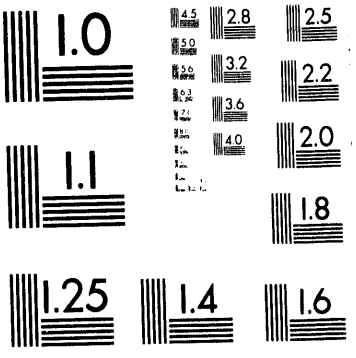
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Densification and Crystallization of Zirconia Thin Films Prepared By Sol-Gel Processing

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Abstract

We have investigated the effects of precursor nature and heat treatment schedule on the densification and crystallization behavior of sol-gel derived zirconia thin films. Precursor solutions were prepared from *n*-propanol, zirconium (IV) *n*-propoxide, and either acetic acid, or 2,4-pentanedione (acac) and water additions. By controlling the ligand type and ligand-to-metal ratio, we were able to prepare films which displayed significant differences in densification behavior. We attribute the dissimilarity in densification to variations in the nature of the as-deposited films, as influenced by ligand type and concentration. While the acac-derived film was a physical gel, (i.e., a physical aggregation of the oligomeric species), the acetic acid-derived film, which exhibited less consolidation, was a chemical gel that could not be redissolved in the parent solvent. Films prepared with large acac/metal ratios and small water additions exhibited minimal crosslinking at 25°C, displayed the greatest consolidation (~ 86% shrinkage) and the highest refractive index (n = 2.071) when heat treated. These results indicate the importance that M-O-M bonds (crosslinks) formed at low temperature can have on densification behavior. We also report on the effects of heat-treatment schedules and ramp rates on densification behavior. All of the films of the present study crystallized into the cubic phase, at temperatures ranging from ~ 400°C to greater than 700°C, depending on the heating rate.

Introduction

Sol-gel derived ceramic thin films are under investigation for a variety of different applications. Multicomponent systems, such as lead zirconate titanate (PZT), are being studied for uses ranging from decoupling capacitors[1] to optical storage discs,[2] while single component systems are being investigated for use as porous[3] and dense membranes.[4] The successful development of ceramic thin films for many of these applications requires that the as-deposited amorphous film be transformed into the desired crystalline phase, and for certain applications, completely densified.

In the preparation of ceramic thin films by sol-gel processing, effects of solution chemistry variations (i.e., differences in precursor type, reaction conditions, solution aging, etc.) on material properties have been noted by many authors.[5-8] Unfortunately, to date, the pathways by which these effects are manifested are poorly understood. While thin films with properties acceptable for several of the applications discussed above have been prepared, a true understanding of the ability to use controlled solution chemistry variations to influence final ceramic properties has yet to be realized. For example, for the fabrication of electronic ceramic thin films, it would be desirable to utilize precursors that produce films which display a tendency toward consolidation, rather than low temperature crystallization. By selecting appropriate precursors, it should be possible to completely densify the thin film prior to the onset of crystallization, producing films with minimal porosity. Since pores can act as light scattering centers, the ability to completely densify the film could lead to the fabrication of non-porous crystalline films suitable for optical storage devices. Alternatively, for the fabrication of porous membranes, chemical precursors and/or fabrication conditions which result in residual porosity should be employed. One strategy for inducing porosity is to use precursors which undergo hydrolysis during deposition. [9] A second approach is to prepare films which tend to

crystallize at low temperatures during firing. This leads to crystalline inclusions in the film which can significantly hinder shrinkage, even when present in small quantities. [10]

In the present study, we have attempted to develop an understanding of the pathways by which solution chemistry variations impact ceramic thin film properties. The technical approach we employed was to generate known differences in oligomeric precursor structure, and then relate these structural variations to observed differences in film densification and crystallization behavior. Our precursors were synthesized by reacting metal alkoxide compounds with different chelating ligands and chelating ligand/metal ratios.[11-14] We have selected zirconia as a model system for this investigation for a variety of reasons. First, in doped form, it is being studied for use as a dense oxygen separation membrane;[4] and second, it is an end-member of the technologically significant electronic material, lead zirconate titanate.

Experimental

Zirconium (IV) *n*-propoxide•*n*-propanol* was used as the starting compound for synthesis of the 0.4 M *n*-propanol solutions of the present study. Two chelating ligands, acetic acid* and 2,4-pentanedione§ (acac; $CH_3COCH_2COCH_3$) were used to generate different oligomeric solution species which were used for film fabrication.

The acetic acid based solution was prepared by reacting neat zirconium *n*-propoxide•*n*-propanol with purified acetic acid[15] in a molar ratio of 1:1.5, in a glove box. The reaction mixture was then removed from the glove box, and after approximately five minutes, sufficient dry *n*-propanol§ was added to yield a 0.4 M (in zirconium) solution.

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§ Fisher Scientific, Pittsburgh, PA

The solution was allowed to age for three days at 25°C under argon prior to use in film fabrication. This precursor system will be referred to as the HOAc system.

The acac-based precursor solutions were prepared by reacting zirconium (IV) *n*-propoxide•*n*-propanol with an *n*-propanol solution containing the acac ligand. After allowing thirty minutes for the chelation reaction, a solution of water in *n*-propanol of equal volume was added to the zirconium-acac reaction mixture. Solutions were stirred during both phases of the preparation. Final solution concentration was 0.25 M or 0.4 M in zirconium. To generate different oligomers, solutions with two different r (moles acac/mole Zr) and h (moles H_2O/mole Zr) ratios were employed.[16] For the first solution, acac and water additions were used so that r = 2.0, h = 0.5; and for the second solution, r = 0.5, h = 4.0. These solutions will henceforth be referred to as acac-H and acac-L, respectively, for high and low acac/metal ratios. The acac-H solution was aged for 4 days prior to use while the acac-L solution was aged for one day prior to use. Longer aging times for this solution resulted in gelation. As for the HOAc precursor, reactions and aging were again carried out at room temperature under an argon atmosphere. Further details of the preparation procedures are given in Reference 17. Solution viscosities, as a function of concentration, were measured at 30.0°C using a Koehler K-23300 kinematic viscosity bath and calibrated Size 1 Ubbelodhe viscometer tubes.

