 2(a), the TM of pure Sodium Alginate (NaAlg) films is 3.68 GPa, whereas in pure Pectin films, it is about 4 GPa. The TM of a 100% Pectin film is slightly higher than in a pure NaAlg film. The TS of NaAlg is about 61.3 MPa and for Pectin it is 82.6 MPa [Fig. 2(b)]. %E for both polymers is very similar and is in the range of 5–6%. Low elongation at break can be attributed to extended chain conformation of both the polymers and the observed extension may be due to slippage of chains past one another.

NaAlg/Pectin binary blends show synergistic effect in TM and TS up to nearly 40% Pectin, and then there is a decrease in both values up to close to 70% Pectin, and then the values start increasing again [Fig. 2(a,b)]. Percentage elongation increases in blends to a maximum of 8.6% E at 10–15% Pectin [Fig. 2(c)]. From these results, we conclude that the synergism (reported and discussed in "Introduction") in the rheological properties of the gels of the
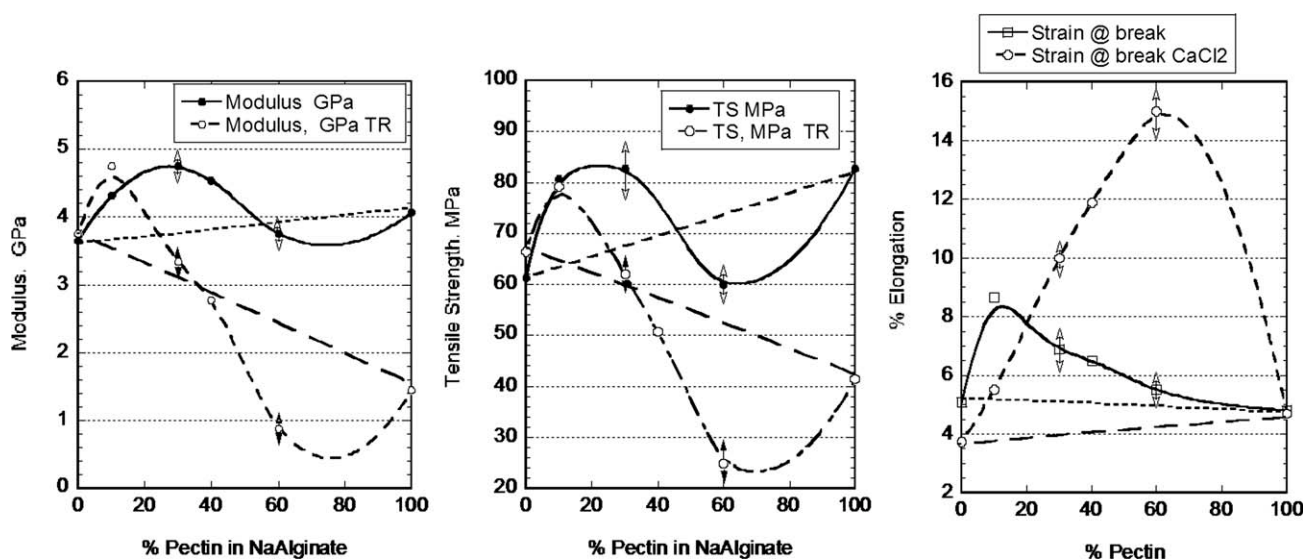
Figure 2 a: Variation of tensile modulus of the films as a function of Pectin content in Sodium Alginate for CaCl$_2$-treated (TR) and -untreated blends. Double arrow indicates standard deviation in all figures. b: Variation of tensile strength of the films as a function of Pectin content in Sodium Alginate for CaCl$_2$-treated (TR) and -untreated blends. c: Variation of percentage elongation of the films as a function of Pectin content in Sodium Alginate for CaCl$_2$-treated (open circles) and -untreated (open squares) blends.

blends of NaAlg/Pectin at low pH (18–20) is also seen in cast films of blend up to 40% Pectin.

Effect of CaCl$_2$ treatment on mechanical properties

Pectin and NaAlg films were made water insoluble by CaCl$_2$ treatment. Within experimental error there is no remarkable change in the TM, TS, or %E of CaCl$_2$-treated and untreated NaAlg films.

In Pectin films, there is a drastic decrease in TM and TS but not in %E (Fig. 2). TM decreases from 4.0 GPa (pure) to 1.45 GPa for CaCl$_2$-treated sample and TS decreases from 82 MPa (pure) to 41.5 MPa (CaCl$_2$-treated). These results suggest that the cross-linked network structure formed by CaCl$_2$ treatment leads to considerable structural reorganization and also destroys some existing crystalline tie points of Pectin leading to an almost 50% reduction in mechanical properties. Pectin has very low crystallinity so its effect on mechanical properties is not expected to be appreciable. The observed drastic change in TM and TS of a CaCl$_2$-treated sample is mainly due to formation of the network structure shown in Figure 1(a). Here, the change in the nature of amorphous phase (relaxed or extended chain conformation), intermolecular interaction after reaction with Ca^{2+}, % crystallinity, nature of interconnecting molecules in network structure, as well as the stability of amorphous micellars can influence mechanical properties.

In blended films, the TM increases from 3.68 (pure sample) to 4.75 GPa at 10% Pectin, then decreases to 0.5 GPA near 70% Pectin, and then increases again.

[Fig. 2(a)]. A similar trend is also noticed in TS where the highest value was 79.5 MPa at 10% Pectin and the lowest was 23.3 MPa near 70% Pectin [Fig. 2(b)]. However, in CaCl$_2$-treated samples, the %E increases up to a maximum of 15% at 60% Pectin and then decreases back down to 5% [Fig. 2(c)].

The large difference in mechanical properties in CaCl$_2$-treated and -untreated NaAlg/Pectin blended films containing more than 10% Pectin suggests a considerable structural change in the continuous matrix (change in molecular interaction) and a change in the size, interface, and morphology of the minor phase.

