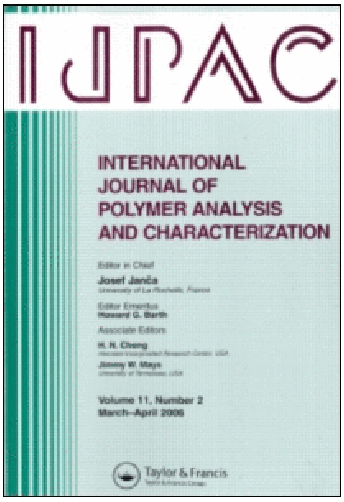

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Chemical Modification of Cellulose Acetate with Titanium Isopropoxide

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This study describes the chemical modification of cellulose acetate (CA) using titanium isopropoxide (TiP) in a sol-gel process for the formation of an organic/inorganic hybrid (OIH) material. The hydrolysis and condensation reactions that characterize this process result in CA cross-linking and formation of inorganic oxide particles. TiP-modified CA gels and membrane materials are characterized by solubility and swelling measurements, Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy, thermogravimetric analysis, differential scanning calorimetry (DSC) and ultrasonic time-domain reflectometry. Whereas the solubility of the CA significantly decreased with increasing TiP exposure consistent with high levels of cross-linking, unambiguous spectroscopic evidence for cross-linking could not be determined. In addition, DSC measurements indicated no significant change in CA glass-transition temperature as a function of TiP exposure. On the other hand, TiP treatment dramatically improved the creep behavior of treated porous CA membranes, whereby the total compressive strain decreases by as much as 70% relative to the untreated materials. Overall, the results suggest that TiP treatment can be used as a post-fabrication processing step to create OIH-modified CA membranes with improved chemical and mechanical stability.

Keywords: Cellulose acetate; Titanium isoproxide; Organic/inorganic hybrid

Cellulose esters are used in a wide range of commercial applications; annual production of these polymers now exceeds 1.5 billion pounds[1]. Cellulose esters have outstanding permselective properties and are extensively used in a variety of industrially important separations. Cellulose acetate (CA) has a particularly attractive combination of physical, chemical, thermal and processing properties that have facilitated its use as a membrane polymer in reverse osmosis, nanofiltration and gas separations[2]. However, CA has several significant limitations in such applications, including a susceptibility to creep and a relatively low resistance to organic solvents[3]. In general, the structure of the CA membranes can be characterized as integrally asymmetric, whereby a thin dense barrier layer is supported by a much thicker porous substrate. Previous studies have reported that the compressive deformation of this porous substrate that occurs over time at high transmembrane pressures may lead to significant flux decline, a process described in the membrane literature as compaction. This phenomenon is of particular concern when the CA is plasticized, as is the case during desalination or gas separations involving CO_2. Consequently, attempts have been made to improve the chemical and mechanical properties of CA via cross-linking. Although these efforts have demonstrated that solvent resistance can be significantly increased, the resulting improvements in mechanical behavior have been much more limited[4].

An interesting approach to the problem involves the use of sol-gel chemistry to create organic-inorganic hybrids (OIH), which can provide unique combinations of properties that arise from simultaneous polymer cross-linking and particulate reinforcement. OIH materials can be synthesized from organic polymers and inorganic monomers such as metal alkoxides. Cellulose derivatives are ideal candidates for the organic polymer because hydroxyl groups can react with the metal alkoxides[5]. However, relatively little information in the literature involves the chemical modification of cellulose derivatives using an OIH scheme with metal alkoxides. Yano[6] studied hydroxypropyl cellulose and tetraethoxysilane, and Yoshinaga et al.[5] reported results for ethyl cellulose and various metal alkoxides including $Ti(OC_2H_5)_4$, $Ta(OC_2H_5)_5$, $Nb(OC_2H_5)_5$ and $Fe(OC_2H_5)_3$. Shojaie et al.[3] investigated the CA-tetraethyl orthosilicate (TEOS) system and confirmed that the chemical and mechanical properties of the resulting OIH material were significantly altered relative to untreated CA. However, the commercial applicability of their approach is limited because the CA first required modification via a time-intensive grafting reaction before TEOS exposure. In addition, reasonable reaction times of the grafted polymer with TEOS can be obtained only when the polymer is in solution. Moreover, the TEOS reaction tended to interfere with the phase separation required to form a porous substrate.

Consequently, the major objective of this study is to develop a post-fabrication treatment for CA membranes that uses sol-gel chemistry for the efficient formation of an OIH material with improved chemical and mechanical stability. We describe a treatment that uses titanium isopropoxide (TiP) as the metal alkoxide, whereby the hydrolysis and condensation reactions that form the basis of this sol-gel process can be represented schematically as:

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH \qquad \text{Hydrolysis}$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \qquad \text{Condensation}$$

where R is $CH(CH_3)_2$. The $Ti(OH)_4$ can react with the CA hydroxyl groups as well as with other $Ti(OH)_4$ molecules. Therefore, the primary effects of the condensation reaction should be cross-linking of the CA and the formation of discrete metal oxide regions.