A similar acac-based solution chemistry was used to prepare films for low temperature pyrolysis heat treatment studies. For these studies, zirconium (IV) *n*-butoxide•*n*-butanol* was used as the starting compound and *n*-butanol§ was used as the solvent. Identical reaction procedures to those discussed above were used. Reactant ratios were: r = 0.5, h = 2.0. Solutions were aged 2 days prior to use.

Films were fabricated onto silicon wafers by spin-casting at 3000 rpm, unless otherwise noted. Continuous uniform films were prepared for each of the precursor solutions. As deposited, film thicknesses ranged from ~2200 Å to ~3200 Å, depending on the precursor solution. Fired film thicknesses ranged from ~450 Å to ~550Å. Gelation

times of the depositing films (i.e., the time required for stabilization of the interference colors during spinning) varied from 5 to 6 seconds. Ellipsometry (Gaertner L116-C; λ = 6328 Å) was used to monitor changes in film thickness and refractive index as a function of time, or heat treatment conditions. Measured psi and delta values were converted to thickness and refractive index values using Gaertner GC4A software for single layer non-absorbing films. Typically, refractive indices and thicknesses of three different films were measured and then averaged. In general, ellipsometry measurements were very reproducible from sample to sample.

Redissolution experiments were conducted to determine the nature of the gel that was formed during deposition. These experiments consisted of spinning a film under standard conditions, waiting for ten seconds, and then immersing the film in *n*-propanol (the parent solvent) to determine film solubility. Redissolution was also evaluated after the film was dried for 18 hours at 25°C; and after heat treatment at 200°C for 5 minutes. The ability to redissolve a film was taken as an indication that primarily a physical aggregation process had occurred during gelation.[18] Alternatively, when as-deposited films did not redissolve, it was assumed that extensive chemical gelation (i.e., the formation of M-O-M bonds between the oligomers) had occurred during deposition.[18]

Three different firing strategies were used for heat treatment of the films. Low temperature isothermal consolidation was studied by placing the films on a hot plate held at the desired temperature, and measuring the changes in thickness and refractive index for different heat treatment times. The effects of ramp rate on shrinkage and densification at higher temperatures were determined by heating the films to 700°C at three different rates: 5°C/min, 50°C/min and ~ 100°C/min (i.e., simply inserting the film into the furnace at T). A hold time of ten minutes was employed. Finally, an AET Addax RMV-04 rapid thermal processing (RTP) furnace was used to heat films to various temperatures at 300°C/min and 3000°C/min. Once the desired temperature was attained, samples were rapidly quenched to

< 150°C. This last procedure allowed for determination of the non-isothermal shrinkage and crystallization behavior of the films.[19]

Results and Discussion

Solution Characteristics and Precursor Nature

From the dependence of solution viscosity on concentration, kinematic viscosity measurements may be used to determine the relative extent of oligomer interaction.[20] We have measured the viscosities of the three precursor systems at concentrations ranging from 0.05 M to 0.4 M, and the results are shown in Figure 1. The acac-L solution showed a strong dependence of viscosity on concentration, indicating that as concentration was increased, this precursor system exhibited a much stronger interaction between solution oligomeric species than the other two systems. This result implies that the oligomers formed in this process are either larger, or more ramified (or both), than the oligomers generated in the other two chemical systems.[21] Based on the known reactions of acac and water with alkoxide compounds, this result is expected.[16] For small additions of acac, the alkoxy ligands of the starting compound that are not replaced by acac are free to react with the water added in the subsequent reaction step. Hydrolysis and condensation occurs, leading to M-O-M bond formation. Under these reaction conditions, i.e., small acac/metal and large water/metal ratios, the extensive hydrolysis and condensation reactions of the remaining alkoxy groups lead to the generation of comparatively large oligomeric species, as has previously been determined by small angle X-ray scattering.[13, 14, 16]

In contrast, the acac-H precursor solution displayed only a minor dependence of viscosity on solution concentration, indicating the presence of relatively non-interacting species. Again, this is an expected result. With large acac additions, the original alkoxide

compounds become highly chelated. Since the acac ligand is stable toward hydrolysis, the number of remaining (alkoxy) ligands available for subsequent hydrolysis and condensation reactions is greatly reduced. Therefore, there are fewer reaction sites for M-O-M bond formation, and smaller oligomeric species are produced.[13, 14, 16]

From the minimal dependence of viscosity on concentration, kinematic viscosity measurements of the oligomers formed from the HOAc system imply that these species are also relatively non-interacting.

Nature of the As-Deposited Film

To investigate the effects of precursor nature on the characteristics of the deposited films, the solubilities of selected films in the parent solvent were characterized. These experiments were conducted to determine whether a chemical or physical gel was formed during deposition. Results are presented in Table I. Films prepared from both acac systems formed only physical gels. This indicates that primarily a physical aggregation process was responsible for gelation, rather than extensive crosslinking between oligomers. This may be due to the stability of the acac ligand to hydrolysis,[22] the relative extent of alkoxy replacement by acac, and/or to the role that acac plays in sterically limiting the accessibility to any remaining alkoxy ligands. In contrast, it was not possible to redissolve the film formed from the HOAc precursor, implying that true chemical gelation, or M-O-M bond formation via hydrolysis and condensation between the oligomeric solution species, had occurred during deposition. Evidently, either the acetate ligands are less stable toward hydrolysis during deposition,[22] or the accessibility of remaining alkoxy (or hydroxy) ligands is not as diminished as for the acac based precursors. Results for films prepared from precursor solutions synthesized with alkoxide compounds modified by sterically large ligands (1-adamantanol) seem to indicate that the accessibility of remaining alkoxy ligands to ambient moisture initiated hydrolysis and condensation is very important

in defining the nature of the as-deposited film.[23] These results indicate the importance that ligand type can have in defining precursor reactivity and consequently, the nature of the as-deposited film.

With extended hold times at room temperature, the dissolution behavior of the acac-derived films changes; the acac-L film no longer dissolves and the acac-H film only partially dissolves. This change in dissolution behavior indicates that the films are transforming to chemical gels through continued condensation reactions. With heat treatment at 200°C, it becomes no longer possible to dissolve any of the films. We believe this is an indication of still more extensive condensation reactions. As discussed below, the extent of chemical crosslinking between oligomeric species in the as-deposited films is key in defining film densification behavior.