To understand the above trend of mechanical properties after CaCl$_2$ treatment at various blend compositions, it is necessary to investigate the possibility of phase separation, a change in crystalline nature of the blends, and its effect on short and long range molecular motions measured by DMA. These parameters also control WVPR (water barrier) of the blends. Thus, the observed trend in mechanical properties as a function of % of Pectin is also expected in the WVPR of the blends. To explain the observed trends in mechanical and other properties, the effects of various parameters on the properties were investigated using several analytical techniques.

Water vapor permeation rate of CaCl$_2$-treated film

The WVPR as a function of % Pectin in the blended and CaCl$_2$-treated films is shown in (Fig. 3). The data for the wet cup measurement is also included. The WVPR of NaAlg and Pectin films are, respectively, 31 g mm/m^2 day KPa and 22 g mm/m^2 day KPa.
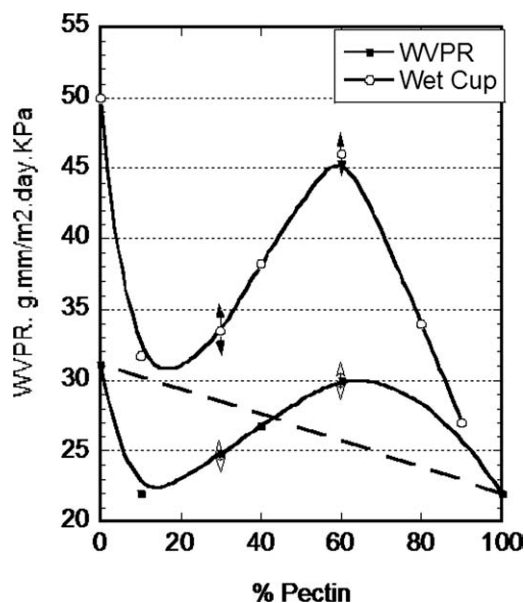
Figure 3 Variation of water vapor permeation Rate (WVPR) as a function of Pectin content in Sodium Alginate for CaCl₂-treated films by Dry (black squares) and Wet Cup (open circles) measurement.

Initially, WVPR decreases with addition of Pectin (Fig. 3) up to 10% and then starts increasing slowly up to 60% Pectin and then again decreases. The maximum synergistic effect in water barrier, TM, and TS is observed in NaAlg film containing 10–15% Pectin and these properties worsen at 60% Pectin. Our observed trend for WVPR is similar to that observed by Perez-Lambrech et al.[19] Results of Parris et al.[29] indicate lower WVP for NaAlg than either low or high methoxylated Pectin.

The WVPR in wet cup measurement follows the trend observed in dry cup measurement, but WVPR has considerably increased. This can be attributed to an increase in molecular mobility when the film is directly in contact with water. It was reported that CaCl₂-treated films swell in aqueous solution[30,31] which breaks hydrogen bonds among the polymer chains and increases molecular mobility. In the blends, it is also possible that water dissolves Pectin crystals leaving a network structure consisting of only amorphous physical tie points.

Even though we can achieve water-insoluble films having good mechanical properties from the present blending system, the observed water barrier in Pectin/NaAlg blends (Fig. 3) is too low for commercial packaging application. Further improvement in barrier properties was brought about by making bilayer films of NaAlg and Pectin using Grindsted Barrier System 2000B (product from Danisco Co.) This edible coating is based on a specially designed beeswax-based product. We mixed 6.5 g Grindsted 2000B, 0.5 g Sodium laurate, and 200 g water and heated at 90°C. The resulting emulsion was coated

at room temperature onto a NaAlg/30% Pectin blend film. Micron thick coated bilayer films showed water permeation rate of 4.5 g mm/m² day Kpa for Dry-Cup measurements and 4.2 g mm/m² day Kpa for Wet-Cup measurement. It was noted that coating of a 1.0 μm layer on the films does not change the mechanical properties of the films. It means that the mechanical properties of NaAlg and blends shown in Figure 2(a–c) do not change after coating with the Grindsted barrier formulation. Results indicate that a thin coating of this type is capable of providing higher water barrier films than commercial Cellophane films. For cellophane film, the WVPR is 11.5 g mm/m² day Kpa, whereas the wet cup value is 26.4 g mm/m² day Kpa. The TM, TS, and %E of cellophane are, respectively, 1586 MPa, 51.1 MPa, and 56%. Elongation of cellophane film is much higher than NaAlg/Pectin films which is required for most of the packaging film applications where enclosed food products have low water activity.

We made three bilayer films of NaAlg blended with 30% hydroxyethylcellulose (TM = 1344.0 MPa, TS = 30.8 MPa, %E = 7.9%), 30% Chitosan (YM = 1106.0 MPa, TS = 19.6 MPa, %elongation = 4.2%), and 30% gelatin (TM = 3367.0 MPa, TS = 52.5 MPa, %E = 6.5%). All three films showed the same WVPR of about 4.8 g mm/m² day Kpa. This shows that the observed high water-barrier of the films can be attributed to the Grindsted coating regardless of the barrier properties of the NaAlg blend system. A NaAlg/30% gelatin blend film gave a very high TM and TS.

The observed trend in WVPR with composition is similar to that observed in mechanical properties. The reduction in WVPR is concomitant with a decrease in molecular mobility. The changes occurring in the molecular mobility of the blends with composition and CaCl₂ treatment of the films are investigated using DSC and DMA, whereas the change in crystalline content is investigated with Wide-angle X-ray scattering (WAXS).

Differential scanning calorimeter (DSC)

The measurement of mechanical properties was carried out on samples conditioned at 23°C at 50% RH, following the procedure discussed in "Instron (Mechanical Properties Measurement)." All the DSC scans were made on samples that were similarly conditioned for measurement of mechanical properties.