In order to gain a better understanding about the nature of the chemical modifications produced by the CA-TiP reaction, we studied solutions prepared from CA polymer gels and CA membranes. These TiP-modified CA materials are characterized by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR), thermal analysis techniques including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and ultrasonic time-domain reflectometry (UTDR). The latter was recently introduced as a means of evaluating creep behavior of membranes under realistic conditions[7,8].

EXPERIMENTAL

Preparation of OIH Materials

Cellulose acetate (CA 398-30) was obtained from Eastman Chemical Co. All other reagents were obtained from Aldrich and used as received.

Gels were prepared from CA solutions that were then treated with TiP. For example, 1.0 g of CA dissolved in 10 mL of acetone in a screw-capped jar, then 0.04 to 0.1 mL (0.14 to 0.34 mmol) of TiP was dissolved in 2 mL acetone. The jar was closed and shaken vigorously; a gel was set up immediately, which was removed with a spatula and allowed to air dry to yield a tough yellow solid. Alternatively, the gel was removed and placed directly in a beaker containing distilled water for 24 h at room temperature before being air-dried.

Dense CA/TiP films were made in a two-step process. First, a dense CA film was cast from acetone and allowed to dry in an acetone-saturated atmosphere. The dry film (approximately 0.1 to 0.5 mm thick) was then allowed to incubate in a 15 vol% solution of TiP in tetrahydrofuran (THF) for up to 3 h at 23°C. The film was removed and immediately plunged into 23°C distilled water, where it was allowed to incubate for at least 3 h. No obvious structural or visible changes occurred aside from slight fogging that presumably resulted from the presence of TiO_2 on the surface of the film. The film was then air-dried and stored in a sealed plastic bag before use.

Dense films used for the infrared studies were very thin, and supported on a melt frame. The films were formed by immersing the frame in a 10% solution of CA in acetone, slowing removing the frame and letting the film dry overnight. These supported films were then immersed in the TiP/acetone solution for 10 to 60 s, removed and soaked in distilled water 1 h, then removed and air-dried.

Microporous CA membranes were prepared by a dry-cast process described in detail elsewhere[9]. The membranes were cast at 23°C using an initial casting-solution composition of 15–20–65 wt% CA-water-acetone in a mold 10 cm in diameter × 1 mm deep. Each cast solution was allowed to dry for 2 h, after which the membrane was stored under vacuum to completely remove any residual solvent or nonsolvent. The membranes, which had a final thickness of 170–180 mm and an overall porosity of approximately 36%, were then treated in a bath of 10 vol% TiP in methyl ethyl ketone (MEK) at 23°C. The treatment protocol used exposure times of 0, 15, 30, 60 and 120 min to control the extent of the reaction. After treatment, the samples were washed with isopropyl alcohol to remove any residual TiP solution.

Characterization Studies

Solubility values were obtained from specimen dry-mass measurements before and after 24 h immersion in dimethyl sulfoxide (DMSO), MEK and toluene. For samples rendered insoluble, implying sufficiently high degrees of cross-linking, equilibrium swelling data were calculated from the weight gain during long-term immersion in MEK.

Liquid and solid-state ^{13}C-NMR spectra were generated using a Varian 300 and a Bruker CP/MAS NMR spectrometer, respectively. Relaxation times, T_1, were measured with a variable contact time experiment. Infrared spectra were obtained with a Nicolet 5SXC FT-IR spectrometer. TGA and DSC studies were conducted using a TA Instruments 2950 TGA and model 2910 DSC, respectively. TGA experiments were conducted over the temperature range 50–850°C using a heating rate of 20°C/min with constant air flow. The DSC runs were conducted in sealed aluminum pans under a nitrogen atmosphere. Samples of approximately 10 mg were first heated to 250°C at 20°C/min then cooled at the same rate (run 1), reheated at 20°C/min to obtain a well-defined glass-transition (T_g) curve (run 2), cooled at 1°C/min, then heated a third time at 20°C/min (run 3). Annealing experiments were performed by heating the samples to 175°C and holding them at temperature for 18 h, cooling to 50°C at 20°C/min, then reheating at 20°C/min to approximately 225°C.

Membranes were placed in a high-pressure separation cell in which the pressure was ramped to 4.14 MPa (600 psi) in less than 1 min. The pressure was maintained at 600 ± 1 psi for the duration of the experiments that ranged from 120 to 200 min. Compaction behavior of the membranes was monitored using the UTDR technique developed by our research group and described in a recent paper[7]. With this technique the thickness change of the membrane can be related to the change in arrival time of an ultrasonic signal reflected from the membrane surface, if the velocity of the propagating ultrasonic wave is known. For each membrane, compressive strain as a function of time was determined from the real-time measurement of membrane thickness changes with a resolution of ± 1 μm.

Overall membrane morphology, including the percent porosity, was evaluated using a Cambridge 250 MK3 scanning electron microscope (SEM). Representative cross-sections were obtained by freeze-fracturing in liquid nitrogen and coating with a Technics vacuum evaporator. All specimens were carefully dried before examination to minimize shrinkage artifacts.