Film Shrinkage and Densification Behavior

Our initial investigations of film shrinkage (consolidation) and densification focused on the effects of precursor nature on room temperature consolidation following deposition. Results presented in Figure 2, illustrate the variation in normalized film thickness as a function of time after t_g. Consolidation at room temperature is most likely due to the capillary contraction associated with removal of residual solvent,[24] and continued condensation reactions.[24] We feel that the change in dissolution behavior of the films with long hold times at 25°C provides strong evidence for the occurrence of continued condensation reactions.

It is evident that while all of the films exhibit significant shrinkage at room temperature, the film prepared from the acac-H precursor consolidates to the greatest extent. After three hours, its thickness has decreased by about 40%, compared to approximately 25% for the acac-L and HOAc-based films. We feel that the greater shrinkage of the acac-H film is due to the initial absence of M-O-M bonds between

oligomeric clusters, as discussed above. Since the interaction of the oligomers in this film may best be described as occurring via a simple physical aggregation process, the oligomers are less constrained to rearrange during drying at 25°C, resulting in extensive film consolidation. As the redissolution data indicate, however, M-O-M bond formation does occur with time. On the other hand, the HOAc derived film is already chemically crosslinked immediately after deposition. Because of this, the oligomers are less free to rearrange through capillary contraction, and the film consolidates less at this temperature.

Based on this explanation, we might expect the acac-L film, which also displays little crosslinking in the as-deposited state, to behave more like the acac-H film than the HOAc film. The observed behavior may be due to the greater tendency of this system to exhibit more extensive condensation reactions at 25°C than the acac-H system, thus inhibiting densification. An indication of this tendency may be noted in Table I, where after 18 hours at room temperature, the acac-H film still partially dissolved, while the acac-L film did not dissolve. Refractive indices for the films at this point of the fabrication process ranged from 1.55 to 1.58.

To obtain information regarding the importance of the processes which can contribute to densification and/or consolidation, i.e., capillary contraction, continued condensation reactions, structural relaxation and crystallization,[24] we have studied the isothermal consolidation of the thin films at three different temperatures. Figure 3 shows typical results for film consolidation at 25°C, 200°C, and 400°C, for the acetic acid derived films. The films were heat treated by placing on a hot plate at the desired temperature. As expected, as the heat treatment temperature is increased and more of the physical processes described above become active, consolidation of the film increases. For this precursor, at 400°C, the film thickness has decreased to approximately 20% of its thickness at t_g.

To further analyze the contributions of the various physical processes to overall consolidation, we have calculated the relative consolidation which occurred after heat treatment for two hours in three different temperature regimes, as shown by the arrows in

Figure 3. Results of this analysis are presented in Figure 4 for the three different precursor systems. It can be seen that significant consolidation occurs at very low temperatures for each of the three precursors. Since it is expected that the only active processes at low temperature (25°C) would be capillary contraction and continued condensation reactions,[24] we may state that these two processes contribute significantly to the overall consolidation of the thin films. In the temperature regime from 25 to 200°C, still greater shrinkage (~40 - 50%) occurs. We again believe that the primary active mechanism in this regime is continued condensation, although potentially, structural relaxation may also play a role. Between 200 and 400°C, we would expect still further condensation reactions, as organic pyrolysis is completed, as well as structural relaxation. Also, by 400°C, all of the films crystallized into the cubic zirconia phase, as determined by X-ray diffraction experiments. Thus, crystallization also contributes to consolidation in this temperature regime. While we have yet to determine whether organic pyrolysis is completed prior to the onset of crystallization, we plan to evaluate this by using TGA and FT-IR reflectance spectroscopy to study organic pyrolysis, as well as hot stage X-ray diffraction, to determine crystallization onset.

The variation in "total" film shrinkage for the three precursors as a function of temperature is further illustrated in Figure 5. As observed for room temperature consolidation, the film prepared from the acac-H precursor exhibited the greatest total shrinkage, consolidating to ~14% of its original thickness. Again, we attribute the greater consolidation of this film, which persists to high process temperatures, to the physical gel nature of the as-deposited film and the initial absence of chemical crosslinks between oligomers.

The observed differences in film consolidation were paralleled by the variations in film density (refractive index) for films heat treated to 700°C at ~ 100°C/min. The acac-H precursor yielded the film with the highest refractive index, 1.948. The film prepared from the acac-L precursor solution displayed a refractive index of 1.897 and the HOAc derived

film displayed a refractive index of 1.908. Since all of the films of the present study crystallized in the same phase, cubic zirconia, we can use refractive index as an indicator of material density. The refractive index value for the acac-H film corresponds to a density of ~88%, as determined from the Lorentz-Lorentz equation,[25] assuming a refractive index of 2.150 for theoretically dense cubic zirconia.[26,27] Using this same approach, the acac-L and the HOAc derived films are ~85% dense. Higher film densities were obtained for both acac and acetic acid precursors by utilizing the faster heating rates accessible with the AET Addax furnace. (see below)

Typical X-ray diffraction patterns for films heated to 700°C are shown in Figure 6. As mentioned, all of the films, regardless of the chemical precursor system, crystallized in the cubic phase. There were, however, minor differences in the crystallite sizes of the films prepared from the different precursors. The acac-H precursor system yielded a grain size of ~130Å, while the HOAc derived films exhibited a grain size of only ~100Å, as determined by X-ray line broadening analysis using the Scherrer equation. For the conventionally fired materials, all of the films were highly microstrained, as determined by line broadening analysis using the Gauss squared technique. We observed no apparent effects of heating rate, or low temperature pyrolysis hold, on the crystalline nature of the films fired to 700°C using a tube furnace. Films prepared by rapid thermal processing with the AET Addax furnace displayed delayed crystallization onsets, as expected.[28] For example, when using a heating rate of 3000°C/min, the acac-H film crystallized at ~700°C, compared with ~400°C for isothermal heat treatment.