Modulated DSC scans of the blends show the endothermic peak temperatures for 100% NaAlg, 10% Pectin, 30% Pectin, 60% Pectin, and 100% Pectin are 110, 109.8, 114.8, 101.0, and 104.90°C, respectively. In reversible heat flow scans, we do not observe another T_g. This indicates the miscibility of the polymers in the amorphous phase. However, it
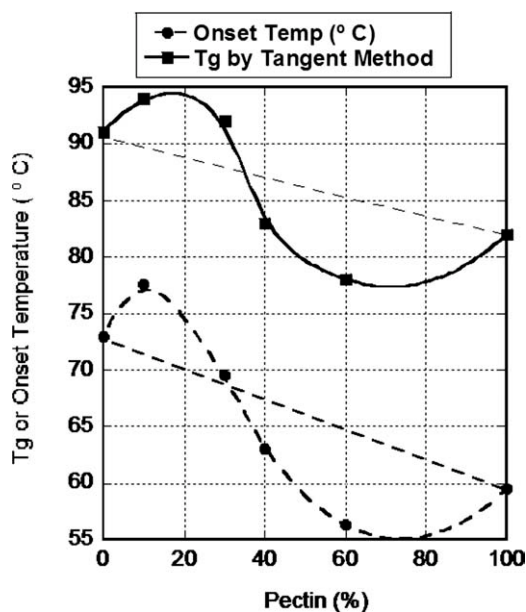
Figure 4 Variation of T_g and onset temperature as a function of Pectin content in Sodium Alginate for untreated blends.

is possible that the peak observed just above 100°C may either be due to overlapping of peaks from water and polysaccharides or just from water. Also, water could have a plasticizing effect.

To avoid confusion, we have determined the onset temperature from DSC scans (the temperature at which heat flow starts to change) which will provide us the lower limit of T_g. We have also determined the T_g from the mid-point between the onset temperature and the observed endothermic peak temperature. Composition-dependent T_g and onset temperatures are shown in Figure 4. These follow the trend observed in the mechanical and barrier properties seen in Figures 2(a,b), and 3. The observed trend in properties with Pectin composition is apparently related to the long-range molecular motion (T_g) of the continuous matrix of the blends and the change in magnitude of the tanδ peak. These results are confirmed from DMA measurements that are discussed in detail in "Dynamic Mechanical Analysis (DMA)."

Representative modulated DSC scans for NaAlg and Pectin are shown in Figure 5, whereas the derivative of weight loss (%/°C) determined from TGA scans are shown in Figure 6. In the case of Pectin, we have not observed any endothermic peak related to melting of Pectin crystals. TGA of Pectin shows the onset of decomposition at 197°C and occurrence of maximum weight loss at 220°C. There is no melting endotherm below 220°C.

Siddaramaiah et al.[10] observed a melting peak for NaAlg at about 220°C. Our DSC scans in Figure 5 shows a very weak endothermic peak at this temperature (Fig. 5) but this peak may not be related to the
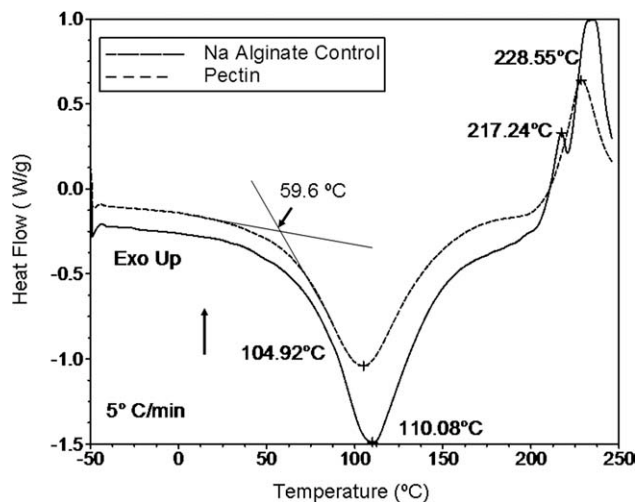

Figure 5 Modulated DSC scan for Sodium Alginate and Pectin samples. Arrow indicates the onset temperature.

melting of NaAlg. To confirm this, we have run TGA. Derivative of weight loss (%/°C) determined from TGA scans of NaAlg (Fig. 6) shows two peaks, which is also seen in DSC (Fig. 5). The onset of decomposition in NaAlg occurs also at 197°C which is similar to Pectin. Figure 6 shows two peaks, at 206.7 and 231.0°C, showing occurrence in maximum in decomposition rate at these two temperatures. So, previously classified melting temperature of 220°C falls in the decomposition range and it is difficult to assign it as a melting temperature.

Humidity dependence of the area of the endotherm observed in DSC scans at about 100°C was also investigated. This allowed us to check the plasticizing effect of water content on the glass-transition temperature. We heated a blend sample (60% Pectin/40% NaAlg) in conventional DSC up to 150°C, then the sample was cooled down to room temperature and reheated up to 250°C. DSC scan shows
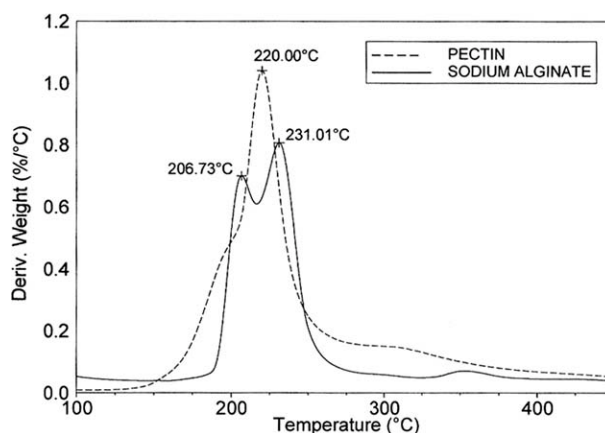
Figure 6 Derivative of weight loss (%/°C), which is derived from thermogravimetric scans (TGA) of Pectin and NaAlginate as a function of temperature.
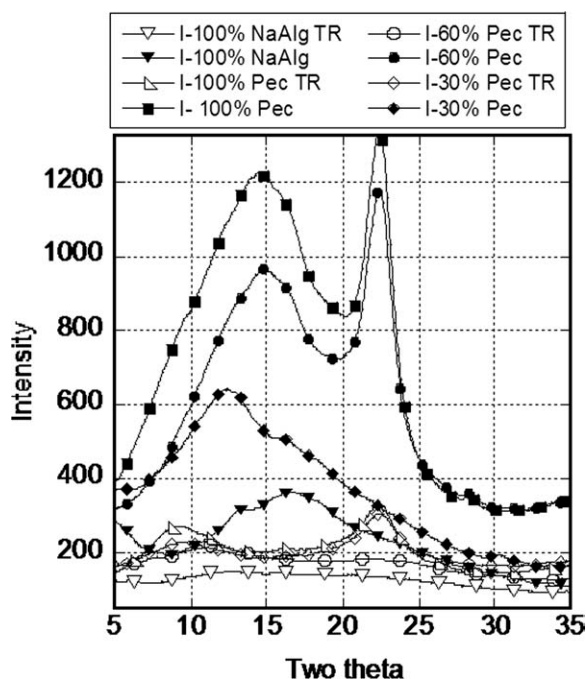
Figure 7 Comparison of Wide-angle X-ray scattering (WAXS) scans for CaCl$_2$-treated and -untreated Pectin and Sodium Alginate and their blends.