RESULTS

Solubility and Swelling

The reaction between CA and TiP produced significant changes in the solubility of gels, and in dense and microporous films. Whereas the injection of a homogeneous CA/acetone solution into pure acetone results in the rapid dilution of the CA solution, the injection of a homogeneous CA/acetone solution into acetone containing TiP results in the immediate gelation of the polymer. Gelation of the CA limits further mixing of the CA and TiP and results in the formation of a heterogeneous material. If the gelled CA is removed from the TiP solution and immersed in a fresh aliquot of acetone, the CA will not redissolve. The same results were obtained for CA/acetone solutions injected into TiP dissolved in THF, toluene and mixtures of these solvents. The CA that gelled in TiP solutions could not be redissolved in several "good" solvents including acetone, THF and DMSO. If the TiP exposure times were brief, the gelled CA would disintegrate but not dissolve completely.

To estimate the minimum amount of TiP needed to cross-link CA, the CA solution was injected into acetone solutions containing decreasing concentrations of TiP. The lowest level of TiP that caused gelation was 0.14 mmol/g, which amounts to one Ti atom for approximately every 30 glucose residues. Although TiP was probably not uniformly mixed throughout the gel, this experiment provides an estimate of the minimum number of reactions that must occur to form a cross-linked material. It also indicates that the required number of cross-links is quite small.

Similar changes in solubility were also observed for dense CA films immersed in TiP for varying lengths of time. In the case of thin, dense CA films, 10–50 μm thick, even short TiP immersion times caused insoluble CA films to form. In the case of thicker, dense CA films, 100–500 μm, only a portion of the TiP-treated CA film was insoluble following short exposure times. These films appeared to have an insoluble skin and a soluble core. In many cases, when TiP-treated thick CA films were exposed to pure solvent, the center of the thick film could be extruded from between the two insoluble outer layers.

In an attempt to quantify the relationship between the swelling of the CA films and the exposure time to TiP, a series of thin, dense films was immersed in a solution of THF containing 10% TiP. The resulting materials were insoluble in common solvents for CA and remained transparent and flexible. Swelling experiments were used to assess the degree of cross-linking by monitoring the weight gain of the films after soaking them for 24 h in MEK. These same films were also evaluated using TGA to measure the weight of inorganic residue that remained after the organic CA was combusted. The relationship between the weight gain, the amount of inorganic residue and the TiP exposure is shown in Table I. The weight gain due to solvent decreases and the inorganic residue increases with increasing TiP exposure, which is consistent with the formation of a TiP-cross-linked CA network. This analysis cannot distinguish the homogeneity of the Ti distribution through the CA film; indeed, the presence of a cross-linked skin undoubtedly accounts for the slight changes in the weight gain and Ti incorporation for exposure times longer than 5 min.

Changes in the chemical stability of the CA membranes were evaluated as a function of exposure time in a 10 wt% solution of TiP in MEK. After treatment with TiP, membrane specimens were dried, immersed in acetone for 12 h and re-dried, and changes in mass measured. The extent of mass loss decreases with increasing TiP exposure time, reaching an "equilibrium" value with a 60 min exposure (Table II). Membranes treated with TiP for varying lengths of time were examined also via TGA (Table II). These data show a monotonic increase in the amount of noncombustible residue as the TiP treatment time increases. Although this trend is similar to that seen for the dense CA films and is consistent with an increase in the amount of Ti in the microporous CA membranes as the TiP exposure time increases, the amount of inorganic residue is considerably less than for the dense films. The microporous nature of the membranes apparently creates sufficient surface area that all the pore surfaces are not completely reacted. Consequently, the membranes evidence overall mass loss in contrast to the weight gain of the dense films;

TABLE I Effect of TiP-treatment time on CA dense film properties.

Treatment time (min)	Film weight gain (%)	Inorganic residue (%)
0	∞	0
5	18	11
30	17	13
60	13	14
120	12	24

TABLE II Effect of TiP-treatment time on CA membrane properties.

Treatment time (min)	Mass loss (%)	Inorganic residue (%)
0	100	0
10		3.5
15	27.1 ± 2.6	
20		5.3
30	7.2 ± 2.9	
40		7.3
60	5.4 ± 0.1	
80		8.8
120	6.0 ± 0.2	

in addition, the amount of Ti incorporated is lower for the membranes when compared with the films.

Observations on both the gels created by the injection of CA solution into TiP solution and the immersion of dense CA films and membranes in TiP solutions are consistent with the formation of a TiP-cross-linked CA network. Based on the rapid formation of gels, the cross-linking reaction appears to be very rapid and results in the formation of an insoluble CA network. The rapid formation of the cross-linked structure can limit the subsequent diffusion of TiP into the unreacted portions of the CA films and membranes, and thereby produces complex, heterogeneous materials. Because of the rapid reaction rate, the extent of cross-linking appears to be controlled by the rate at which TiP diffuses into the material.