Effect of Ramp Rate and Heat Treatment Conditions on Densification

As a final area of investigation, we have studied the effects of low temperature pyrolysis holds and ramp rates on film densification. Results for the effects of ramp rate are shown in Figure 7. As expected, greater consolidation and higher refractive indices

(i.e., higher densities) are obtained for higher heating rates. This result is believed to arise from the retention of a lower viscosity structure to higher temperatures as condensation reactions are delayed because of kinetic considerations.[29] Because the lower viscosity structure is retained, greater consolidation and densification occurs prior to the onset of crystallization.

The effect of heating rate on densification is most significant for the acac-H film. This film should be most amenable to densification due to the comparative absence of chemical crosslinks at room temperature. By simply inserting this film into the furnace at temperature, a film with density of ~88% was obtained. Films prepared from the other precursor systems also displayed higher densities for faster heating rates, although, as seen in this figure, the effect was not as pronounced as for the acac-H precursor.

We have also investigated the effects of faster ramp rates on the densification behavior of the acac-H and the HOAc derived films using the AET furnace. At a heating rate of 300°C/min, films prepared from both precursors exhibited higher densities than those prepared by conventional firing strategies. Using this higher ramp rate to heat the films to 700°C, it was possible to prepare an HOAc derived film with a refractive index of 1.943 (ρ ~88%) and an acac-H film with an index of 2.064 (ρ ~95%). The greater densification of the films at the faster heating rates is again attributable to retention of the high free energy, low viscosity material structure to higher process temperatures.[29] The highest density obtained was for an acac-H film heated to 800°C at 3000°C/min. Under these conditions, we were able to prepare a film with a refractive index of 2.071 (ρ ~96% of theoretical). Higher density acetic acid derived films were also produced at the higher heating rates, but for similar heat treatment conditions the densities of these films were always lower than those of the acac-H derived films. The highest density HOAc-based film, prepared by firing to 700°C at 3000°C/min, was ~89% dense.

The use of low temperature pyrolysis holds also affected the densification behavior of zirconium (IV) *n*-butoxide, acac-based films. Prior to ramping the films to 700°C for

crystallization, these films were subjected to low temperature holds for pyrolysis of organic species. In Figure 8 it may be seen that, in general, as the pyrolysis temperature is increased, the refractive index of the film decreases. The magnitude of the variation is also significant, with film densities decreasing by about 3 to 5%, for the higher temperature pyrolysis heat treatments. As the pyrolysis temperature is increased, it is expected that more condensation reactions would take place as organic pyrolysis is more extensive. As these reactions occur to greater and greater extents, subsequent densification with heat treatment to higher temperatures is inhibited, as is evident in the data.

Conclusions

Zirconia thin films were prepared from three different chemical precursor systems. The general nature of the films, as well as the film consolidation and densification behavior, were highly dependent on the ligand used to modify the alkoxide starting compound, and on the modifying ligand/metal ratio. Films prepared from precursors using more hydrolytically stable chelating agents or high chelate/metal ratios densified to the greatest extent. This presumably occurs because the gelled film that was formed was more the result of a simple physical aggregation of oligomeric species, rather than chemical crosslinking. Because of this characteristic, these films were able to consolidate to a greater extent; not only at room temperature, but also as the heat treatment temperature was increased.

Films prepared from precursors which underwent more extensive chemical crosslinking during deposition, i.e., the HOAc-based sols, consolidated to a lesser extent, presumably because of the existence of the M-O-M bonds between the oligomeric clusters. The results of low temperature pyrolysis experiments would also seem to support this conclusion. Films prepared with higher temperature pyrolysis holds, i.e., conditions

expected to lead to more extensive condensation reactions and M-O-M crosslink formation, densified to a lesser extent on subsequent heating.

Heating rate also impacted densification behavior and crystallization temperature. As heating rate was increased, higher density films were obtained. Very rapid heating rates, attained using the rapid thermal processor, produced films of the highest density, ~96%. All of the films prepared from the three precursors crystallized into the cubic phase, at temperatures as low as 400°C.

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Table I. Results of redissolution experiments for acetic acid and acac derived sol-gel thin films.

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Figure 7. Effect of ramp rate on the refractive index and relative density of sol-gel derived zirconia thin films. Lower ramp rates (5, 50 and ~ 100°C) were obtained by firing in a tube furnace; highest ramp rate (300°C/min, 5°C/sec) obtained by firing with AET Addax RTP furnace.

Figure 8. Effect of spinning speed and low temperature pyrolysis heat treatment on the refractive index of zirconia thin films fired at 700°C for 10 minutes, using a ramp rate of ~ 100°C/min.

Table I.

Results of redissolution experiments for acac and acetic acid derived thin films.

Precursor	Temp (°C)	Time	Dissolution Behavior	Gel Nature
acac-H	25	10 seconds	Dissolved	Physical
acac-H	25	18 hours	Partially Dissolved	Intermediate
acac-H	200	5 minutes	Insoluble	Chemical
acac-L	25	10 seconds	Dissolved	Physical
acac-L	25	18 hours	Insoluble	Chemical
acac-L	200	5 minutes	Insoluble	Chemical
HOAc	25	10 seconds	Insoluble	Chemical
HOAc	25	18 hours	Insoluble	Chemical
HOAc	200	5 minutes	Insoluble	Chemical

