Epoxidized Soybean Oil-Based Ceramer Coatings

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ABSTRACT: New inorganic/organic hybrid coatings containing epoxidized soybean oil were prepared. Three sol-gel precursors [titanium (IV) *i*-propoxide, titanium (IV) di-*i*-propoxide bis-acetoacetonate, and zirconium *n*-propoxide] were utilized as the inorganic phase. Various coating properties, including adhesion, hardness, impact resistance, flexibility and tensile properties, were investigated as a function of sol-gel precursor type and concentration. All ceramer coatings exhibited excellent flexibility and hardness. Tensile strength and hardness increased with sol-gel precursor concentration. A slight decrease in adhesion and impact resistance was observed with increasing precursor content.

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KEY WORDS: Epoxidized soybean oil, sol-gel precursor, ceramer coatings.

Soybean oil is one of the most widely used drying oils in coatings and varnishes (1–4). Raw soybean oil consists of glycerol esters of linolenic, linoleic, oleic, and saturated acid. The reactivity of drying oil is determined by the linoleic and linolenic acid content, and thereby can be quantified from the drying index:

$$D.I. = \text{Linoleic \%} + 2\text{Linolenic \%} \qquad [1]$$

where D.I. is the drying index and Linoleic % and Linolenic % are expressed in weight percentages. Typically, soybean oil contains a lower level of linolenic acid than linseed oil. As a consequence, its reactivity is relatively low in comparison, and it is often called a semidrying oil. This lower reactivity leads to lack of hardness, chemical resistance, and durability after coating formulation (2). Several chemical methods have been employed in the modification of soybean oil to overcome these deficiencies (4). Among them, epoxidation is one of the most widely used. The unsaturated double bonds of the fatty acids react with peroxide to afford oxirane groups (5).

The oxirane groups can react with a variety of compounds with an active hydrogen, including alcohol, amine, and carboxylic acid (Scheme 1). In addition, epoxidized oil can undergo homopolymerization as shown in Scheme 2. This versatility has led to a wide range of applications and properties (5). Epoxidized soybean oils have been used extensively in plasticizing and stabilizing polyvinyl resins (1). In the coatings industry, epoxidized soybean oils have been employed in the preparation of alkyds, in which epoxide groups serve as latent polyols (4,5).

Ceramers are inorganic/organic hybrid materials in which the organic phase is usually bound to an inorganic phase through a siloxane linkage. The inorganic phase, which has ceramic character, generally consists of metal-oxo clusters. The combination of the hardness of the inorganic phase and the flexibility of the organic phase can provide unique properties that surpass those of the individual components. The inorganic phase of ceramer coatings is prepared *via* a relatively new method called the sol-gel process (6,7). With this process, the inorganic phase can concurrently cure with the organic cross-linking reactions through a succession of hydrolysis and condensation reactions, leading to the formation of a metal oxide network as shown in Scheme 3. The ceramer coatings are suitable for protecting optical and electronic devices because the sol-gel method offers advantages of easy film formation and lower processing temperatures over traditional techniques (8).

Recently, ceramer coatings based on linseed and sunflower oils as the organic phase, and titanium (IV) *i*-propoxide (TIP), titanium (IV) di-*i*-propoxide bis-acetoacetonate (TIA), and zirconium *n*-propoxide (ZRP) as the inorganic phase were developed by Soucek and co-workers (9,10). Ceramer coatings were obtained at a 5–25 wt% sol-gel precursor loading with optimal coatings at a 10–15 wt% sol-gel precursor loading. They also studied the catalytic effect of sol-gel precursors on
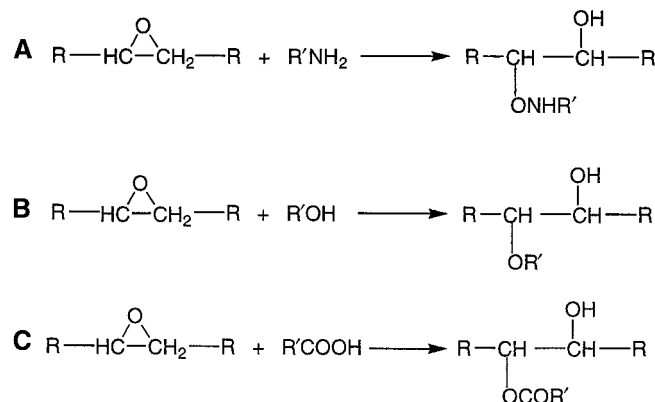
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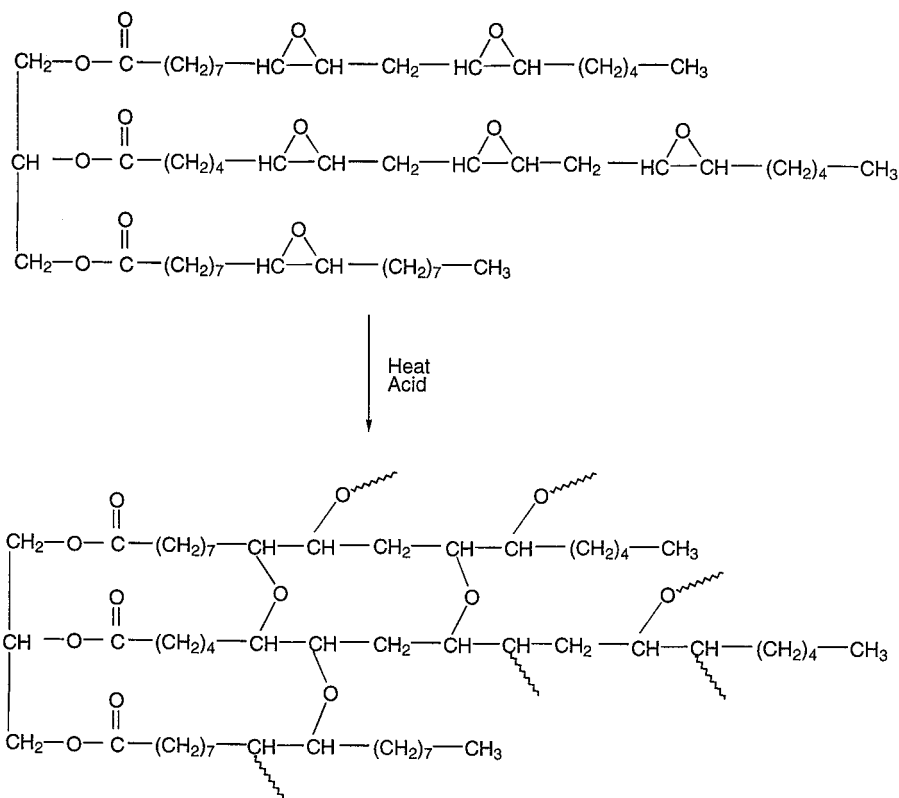
SCHEME 2