Spectroscopic Characterization

Initial ^{13}C-NMR spectroscopic studies were conducted on the gels formed by the reaction of a CA solution with a TiP/acetone solution (not shown). These gels were dried and their chemical compositions evaluated using solid-state NMR. Peaks assigned to the carbons of the anhydroglucose are seen between 60 and 90 ppm, and at 103 ppm. The carbons associated with the acetyl methyl groups (22 ppm) and the acetyl carbonyl groups (176 ppm) are also observed. Close inspection of the signals associated with the CA polymer shows no evidence of hydrolysis of the polymer backbone or deacetylation. Two additional peaks that can be assigned to the methyl and methine carbons of the isopropoxide groups attached to the TiP are seen at 29 ppm and 35 ppm, respectively. The absence of signals associated with acetone suggests that the isopropoxide groups are still attached to the titanium and are not present as free isopropyl alcohol.

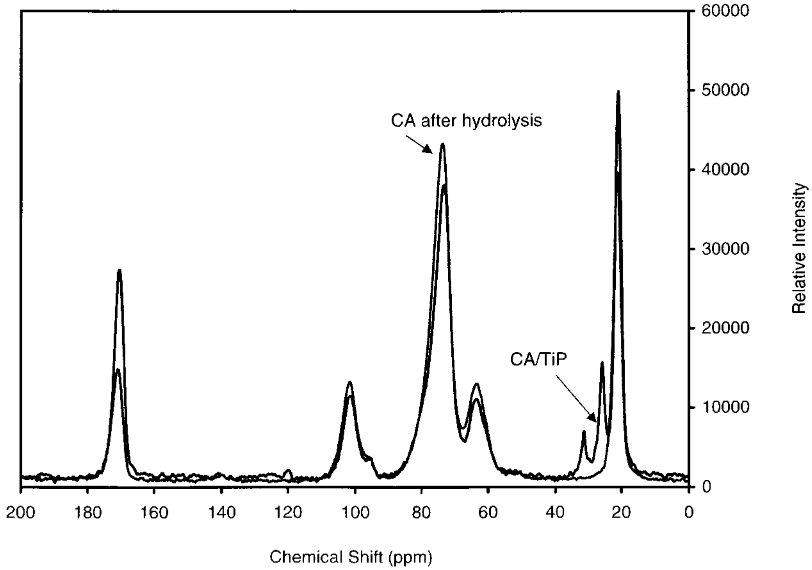

FIGURE 1 ^{13}C-NMR spectra of CA/TiP before and after hydrolysis.

The gels were then subjected to aqueous hydrolysis for 24 h at room temperature, dried and evaluated via solid-state ^{13}C-NMR (Figure 1). The peaks associated with CA remained; those associated with the isopropoxide disappeared. This analysis shows that the residual isopropoxide groups can be hydrolyzed and removed from the CA/TiP hybrid. None of the solid-state NMR analyses revealed additional peaks that could be assigned to carbons that are covalently bonded to titanium. This suggests that either the titanium cross-links are present in low concentration or that the chemical shift of a cellulose ring carbon atom attached to a hydroxyl does not differ significantly from the chemical shift of a cellulose ring carbon atom bonded to titanium.

The NMR data were also analyzed to determine the effect of TiP treatment on the ^{13}C T_1 relaxation time of the CA/TiP OIH materials. Analysis indicated that the ^{13}C relaxation time systematically increased from 19.4 to 25.2 s as the TiP exposure time increased from 0 to 180 min. This 30% increase in relaxation time indicates a significant decrease in molecular mobility. Such a decrease is consistent with the effects of cross-linking.

FT-IR spectra were evaluated to determine the effect on CA films of systematically increasing the TiP exposure times. The spectral region from 900 to 1800 cm^{-1} is shown in Figure 2. These spectra show a

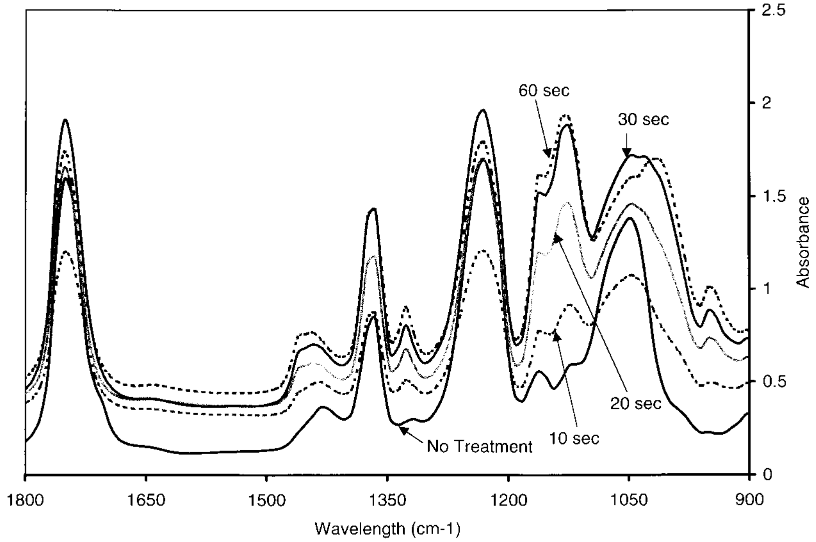

FIGURE 2 FT-IR spectra of thin CA films exposed to TiP for varying lengths of time.