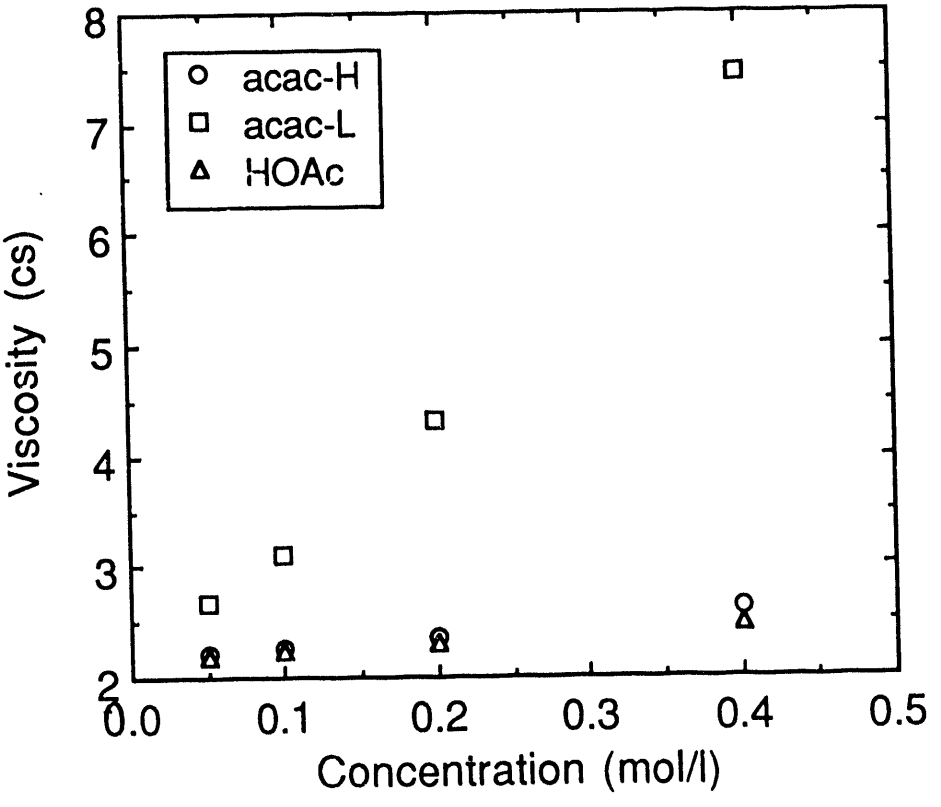
acac-H
acac-L
HOAc
Viscosity (cs)
Concentration (mol/l)
8
7
6
5
4
3
2
0.0
0.1
0.2
0.3
0.4
0.5

Figure 1.

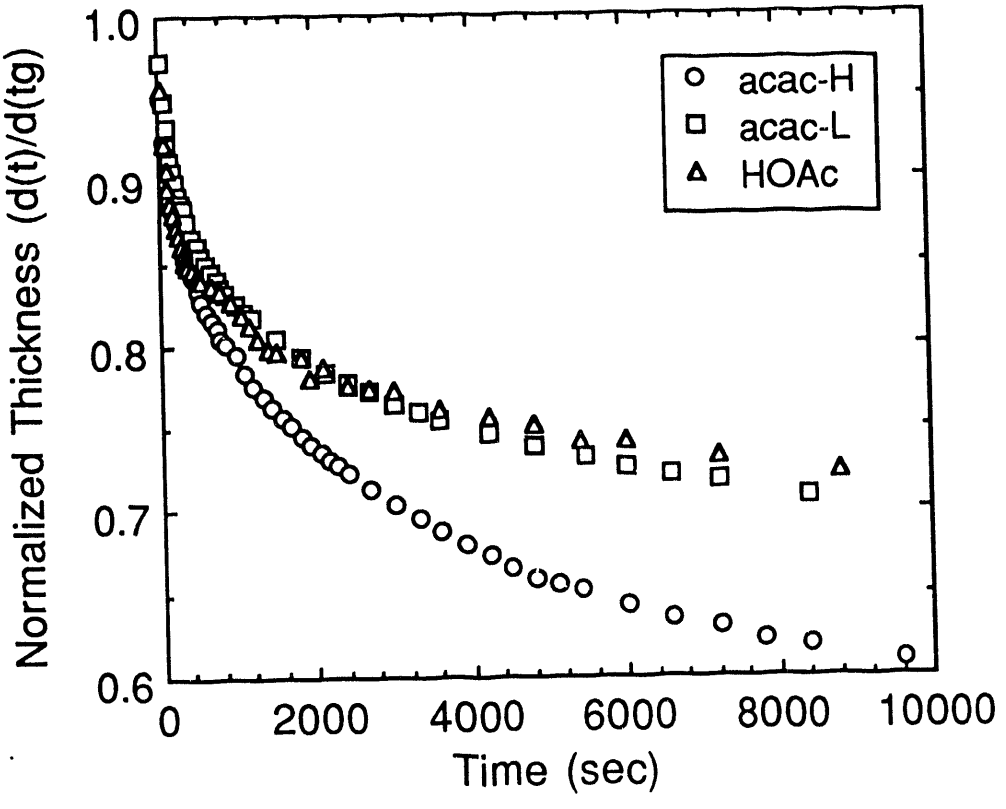
1.0
0.9
0.8
0.7
0.6
Normalized Thickness (d(t)/d(tg)
0
2000
4000
6000
8000
10000
Time (sec)
acac-H
acac-L
HOAc

Figure 2.