disappearance of the endothermic peak observed at 106.24°C. The observed baseline change in the reheated scan occurs at 118.6°C. Thus, the T_g and mechanical properties of the NaAlg/Pectin blend samples will be humidity dependent.

The observed trend in water barrier and in the mechanical properties follows the trend observed in T_g-% Pectin relation (Fig. 4). Thus, change in various properties of the blends with the compositions is therefore related with the change in molecular mobility. The molecular mobility was lower in the composition range showing synergism in properties, whereas mobility increases for the compositions manifesting properties below the rule of mixing line.

Wide angle X-ray scattering

Wide angle X-ray scattering was performed on films before and after CaCl$_2$ treatment. Figure 7 shows some representative X-ray scans of treated and untreated blend films and also pure NaAlg and Pectin films. Normally, NaAlg is considered an amorphous polymer. Our 100% NaAlg sample showed very weak peaks at 2θ values of 14° and 16.25°. However, crystalline peaks sit on the top of the amorphous halo so the peak area reveals the presence of very low crystalline ordered structures. These peaks, which are related to the ordered structure of NaAlg, disappear after addition of 10% Pectin. This phenomenon indicates good molecular interaction or miscibility of two chemically different

polymers at low Pectin levels. As seen from Figure 7, with increasing percentage of Pectin in NaAlg the crystalline content of the blends increases.

CaCl$_2$-treated films of NaAlg do not show any crystalline peak. This indicates total destruction of the ordered phase. Note that the X-ray intensity of the CaCl$_2$-treated and -nontreated samples cannot be compared because the Ca^{2+} can absorb X-rays.

X-ray scans of 100% NaAlg and the blend containing 10% Pectin show a weak peak at 2θ = 14° which is retained in the CaCl$_2$-treated sample. The addition of 10% Pectin in NaAlg considerably reduces the peak intensity versus 100% NaAlg, showing destruction of the ordered phase or an increase in amorphous content. If this is the case, then CaCl$_2$ treatment of the 10% Pectin sample (which has higher amorphous content) can increase the rate of Ca^{2+} ion diffusion leading to an increase in amorphous physical tie points (ATP) in the molecular network structure. This can be responsible for the reduction in molecular mobility and also leads to an increase in the TM and TS of the NaAlg continuous matrix containing 10% Pectin. Reduction in the values of WVPR and corresponding increase in T_g support the conclusion.

On the other side of the phase diagram, Pectin shows two distinct peaks at 2θ values of 15° and 22.5° (Fig. 7). These peak values were previously observed for Pectin.[32] WAXS of Pectin from apple peel showed peak at 12.5° and 21.5°.[3] This peak position is retained in the blend containing 60% Pectin indicating that the blend is phase separated. These results show that the crystalline character of NaAlg blend films increases with % Pectin.

On CaCl$_2$ treatment, the peak observed in 100% Pectin at 15° disappeared and a new peak appeared at 9.2° (Fig. 7). There are peaks observed at 2θ values at 7.75° (I = 189.00), 11.3° (I = 218), and 22.2° (I = 138.0) in the CaCl$_2$-treated sample containing 60% Pectin. This would indicate that the 60% Pectin sample has lost much of the ordered structure and is becoming more amorphous than the 30% or 100% Pectin samples. In a 60% Pectin blend, more Pectin crystals are replaced by amorphous physical tie points than in CaCl$_2$-treated 100% Pectin (it contains a mixture of crystalline and amorphous network structures). The amorphous crosslinked network structure so formed has low mechanical properties, as seen in CaCl$_2$-treated 100% Pectin (Fig. 2). It became apparent at this stage that in the CaCl$_2$-treated 60% Pectin blend, the continuous Pectin matrix has much lower mechanical properties than those observed in the blends having a continuous NaAlg matrix. In a continuous Pectin matrix consisting of phase separated high modulus NaAlg phase, two things can happen; (a) addition of NaAlg can progressively break down interconnecting network
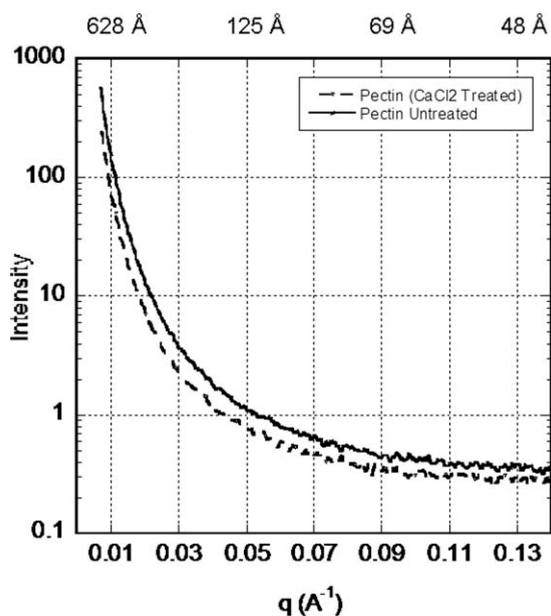
Figure 8 Small-angle X-ray scattering (SAXS) scans for CaCl$_2$-treated and -untreated Pectin films showing absence of periodicity.

structure creating loose molecules; (b) the nature of the interface between the phases gets modified; load will not transfer efficiently if the interface is poor.