decrease in the vibrations at 1751, 1234 and 1130 cm^{-1} associated with the carbonyl and ether vibrations present in the CA[10]. To obtain more information from these spectra, projection of latent structure (PLS) regression was performed to identify correlations between changes on the FT-IR spectra and exposure to TiP. The PLS regression model confirms the qualitative changes noted in Figure 2. Specifically, the vibrations at 1751, 1234 and 1130 cm^{-1} decrease with increasing exposure to TiP. A complex set of vibrations at 900 and 1400 cm^{-1} increases with increasing exposure to TiP. A careful examination of the PLS regression model also shows that the vibrations at 1751, 1234 and 1130 cm^{-1} are broadened with exposure to TiP, that is, the intensity of the peak maximum decreases, while the intensity on both shoulders is increased. This broadening is particularly evident for the acetyl carbonyl vibration at 1751 cm^{-1} and is consistent with a more heterogeneous environment around the acetyl carbonyls with increasing TiP exposure. The vibration at 1234 cm^{-1} is associated with stretching of the ester oxygen. Again, the broadening is consistent with a more heterogeneous environment around the acetyl groups.

The results of a Projection to Latent Structures (PLS) regression of the spectral changes as a function of TiP exposure time are shown in Figure 3. PLS models can be used to interpret complex data sets where many

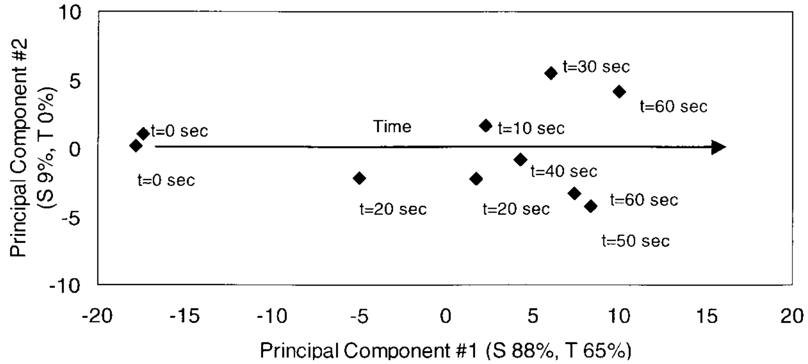

FIGURE 3 Results of PLS analysis: the FT-IR spectra of CA films exposed to TiP showing the overall correlation between TiP exposure time and changes in the FT-IR spectra.

spectral features are changing in response to a treatment[11,12]. The traditional approach to interpreting spectral data is to focus a few selected peaks, commonly those that can be easily interpreted by the spectroscopist. PLS models consider all of the individual vibrations regardless of their intensity and determine correlations between all of the wavelengths and the response of interest. The PLS analysis shows that 88% of the spectral variation and 65% of the time variation can be explained with changes in TiP exposure time along principal component one (the x axis). The PLS model also shows that only 9% of the spectral variation and none of the time variation can be accounted for by principal component two (the y axis). The regression coefficients for the PLS model (not shown) reinforce the spectral changes discussed above.

Although FT-IR analysis showed changes in the acetyl carbonyl vibrations consistent with the creation of a more heterogeneous environment, it did not allow the identification of any peaks that could be specifically assigned to CA-Ti bonds.

Thermal Analysis

Cross-linking can frequently have an impact on the glass-transition temperature (T_g) of a material. Cross-links can decrease the molecular mobility of the polymer chains thereby increasing the amount of thermal energy required for the large-scale segmental motions associated with the T_g[13]. However, DSC analysis indicated that exposure of the microporous membranes to TiP did not have a significant impact on the T_g

of the membranes; indeed, even with exposure times as long as 120 min the measured T_g of 190°C did not differ significantly from that of the untreated membranes. The lack of significant change in the T_g is somewhat surprising and suggests that the titanium cross-links are far apart or that cross-linking is confined to a thin surface region.

Changes in T_g constitute only one way to measure changes in the molecular mobility of a polymer system. Annealing a sample slightly below T_g can lead to a reduction in the free volume. This decrease in free volume, also known as physical aging or enthalpy relaxation, can be detected by DSC. The four microporous CA/TiP samples were aged at 175°C for 18 h and then rescanned (Figure 4). These scans show a monotonic decrease in the size of the enthalpy relaxation peak with increasing TiP exposure times, which is consistent with a more restricted molecular mobility. Such restricted molecular mobility can arise from the formation of cross-links that constrain the mobility of the chains.

The TGA response of a pure CA, a CA/TiP hybrid and physical mixture of TiO_2 and CA was also examined to observe changes in the molecular level interactions between the two components caused by the incorporation of TiP into the CA structure. The differential TGA response for these samples is shown in Figure 5. The pure CA shows a peak at approximately 360°C and a second small peak at 480°C, while the CA-

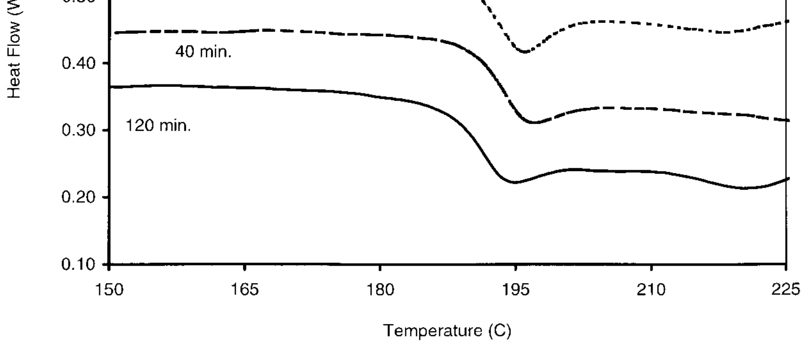

FIGURE 4 DSC scans showing the enthalpy relaxation peak of microporous CA/TiP membranes exposed to TiP for varying lengths of time.