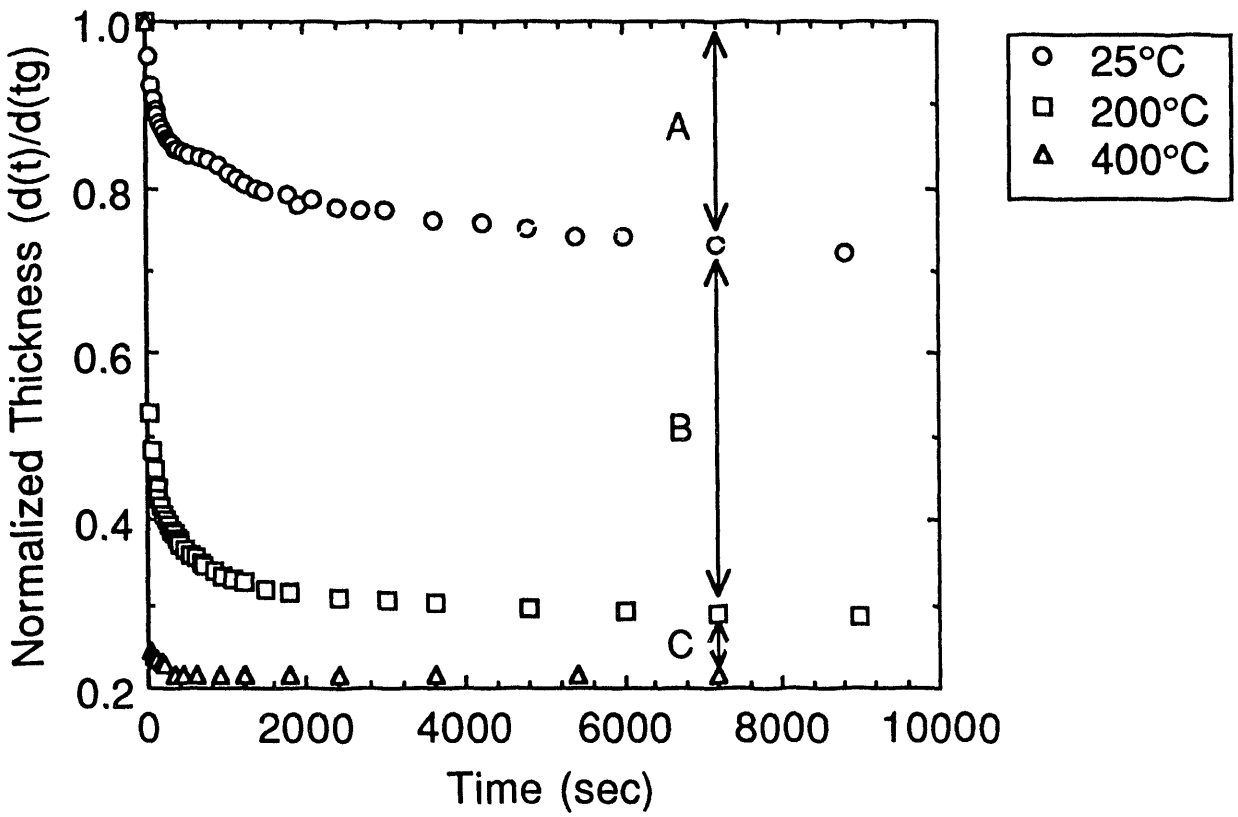
Normalized Thickness (d(t)/d(tg)
1.0
0.8
0.6
0.4
0.2
0
2000
4000
6000
8000
10000
Time (sec)
A
B
C
25°C
200°C
400°C

Figure 3.

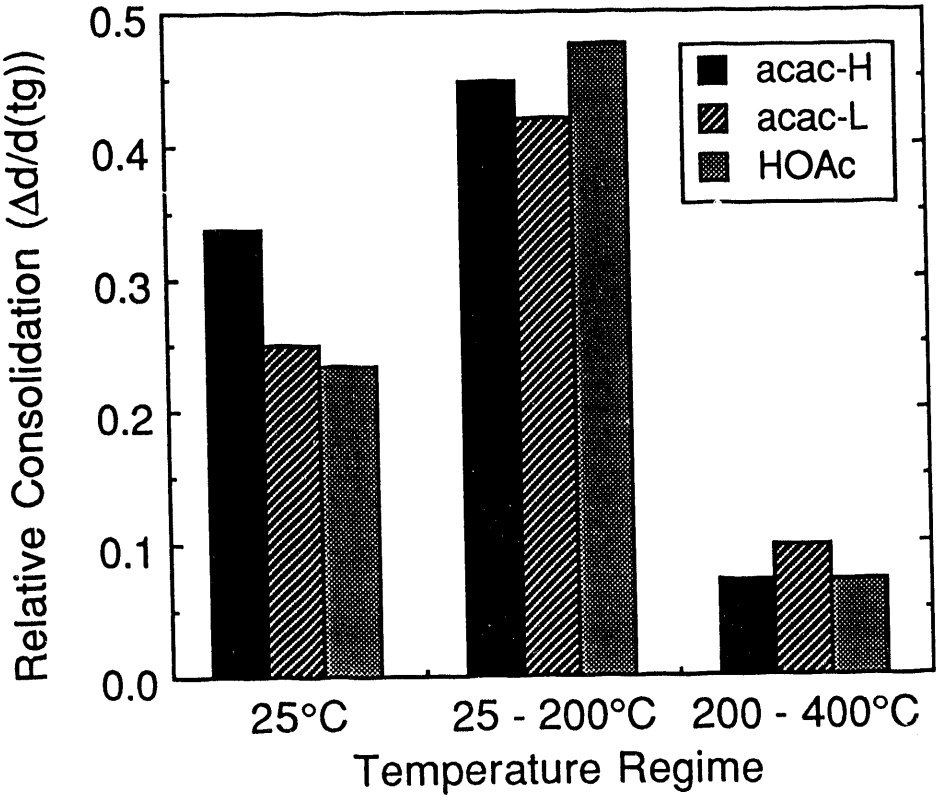
0.5
0.4
0.3
0.2
0.1
0.0
Relative Consolidation (Δd/d(tg))
acac-H
acac-L
HOAc
25°C
25 - 200°C
200 - 400°C
Temperature Regime

Figure 4.

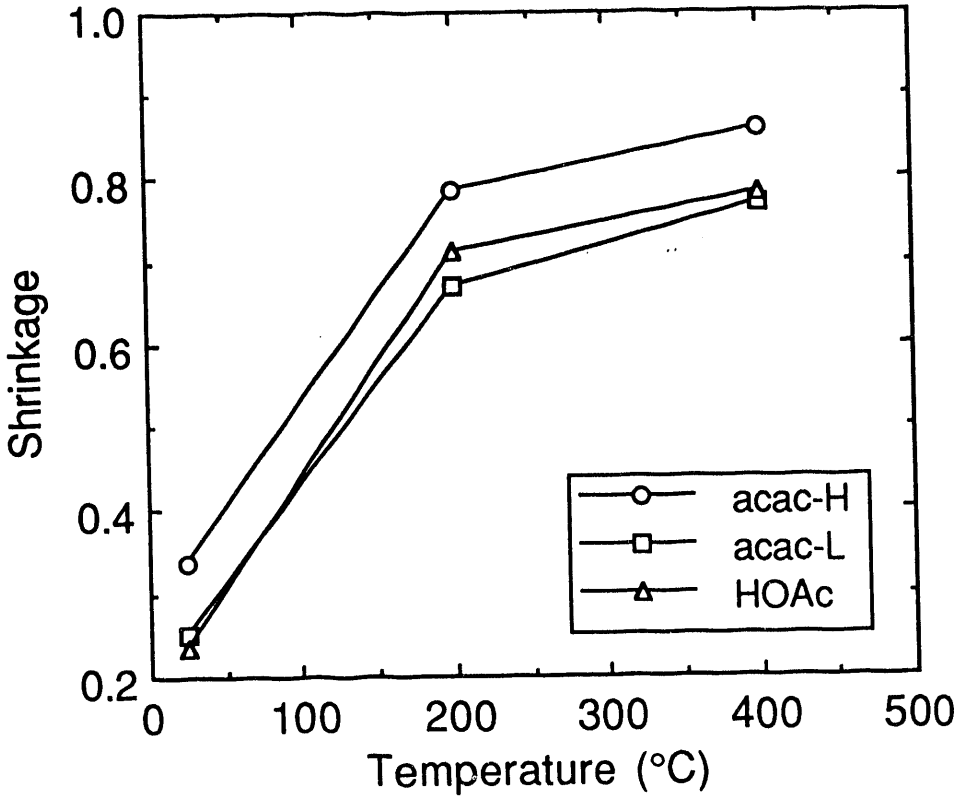
1.0
0.8
0.6
0.4
0.2
Shrinkage
0
100
200
300
400
500
Temperature (°C)
acac-H
acac-L
HOAc