For both the CaCl$_2$-treated films of 30% Pectin blend and pure Pectin, we observed weak crystalline peaks having similar areas at 2θ values of 9° and 22.5° (Fig. 7). However, both the blended film samples have different mechanical properties (Fig. 2). This indicates that Pectin is almost amorphous in both cases. The 30% Pectin blend contains low modulus Pectin in a relatively stiffer NaAlg continuous matrix which enhances the toughness of the film. After inversion of the continuous matrix above 50% Pectin, low modulus Pectin dictates the mechanical response.

SAXS scans of treated and untreated Pectin are shown in Figure 8. Absence of periodicity arising from lamellar crystalline and amorphous phases reveals the absence of supermolecular structure (spherulitic growth features) in the range from 48 to 500Å (refer to values above the plot). TEM study of films and gels supports this conclusion.[18,19] Thus, the morphology of crystalline Pectin may be similar to that described by the "Fringed Micellar model."

Even though the % crystallinity of Pectin is very low and its effect on film properties may not be appreciable, it plays a vital role in understanding the nature of the resulting blend as well as the type of network structure formed after CaCl$_2$ treatment. For the blends of crystalline and amorphous natural molecules, the X-ray study helps to discern the nature of the resulting blends, composition ranges of compatible and noncompatible blends, the types of

molecular network structure present in the blends, extent of diffusion of Ca^{2+} in films, cause of increasing or decreasing physical crosslinking, occurrence of skin-core effect, etc.

Dynamic mechanical analysis

To understand the observed trend in mechanical and thermal properties, it is useful to examine changes in molecular mobility of the matrices both before and after CaCl$_2$ treatment, which is reflected in changes in storage modulus with temperature, mechanical dispersion (alpha, beta, and gamma), change in magnitude of tanδ peaks, and comparison of T_g from tanδ peak and storage modulus-temperature scans.

The observed tanδ peak temperatures for NaAlg, Pectin, and the blends before and after CaCl$_2$ treatment and the change in magnitude of tanδ peaks compared with untreated samples are compiled in Table I and some representative tanδ curves are shown in Figures 9 and 10. For the same composition, more than one peak was observed and a peak having the highest temperature was taken as T_g. As seen from Table I, T_g increases initially up to 30% Pectin and then decreases. This trend is very similar to that noted in T_g observed from DSC (Fig. 4).

A similar trend is also seen in the blends treated with CaCl$_2$. Following CaCl$_2$ treatment, the magnitude of tanδ peak initially decreases up to 30% Pectin addition and then increases (Table I). These results indicate that long range molecular motion initially decreases making the NaAlg continuous matrix stiffer. The decrease in motion is due to increases in intermolecular interaction and physically crosslinked tie points.

Table I shows that upon CaCl$_2$ treatment molecular mobility in samples having 40% or more Pectin content increases with increasing Pectin content (increase in peak area (PA) of tanδ peak). Increase in molecular mobility reveals the softening of the continuous Pectin matrix. Compared with a 60% Pectin blend, the magnitude of the tanδ peak in 100% treated Pectin is decreased. Thus, molecular mobility is more restricted in pure Pectin than the blend

TABLE 1
Effect of CaCl$_2$-treatment on Tg and tanδ Peak Area

| Pectin content (%)	Tanδ PT, (°C) untreated	Tanδ PT, (°C) treated	Change in Tanδ PA
0%	54	44, 55	Decreased
10% Pectin	46,76	65	Decreased
30% Pectin	68, 87, 139, 150	23, 66, 76	Decreased
40% Pectin	64	100, 139	Increased
60% Pectin	28,76	33, 51	Increased
100% Pectin	26,58	27,68	Decreased
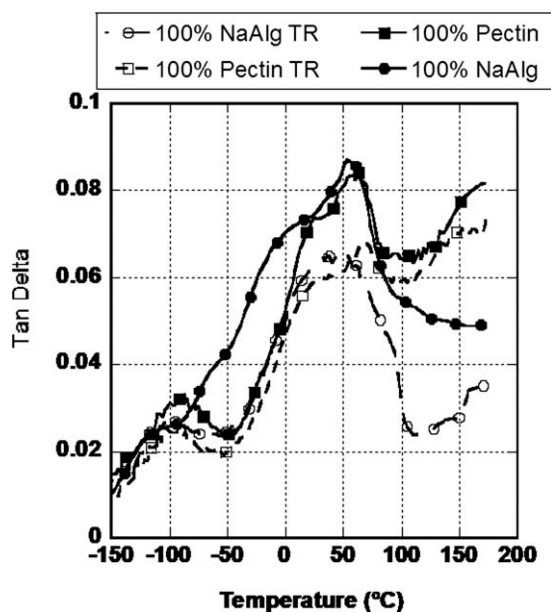
Figure 9 Tanδ—Temperature scans for CaCl₂-treated (dashed lines) and -untreated (solid lines) pure Sodium Alginate and Pectin films.