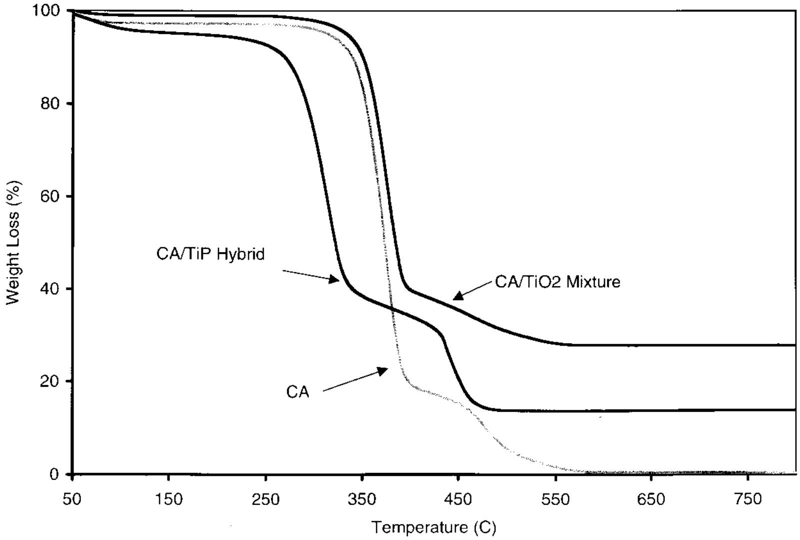

FIGURE 5 TGA thermograms showing the weight loss of CA, a physical mixture of TiO_2 and CA and a CA/TiP hybrid.

TiP OIH film has peaks at about 300 and 440°C, respectively. In contrast, the CA-TiO_2 physical mixture shows a peak corresponding to the CA portion, i.e., 360°C. This analysis does not provide molecular level information on the type of interactions between the CA and TiP in the OIH materials, but it is consistent with all the other analyses that suggest that the TiP-treated CA is not a simple physical mixture of the two components.

All the physical and chemical observations are consistent with the rapid formation of Ti cross-links between CA chains. These cross-links prevent dissolution of the TiP-treated CA. Although spectral analysis showed no direct evidence for the formation of Ti cross-links, indirect evidence from NMR, FT-IR and thermal analysis suggests that by varying the length of TiP exposure, the number of cross-linking sites can be increased. All these effects should affect the mechanical behavior of the CA/TiP OIH membranes.

Mechanical Behavior

Figure 6 shows representative changes in mechanical behavior for four membrane samples treated in TiP for increasing periods of time as well as an untreated membrane that serves as a control. The results are obtained