Figure 5.

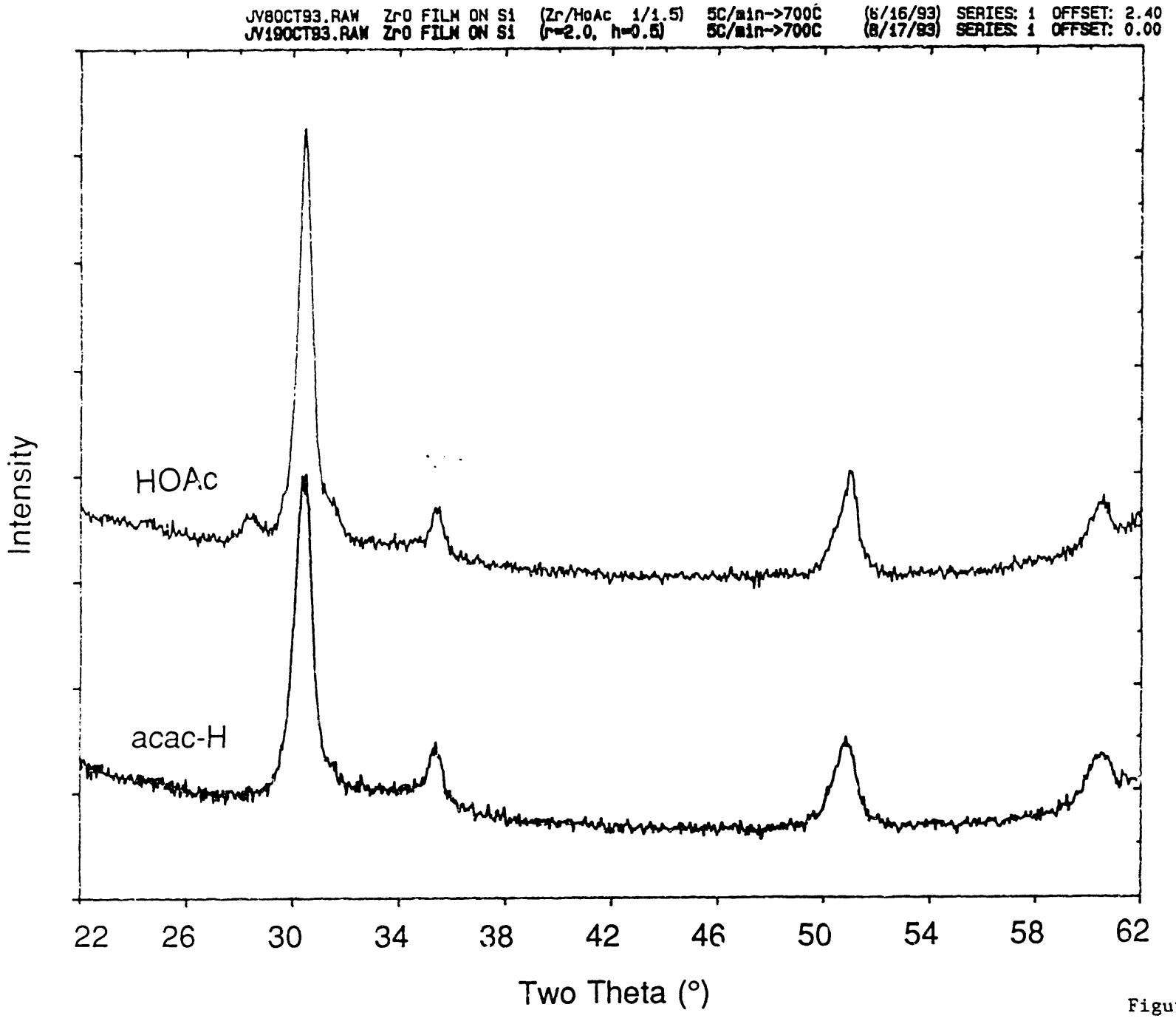
JV80CT93.RAW ZrO FILM ON Si (Zr/HoAc 1/1.5) 5C/min->700C (6/16/93) SERIES: 1 OFFSET: 2.40
JV190CT93.RAW ZrO FILM ON Si (r=2.0, h=0.5) 5C/min->700C (8/17/93) SERIES: 1 OFFSET: 0.00
Intensity
HOAc
acac-H
22
26
30
34
38
42
46
50
54
58
62
Two Theta (°)

Figure 6.