having 60% Pectin. It is also seen that addition of a low % of NaAlg in Pectin breaks hydrogen bonds between polymer chains or that initially existing polymer–polymer chain interactions are broken after CaCl₂ treatment. Figure 2(a) demonstrates that the molecular network formed after CaCl₂ treatment of Pectin has very low modulus. The newly formed network structure of Pectin containing Ca²⁺ after CaCl₂ treatment is softer (less stiff) which reflects the change in the cohesive energy or interaction
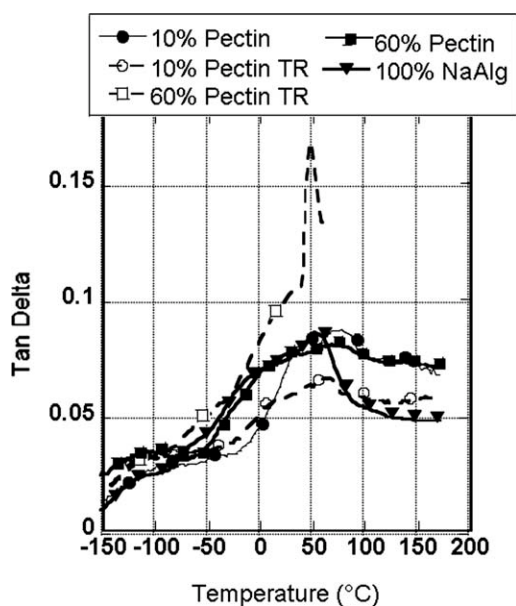
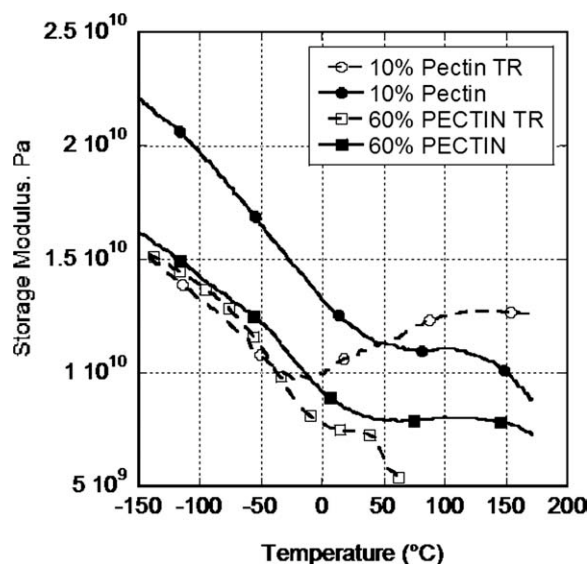**Figure 10** Tanδ—Temperature scans for CaCl₂-treated (dashed lines) and -untreated (solid lines) blends of Sodium Alginate and Pectin.
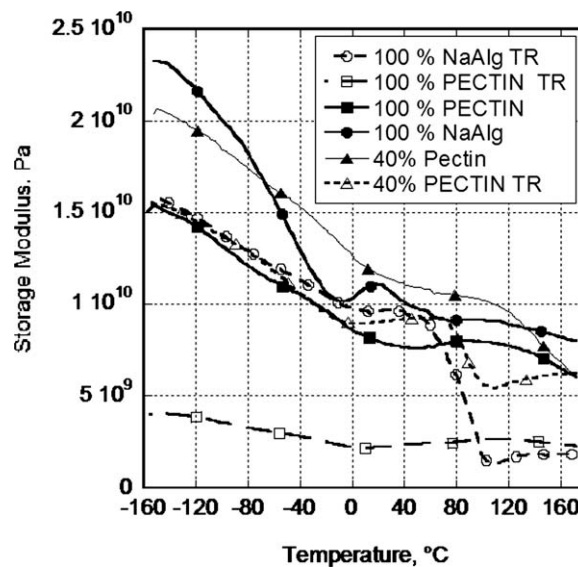
Figure 11 Storage Modulus—Temperature curves for CaCl₂-treated (dashed lines) and -untreated (solid lines) blends of Sodium Alginate and Pectin.

among the polymer chains. In the blends, a continuous flexible Pectin matrix contains a high modulus NaAlg phase. Depending on the interface, these phases can also act as defects in the continuous Pectin matrix. All these factors influence the nature of the network structure and morphology of the phases, and thereby change in mechanical and barrier properties.

As noted previously,[11,16] the discrepancy observed in the values of T_g by DSC and DMA is due to principles involved in the methods of measurement and different constraint on sample and heating rates.

Temperature dependent storage modulus (E')

It is possible to confirm T_g from temperature dependent of storage modulus (E'). Normally at T_g, there is an abrupt change in E' from the brittle glassy state to the rubbery state. This transition is defined as glass transition temperature (T_g) where long range molecular motions occur in amorphous phase and is related to alpha transition observed in loss modulus or tanδ temperature curves. Figures 11 and 12 show the variation in E' as a function of temperature for NaAlg (solid circles), Pectin (solid squares), and blends before and after CaCl₂ treatment. As seen from Figure 11, the transition from glassy to rubbery state is not sharp for NaAlg and Pectin, and in such cases, it becomes very difficult to evaluate correct T_g. Complexity of this type can arise due to continuous reorganization in structure with temperature in treated and untreated samples. Because of complexity near the glass-rubbery transition and on higher temperatures in E'-Temperature curves of the blends, it is difficult to assign correct value of T_g. So, in this

Figure 12 Storage Modulus—Temperature curves for CaCl$_2$-treated (dashed lines) and -untreated (solid lines) films of 10 and 60% Pectin in Sodium Alginate blends.

study, our interpretation regarding molecular mobility is mainly based on the variation in tanδ peak temperatures and change in the magnitude of the tanδ peaks after CaCl$_2$ treatment. Major characteristic features of the curves are briefly summarized here.

NaAlginate

The Storage modulus of NaAlg films rapidly decreases from −150°C, remains constant above room temperature, and then further decreases with increasing temperature (Fig. 11). Transition from glassy to rubbery is not sharp enough to define T_g. The onset in decrease in E' occurs at 55°C and 118°C. Beyond 118°C, decreases in E' with temperature is not appreciable. Miura et al.[11] observed a mechanical dispersion peak around 130°C in the loss modulus curve which was assigned as α-transition corresponding to long range molecular motion, T_g. We do not observe any peak above 100°C either in loss modulus or in tanδ curves. Instead a prominent peak is observed at 55°C (Fig. 9). Sub-T_g is observed at −100°C. Our results are consistent with the previous DMA result of Kumar Naidu et al.[32]

Except in temperature range of 0–40°C, the storage modulus of CaCl$_2$-treated NaAlg films is lower than untreated sample. Storage modulus of CaCl$_2$-treated NaAlg films decreases up to 0°C (Fig. 11); it then remains constant up to 60°C and followed by abrupt decreases until 100°C. The glassy-rubbery transition is sharp and the assigned glass-rubbery transition temperature is 88°C. The observed long rang motions in NaAlg reflect the change in nature of network structure along with the interaction parameter. Comparison of amplitude of both the crosslinked

and native tanδ peaks (Fig. 9) reveals that there is a reduction in the molecular motion on crosslinking with Ca^{2+}. In spite of the similar storage modulus of treated and untreated films at room temperature, its temperature dependence is very different than untreated film.