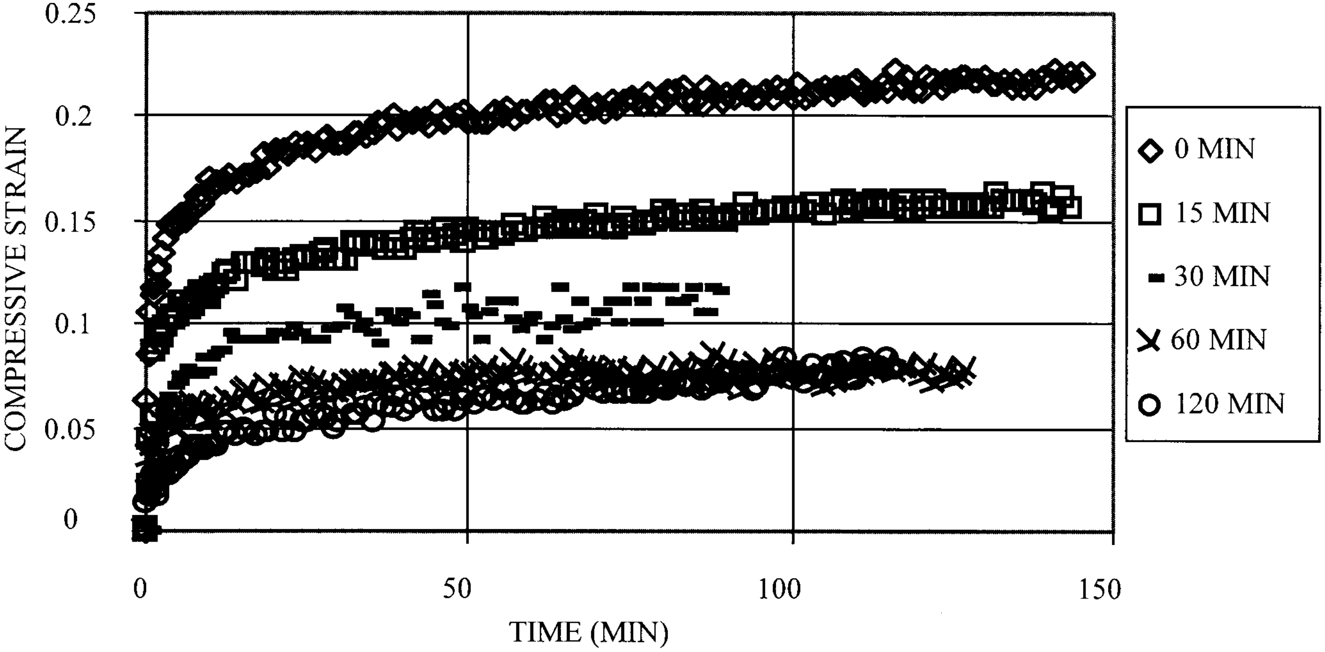

FIGURE 6 Creep response of microporous CA/TiP membranes exposed to TiP for varying lengths of time.

in double-distilled deionized water at a constant transmembrane pressure gradient of 4.14 MPa. The compressive strain response contains elastic, viscoelastic and permanent deformation components[13]. The initial strain response is characterized by a rapid increase from the baseline value caused by an elastic response to the nearly instantaneous application of the pressure gradient. This portion of the curve is well represented as a nearly vertical straight line and predominately represents the elastic response. The data indicate that the initial creep compliance, $J(t) = e(t)/s_0$, systematically decreases as the TiP exposure time increases. The magnitude of additional strain beyond this point also decreases systematically with increasing TiP exposure. The curves all approach an asymptotic value in a relatively short period of time relative to the untreated CA[4]. This study appears to be the first in which the instantaneous as well as the time-dependent portions of the strain behavior during membrane or thin film compaction have been observed.

DISCUSSION

The reaction between CA and TiP involves a complex sequence of physical and chemical changes. These changes include the swelling of the CA by the solvent, rapid cross-linking reactions between the CA and TiP and the formation of a separate TiO_2 phase. Given this complex reaction sequence, it is not surprising that the morphology of the CA film also affects the properties of the CA/TiP hybrid.

The first two reactions, swelling of the CA by the solvent used to dilute the TiP, and cross-linking of the CA by the TiP, compete with one another. The swelling front carries the reactive TiP into the CA, where the solvent begins to separate the CA chains, thereby increasing the diffusion coefficient of the solvent in the CA. In competition with this swelling are the cross-linking reactions that limit further separation of the CA chains as well as increases in the diffusion coefficient of the solvent in the CA. The cross-linking reactions also deplete the local concentration of TiP, which may affect the rate of the cross-linking reaction. As the solvent front moves further into the CA film, the local concentration of TiP increases to that of the bulk solutions. Since the concentration of TiP in the bulk solution is relatively high compared to the number of reactive hydroxyl groups attached to the CA, there is a local excess of TiP. The CA also contains moisture that can react with the local excess of TiP, leading to the formation of discrete TiO_2 domains. Moreover, TiP is a Lewis acid capable of causing hydrolysis of the acetyl groups attached to the cellulose backbone and increasing the number of reactive hydroxyls, which could create additional sites for reaction between the CA and TiP; however, no spectroscopic evidence for hydrolysis was found.

All the competing chemical reactions can be influenced by the morphology of the CA film. A dense CA film may rapidly form a highly cross-linked skin, which limits further diffusion of the TiP solution into the bulk of the CA film. This explains the observation that the swollen CA core could be extruded from between the two gelled surfaces of a thick CA film. Microporous CA membranes with connections between the pores will have fewer barriers to diffusion of the TiP solution into the interior of the membrane. Microporous membranes will also have a higher local concentration of TiP solution relative to the bulk CA and thus a higher local concentration of TiP at the solvent front. This could lead to more uniform penetration of the TiP into the microporous CA membranes. On the other hand, the increased surface area of the microporous membranes may sufficiently reduce the local TiP concentration to the extent that a significant fraction of the CA along the pore walls remains unreacted. This possibility might explain the lower concentrations of inorganic residue and the overall mass loss in solvents for the microporous membranes when compared with the behavior of the dense films.

The properties of the solvent can also affect the properties of the resulting CA/TiP hybrid. The solvent will alter the degree and rate of swelling that the CA undergoes. Many of these effects can be deduced from the known interactions between CA and solvents. In a less well-defined manner the solvent can also influence the reactions of the TiP. The TiP appears to undergo self-polymerization to form TiO_2 oligomers, and at some point these oligomers will precipitate from solution. Additional reactions of the precipitated particles are likely to be slower than that of the soluble oligomers.