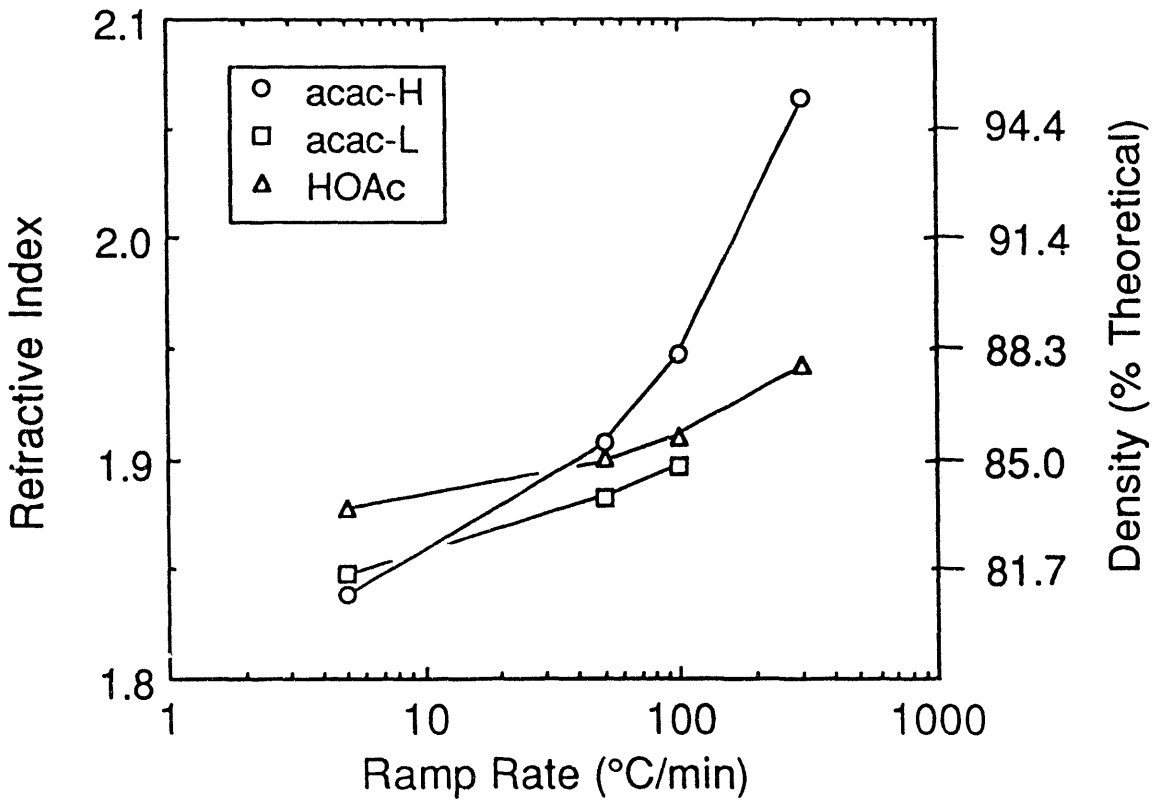
2.1
2.0
1.9
1.8
Refractive Index
acac-H
acac-L
HOAc
94.4
91.4
88.3
85.0
81.7
Density (% Theoretical)
1
10
100
1000
Ramp Rate (°C/min)

Figure 7.

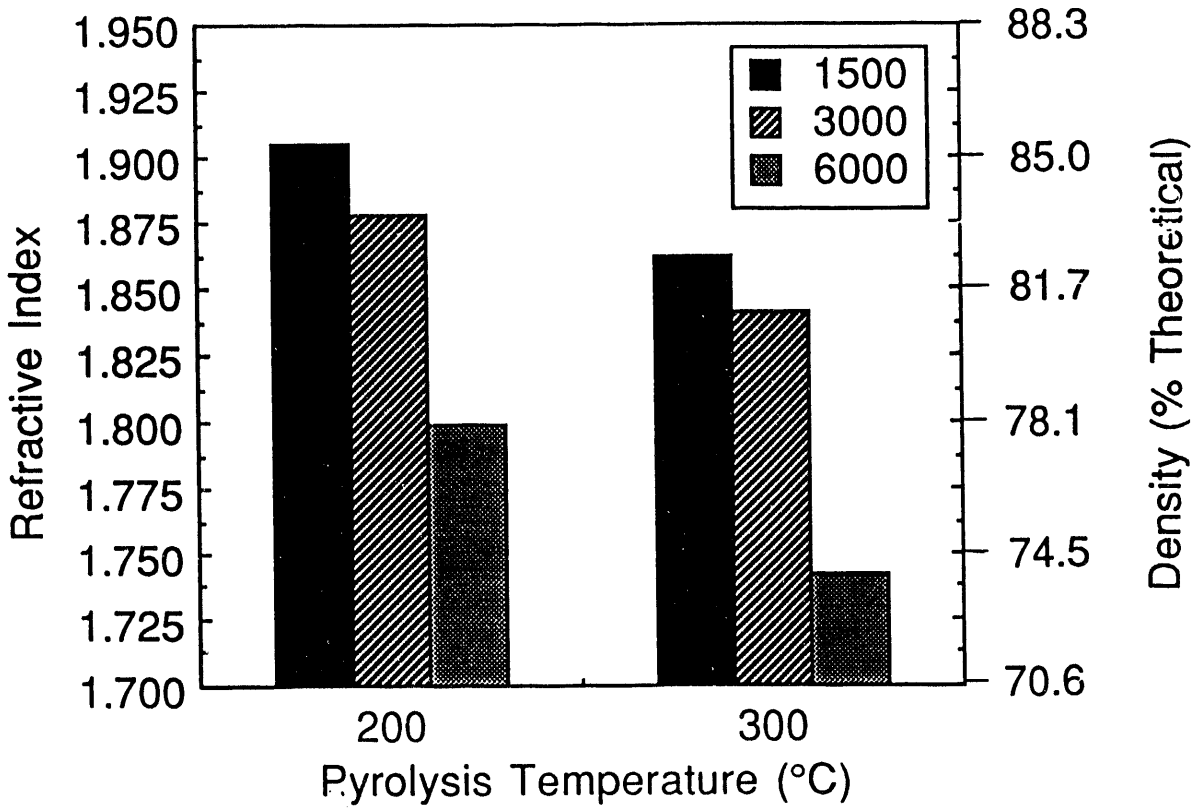
1.950
1.925
1.900
1.875
1.850
1.825
1.800
1.775
1.750
1.725
1.700
Refractive Index
88.3
85.0
81.7
78.1
74.5
70.6
Density (% Theoretical)
1500
3000
6000
200
300
Pyrolysis Temperature (°C)

Figure 8.

DATE
FILMED
3/8/94
END