Pectin

The Storage modulus of Pectin films follows the trend observed in NaAlg; the change in E' occurs at 40°C (Fig. 11). However, this change in E' is not distinct or sharp. In the tanδ temperature curve, the prominent peaks are observed at 26°C and 58°C and the sub-T_g is at −90°C (Fig. 9). DMA study of Fishman and Coffin[33] does not show T_g. At this stage, there is confusion about the nature of the mechanical dispersion noted at high temperature (above 58°C in Fig. 9) as the tanδ curve showed upward increase. However, from the tanδ temperature curve, we defined T_g to be 58°C.

In case of CaCl$_2$-treated Pectin samples, there is drastic reduction in E' at all temperatures and it becomes almost independent of temperature (Fig. 11). There is no transition from glassy to rubbery state. Hence, there is no observable T_g. We do not know if the absence of glassy to rubbery transition is related to structural reorganization taking place as temperature increases. The cause of the considerable drop in the E' in whole temperature range is due to change in interaction parameters. From X-ray study, it is clear that Pectin has a mixture of two types of molecular network structures and CaCl$_2$ treatment destroys crystallites of the network structure; therefore, the original molecular network structure is modified.

As seen in Figure 9, after CaCl$_2$ treatment, the tanδ peaks are at 27°C and 68°C, so we defined 68°C as the T_g. The peak is broad and it fans out with increasing temperature. The low temperature transition (Sub-T_g) occurs at −99°C (Fig. 11) and the amplitude of this peak is decreased upon CaCl$_2$ treatment. This indicates that there is a decrease in short- and long-range molecular motion.

NaAlginate/pectin blends

Figure 12 shows the temperature dependence of E' in the CaCl$_2$-treated and nontreated films of blends containing 10 and 60% Pectin. The Storage modulus of the 10% Pectin blend decreases up to 50°C, then remains constant up to 110°C, and again starts decreasing. CaCl$_2$ treatment of 10% Pectin causes a considerable reduction in E' below 0°C and then it increases with temperature and crosses over the curve for untreated Pectin. The increase in E' above room temperature can be due to shrinkage of the

films or change in perfection and/or increase in density of tie points due to structural reorganization.

As seen in the tanδ temperature curve (Fig. 10), the major peak for 10% Pectin is 76°C, and a shoulder is observed at 46.5°C. The sub-T_g is observed at −100°C. After CaCl$_2$ treatment, the major peak is at 65°C and a shoulder is observed at 30°C. The Sub-T_g is observed at −108°C, however, one should remember that peaks in both CaCl$_2$ treated and untreated at high temperature fan out and are not sharp. The reduction in the magnitude of the tanδ peak upon CaCl$_2$ treatment reveals the reduction in long range molecular motion.

The storage modulus curve of 40% Pectin films follows a trend similar to 100% Pectin, but the E' is higher above −60°C than 100% NaAlg (Fig. 11). After CaCl$_2$ treatment, there is reduction in modulus at all temperatures. The trend in variation in modulus with temperature is the same as CaCl$_2$-treated 100% Pectin film up to 0°C, then remains unchanged up to 80°C; thereafter, there is abrupt decreases until it reaches 100°C. Above 110°C, E' slightly moves upward until 160°C. The T_g is about 90°C. The tanδ curve shows peaks at 100°C and 139°C. At this composition, compared with an untreated sample, the magnitude of tanδ peak is increased which indicate reduction in interaction between polymer–polymer chains or an increase in mobility in molecules.

In the blended samples containing 60% Pectin, E' is lower than in 10% Pectin (Fig. 12). At room temperature and above, E' remains constant up to 150°C and then starts decreasing. Upon CaCl$_2$ treatment, the E' decreased up to 0°C and retains the same value up to 40°C, and then it rapidly decreases. This trend in E' is the opposite of the CaCl$_2$-treated 10% Pectin blend where the modulus increases above room temperature. T_g of this blend is 50°C which is also observed in tanδ peaks (Fig. 10). The high temperature peak for 60% Pectin is at 76°C with a shoulder in the peak at 28°C. The sub-T_g peak is observed at −105°C. After CaCl$_2$ treatment, the high temperature peak is at 51°C with a shoulder in peak at 33°C. The Sub-T_g is observed at −92°C. After CaCl$_2$ treatment, the amplitude of the T_g peak increases drastically. From these results, it can be concluded that compared with 10% Pectin blend, the long range molecular motion (chain mobility or flexibility) increased drastically in the 60% Pectin blend. Thus, Pectin matrix in this blend has low modulus.

From the results, it is seen that T_g of both CaCl$_2$-treated and untreated samples increases up to 30% Pectin content and the magnitude of the tanδ peak decreases (Table I). These results lead to the conclusion that modulus or stiffness of NaAlg continuous matrix in the blends increases. For the blend having 60% Pectin, tanδ magnitude is higher than that observed for 10% Pectin blend. After CaCl$_2$ treatment of 60% Pectin blends, T_g becomes lower than Pectin; the magnitude of tanδ peak drastically increased. Thus, the continuous Pectin matrix of the blend has lower modulus or a softer matrix than the NaAlg matrix. This is the major reason for the decrease in mechanical properties above 50% Pectin.

The relatively lesser change in the mechanical properties of almost amorphous NaAlg film on CaCl$_2$ treatment can be possibly explained by the occurrence of the skin-core effect. A fast reaction of the surface molecules during CaCl$_2$ treatment creates physical tie points on the film surface (skin, several Å thick) which then hinders further diffusion of Ca^{2+} into the interior of the film (core). Hence, this causes the interior of the film to have different mechanical properties than on the surface. However, in this case, the temperature dependence of the storage modulus should have not shown sharp glass-rubbery transition as seen in Figure 11. Thus, occurrence of the skin-core effect can be ruled out.

SUMMARY

Synergistic character of blends; composition dependency of properties

In blends of semicrystalline polymers, the variation of properties with the blend compositions is controlled by parameters such as compatibility of the polymers, phase coarsening with increasing second blend component, short and long range molecular motions, resulting morphology in both the separated phases, size of crystals (aspect ratio), and method of sample preparation.[34–40]

Synergism in mechanical properties in blends of semicrystalline polymers has been investigated in the past (36, 37, and 40). The situation in a compatible blend of an amorphous polymer with a semicrystalline polymer differs as the role of phase coarsening is absent; the property governing factors are % crystallinity, the nature of amorphous and crystalline phases, short and long range molecular motions, and the nature of the molecular network structure.