the auto-oxidative cross-link process of the organic phase. The inclusion of sol-gel processors leads to lower energies of activation and lower heats of reaction. This suggested that the sol-gel precursors had a catalytic effect on the autooxidative cross-linking reaction similar to that of conventional driers.

In this study, epoxidized soybean oils were used to prepare ceramer coatings. For comparison purposes, the cure schedule from a previous study was utilized (9,10). A schedule of shorter time and lower temperature is also suitable (11,12). The effect of sol-gel precursors was studied in terms of precursor type and loading. The chemical composition of the coatings was varied by altering the metal alkoxide-to-oil ratio. The general coatings properties of adhesion, flexibility, impact resistance, and hardness were evaluated as a function of sol-gel precursor type and loading. In addition, mechanical properties, including tensile modulus, tensile strength and tensile strain-at-break, also were studied as a function of precursor content.

MATERIALS AND METHODS

Soybean oil was obtained from Northern Sun Corporation (Enderlin, ND). Epoxidized soybean oil was obtained from Union Carbide Corporation (Danbury, CT). TIP, 95 wt%, and ZRP, 70 wt%, in 1-propanol were obtained from Aldrich Chemical Company (Milwaukee, WI). TIA, 75 wt% in isopropanol, was obtained from Strem Chemicals (Newburyport,

MA). All starting materials were used as received. The nomenclature for these metal oxides in the formulations is summarized briefly here. As an example, consider a metal oxide designated as TIP5. The first three characters signify what metal oxide was used, and the last numbers signify the percentage of the metal oxide used.

A resin solution was prepared by combining the appropriate quantities of oil and sol-gel precursors in a sealable glass vial under inert atmosphere. After removal from the drybox, the formulation was mixed in a small roll mill for at least 3 h. Films of the ceramer coatings were cast with a drawdown bar at 6 mil wet thickness. The films were then placed in a dust-free drying chamber for 48 h, followed by a cure schedule consisting of 1 h at 130°C, 1 h at 180°C and 1 h at 210°C.

The films were prepared on steel and glass panels. The films on steel panels were tested for cross-hatch adhesion, pencil hardness, reverse impact resistance, conical mandrel flexibility, and Tukon hardness (13). After removing the films on glass panels with a razor blade, the Instron Universal Tester (model 1000; Canton, MA) was used to evaluate tensile properties. A crosshead speed of 2 mm/min was used to determine tensile modulus, tensile strength, and strain at break. Pneumatically actuated 1-in. grips with steel face were used for clamping the specimens. More than five samples were tested for each composition, and average values are reported. The test samples were 8 cm long and 1.7 cm wide.