Much information is available in the literature concerning the effects of cross-linking on the measurement of T_g. As the main chain motions associated with the T_g are increasingly restricted by the addition of effective cross-link junctions, the temperature at which the glass transition is observed will also increase. If sufficient cross-link junctions are incorporated into the growing network structure whereby the main chain motions are effectively suppressed, no glass transition will be measured. However, the overall magnitude of this increase in T_g will vary considerably depending upon the polymer and cross-link agent employed as well as the extent to which the cross-links are homogeneously distributed. In the present set of DSC experiments no significant change in the T_g of CA was observed with increasing TiP treatment. The literature confirms that the T_g of CA is generally not well behaved, whereby the glass-transition region is broad and not well defined. This is particularly evident when T_g is measured by DSC as compared with other techniques such as dynamic mechanical analysis (DMA). Whereas T_g is characterized by a step-change in the former, it is more readily observed as a peak in the loss modulus or the ratio of the loss and storage moduli (tanδ) in the latter. Both the loss modulus and tanδ measure the extent of energy dissipation, and peak values are associated with the large-scale molecular motions that define T_g[11]. Interestingly, in other studies of cross-linking in CA by the incorporation of both organic as well as organic-inorganic materials, observations of changes in T_g are detailed only in the work of Shojaie et al.[3] They studied the effects of TEOS additions to CA via DMA and observed that the T_g of the resulting hybrid films increased only slightly based on a shift in the tanδ peak. Whether such results reflect a relatively small number of cross-links, a heterogeneous cross-link distribution or some combination of the two requires additional study.

The effect of filler additions on polymer mechanical behavior is well documented in the literature[14,15]. Many fillers provide reinforcement, whereby properties such as strength and stiffness will increase as a function of filler volume fraction by an amount that can be predicted based on rule-of-mixtures type expressions. Such additions typically have no significant effect on the T_g, but they can provide a physical reinforcing effect. In addition, certain polymer-filler combinations can give rise to chemical interactions that may be manifest via an increase in the T_g. Although such increases are typically small, they can be observed via DSC and by a systematic shift in the tanδ peak obtained using DMTA[14,15].

In order to place the current results in an appropriate perspective, we first consider previous studies of the creep behavior of cellulose acetate[4,7,16]. As indicated in Table III, despite differences in stress level, stress state, temperature and experimental methodology, data for the total creep strain of CA dense films show reasonable consistency, whereby creep strain values at 1-h are in the range of 3–4%. By comparison, the untreated CA membranes used in this study showed a corresponding 1-h creep strain of ~20%. This significantly higher value reflects the influence of an overall porosity level of ~36%.

As indicated by the results of figure 6, the TiP treatment systematically improves the creep behavior of the CA microporous membranes.

TABLE III Creep behavior of cellulose acetate under various experimental and structural conditions.

Stress state	Stress level (MPa)	Temperature (°C)	Specimen structure	1-h total strain (%)	Reference
tension	5.17	60	dense	4	14
compression	10.34	25	dense	3	4
compression	4.14	25	dense	3	7
compression	4.14	25	porous	20	7

With a treatment time of 60 min, the total compressive strain decreases by almost 70% relative to the control. Deanin et al.[4] noted a similar but more modest decrease in the creep response with the addition of titanium acetyl acetonate to CA. Our results indicate that a significant fraction of the overall strain decrease reflects decreased values of the elastic strain. Additional studies with a more sophisticated version of the UTDR technique will provide more precise determination of the elastic component. However, we believe that the observed improvement in the compressive strain behavior with TiP concentration and/or treatment time is due to both cross-linking and filler effects. Because the strain results from the compression of the microporous support layer and an accompanying decrease in the degree of porosity, the transmembrane pressure gradient should reduce the membrane permeability. Although the TiP treatment would be expected to improve membrane performance by limiting this porosity decrease, a corresponding change in membrane selectivity might not represent an acceptable trade-off. In the treatment protocol used in this set of experiments the thin, dense membrane barrier layer is also in contact with the TiP solution. Any significant cross-linking of this layer might decrease the permeability or alter the selectivity. Comprehensive membrane permeability and selectivity experiments were not conducted because of a relatively thick barrier layer; however, preliminary data for other systems suggest that the treatment adversely affects the permeability, presumably by cross-linking the barrier layer. Consequently, a commercially successful use of the TiP treatment would necessitate a protocol whereby only the microporous support was exposed to the TiP so that only the pore walls and not the dense layer would be affected. A possible scheme to accomplish this is currently under investigation.

CONCLUSIONS

All of the physical and spectral observations are consistent with the rapid formation of Ti cross-links between CA chains. These cross-links prevent dissolution of the TiP-treated CA. Although spectral analysis did not show any direct evidence for the formation of Ti cross-links, indirect evidence from NMR and thermal analysis suggests that by varying the length of TiP exposure the number of cross-linking sites can be increased. Thermal analysis evaluation also indicated that discrete regions of metal oxide had formed within the CA. Creep measurements confirmed the systematic improvement of creep resistance with increased TiP exposure caused by cross-link formation and filler reinforcement effects.

The TiP process appears to have significant potential for improving the performance of CA membranes. The unique reaction/diffusion properties of the TiP system can help produce materials with desirable mechanical properties. Using the UTDR technique, simultaneous permeation and compaction experiments can be conducted to evaluate the performance of these cross-linked materials during separation processes. This information should be very useful for further development of improved membrane materials.

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