Our X-ray study reveals that NaAlg is almost amorphous, whereas Pectin has very low crystallinity. Long spacing, a characteristic of spherulites of semicrystalline polymers, is absent. In addition, a previous electron microscopic study shows the absence of any spherulites. These results led us conclude that the morphology of Pectin is like that described by the "Fringe-Micellar" structure [Fig. 1(b)].

The properties of the Pectin and NaAlg blended cast films have been studied before and after CaCl$_2$ treatment. In nontreated film, the synergistic character in mechanical and barrier properties is observed up to 40% Pectin in NaAlg. A similar trend was also seen for T_g with % Pectin in NaAlg for CaCl$_2$-treated

films. This observed increase in properties is attributed to the decrease in long range molecular motions in these blends. Thus, previously observed synergistic properties seen in gels of the blends of these polymers at low pH and which originate from a strong network structure are also seen in our cast films of the blend made at room temperature.

Above 40% Pectin blends, the Pectin becomes a continuous matrix containing NaAlg. Films that have not been $CaCl_2$ treated show a continuous increase in crystallinity in the continuous Pectin phase due to an increase in crystalline Pectin content (refer "Wide Angle X-Ray Scattering (WAXS)"). Thus, the increase in amorphous NaAlg molecules in the crystalline Pectin matrix at high Pectin content leads to the formation of a mixed molecular network structure. In this case, the molecular connectivity in the Pectin network structure can be disrupted or the possibility of development of poor interface at the boundary of the separated phases by NaAlg cannot be ignored. In other words, NaAlg creates defects in the molecular network structure of the continuous Pectin matrix. Our DMA study reveals that the resulting structure has higher molecular mobility which is responsible for the slight decrease in mechanical properties at high Pectin content (refer "Dynamic Mechanical Analysis (DMA)"). These blends showed very high modulus but have lower film flexibility and the films are water soluble. Films become water insoluble after $CaCl_2$ treatment.

Change in properties via structural reorganization after $CaCl_2$ treatment

NaAlg is amorphous while Pectin has low crystallinity. $CaCl_2$ treatment of pure films of both the polymers led to formation of amorphous tie points [Fig. 1(a)]. Interaction of Ca^{2+} with acidic groups forms a complex [Fig. 1(a)] with Pectin and NaAlg which introduces noncrystalline physical crosslinks (tie points) in the molecular network. The resulting morphology is described by the "Egg Box" model.

Even though the mechanical properties of NaAlg and Pectin are very similar, $CaCl_2$ treatment leads to formation of a very different structure resulting in very low modulus Pectin film. Both molecules have very different composition and chain conformation (Introduction). The presence of Ca^{2+} affects molecular interaction more in Pectin than in NaAlg films.

Our X-ray study of the Pectin and its blends before and after $CaCl_2$ treatment also shows the presence of Pectin crystals. Thus, initial "Fringe-Micellar" type molecular network structure of Pectin is partly converted after $CaCl_2$ treatment to "Egg Box" type amorphous molecular network structure. Hence, $CaCl_2$ treatment of films can create a mixed network structure in blends and change in molecular

interaction. Films become water insoluble. Our mechanical property measurements show a drastic decrease in mechanical properties after $CaCl_2$ treatment (Fig. 2) which suggests that the resulting mixed network structures of Pectin is unique and has high molecular mobility and low modulus.

In the blends, the composition range for synergism in mechanical properties is reduced after $CaCl_2$ treatment of the films. The initial increase in mechanical and water barrier properties are attributed to the decrease in molecular mobility of the continuous NaAlg phase due to an increase in physically crosslinked tie points. The increase in amorphous tie molecules is caused by the increase in diffusion of Ca^{2+} due to the breaking down of crystalline content (Wide Angle X-Ray Scattering (WAXS)).

Compared with untreated blends, mechanical properties of the films rapidly deteriorate after $CaCl_2$ treatment in the blends above 20% Pectin as the crystallinity of Pectin is reduced and is converted to an amorphous molecular network structure having high molecular mobility. A similar property trend is also noted in water barrier properties. This situation is clearly seen from the results of a 60% Pectin blend with NaAlg before and after $CaCl_2$ treatment. In brief, reduction in the composition range for synergism in mechanical and water barrier properties after $CaCl_2$ treatment of films is attributed to factors such as, reduction in crystallinity, formation of mixed network structures [Fig. 1(a,b)], change in nature in interconnectivity of network structures and their interface, as well as change in molecular mobility at various blend composition due to change in molecular interaction.

The continuous increase in %E of NaAlg blends above 20% Pectin [Fig. 2(c)] in $CaCl_2$-treated samples can be understood from the conversion of the Pectin phase into a low modulus phase in the NaAlg continuous phase. Increasing the amount of the low-modulus (rubbery-phase), finely dispersed Pectin phase in the relatively high-modulus, continuous NaAlg matrix enhances toughness of the blends up to 50% Pectin. The further increase in %E films having above 50% Pectin is related to the conversion of the continuous high-modulus NaAlg matrix to the very low modulus Pectin matrix and the associated change of morphology of separated phases. Increase in molecular motions observed from DMA results and decrease in water barrier support this conclusion.

Commercial applications of NaAlginate/pectin films

The goal of this study was to make edible films which have mechanical and water barrier properties similar to nonedible Cellophane films. It is possible to achieve high water barrier films of Pectin/NaAlg

blends but those films lack the film flexibility required for several food packaging applications. However, such films have potential use for enhancing shelf life of food products containing various food components (sandwiches, pizza, etc.) that have different water activities.

Further improvement in barrier properties was brought about by making bilayer films of NaAlg and Pectin by using a thin coating of edible beeswax-based formulation at room temperature. Bilayer films showed water vapor permeation rate in the range of 4.0–4.5 g mm/m^2 day Kpa for wet and dry cup measurements. These values of WVPR are better than the values observed for Cellophane (11.5 g mm/m^2 day Kpa.)

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