R = –CH(CH$_3$)$_2$, –C(CH$_3$)CH(CH$_3$)C–, or –CH$_2$CH$_2$CH$_3$
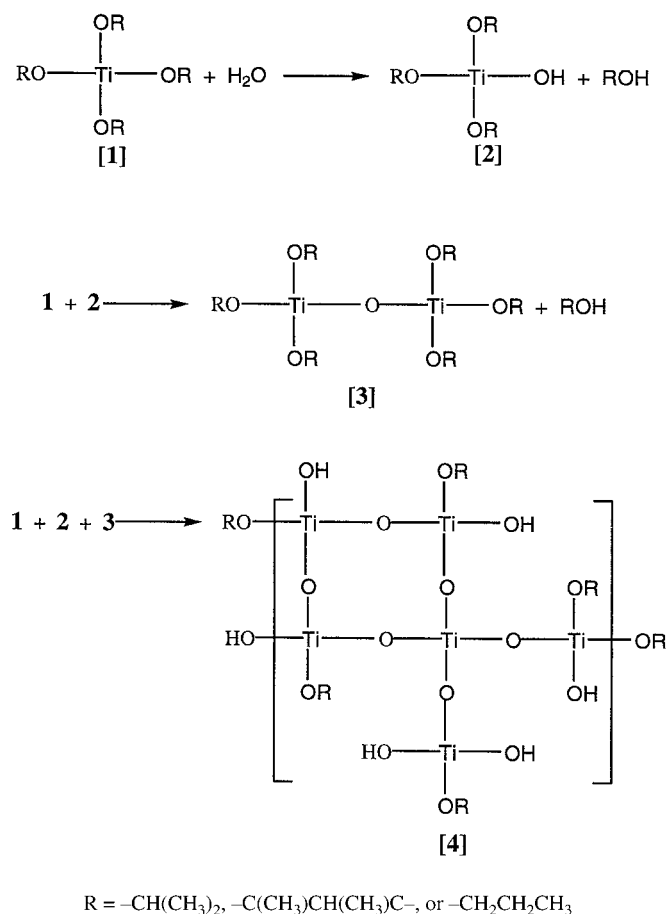
SCHEME 3

RESULTS AND DISCUSSION

The primary objective of this study was to prepare high-performance soybean oil-based ceramer coatings. The three sol-gel precursors, TIP, TIA, and ZRP were used at 5, 10, and 15 wt% loading. The epoxidized soybean oil provides several benefits for the manufacture of ceramer that include low price, versatility, minimal volatile organic content (VOC), and minimal environmental impact. In addition and perhaps more importantly, epoxidized soybean oils have the advantage of a latent hydroxyl group incorporated into the triglycerides. We surmised that this latent group would lead to better interaction between the organic and inorganic phases of the resultant ceramer coatings.

A previous study reported that coatings based on sunflower and linseed oil exhibited relatively low impact resistance and flexibility (9). On the other hand, coatings based on raw soybean oil showed poorer film properties due to its lower reactivity (9). Therefore, epoxidized soybean oil was utilized to formulate the ceramer coatings instead of raw soybean oil. In this preliminary study, the influence of the type and content of sol-gel precursor has been investigated in terms of the general properties and tensile properties of these coatings. Loadings up to 15 wt% sol-gel precursor were used because coatings with 20 wt% or more TIP and ZRP were

brittle. As a consequence, the coatings could not be removed from glass substrate without considerable damage to the films. Moreover, at higher sol-gel precursor loading (20 wt%), the ceramer mixture did not form a homogeneous film. For ZRP-based coatings, even 15 wt% films were difficult to remove from glass substrates without damage to the integrity of the films.

General properties. Table 1 shows the mechanical properties of epoxidized oil-based coatings as a function of sol-gel precursor type and content. All films showed excellent flexibility that was independent of sol-gel precursor type and amount. In contrast, flexibility of the ceramer coatings based on sunflower and linseed oil depended on sol-gel content (9). However, the reverse impact resistance of epoxidized soybean oil ceramer coatings depended on the sol-gel precursors loading. The inclusion of sol-gel precursors decreased the reverse impact resistance in comparison to the epoxidized soybean oil coatings without sol-gel precursor. All three sol-gel precursor ceramer coatings exhibited a decrease in reverse impact resistance at 15 wt% loading. Both TIA- and ZRP-based formulations retained most of the reverse impact resistance, whereas the TIP-based coatings lost almost all reverse impact resistance (15 in.-lb).

Tukon hardness values are shown in Table 2. Both pencil and Tukon hardness of the ceramer coatings significantly increased with increasing sol-gel precursor concentration. The coatings with the greatest pencil hardness were the TIP-based ceramers. The maximum pencil hardness value of 9H was obtained from a 15 wt% TIP loading. There are differences between the Tukon hardness and pencil hardness data of coatings. The Tukon hardness data shows only a slight increase in hardness at 5 and 10 wt% loading for all three precursors, probably due to the different sensitivity of the Tukon tester

TABLE 1
Film Properties of Epoxidized Soybean Oil Ceramers

Chemical composition	Pencil hardness[b]	Cross-hatch adhesion[b]	Reverse impact resistance[b]	Conical mandrel flexibility[b] (%)
Epoxidized soybean oil	F	5B	>80	>32
TIP5	6H	5B	>80	>32
TIP10	7H	5B	>80	>32
TIP15	9H	4B	15	>32
TIA5	5H	4B	>80	>32
TIA10	5H	4B	>80	>32
TIA15	6H	4B	60	>32
ZRP5	5H	4B	>80	>32
ZRP10	5H	4B	>80	>32
ZRP15	6H	4B	70	>32

[a]TIP, titanium (IV) *i*-propoxide; TIA, titanium (IV) di-*i*-propoxide bis-acetoacetonate; ZRP, zirconium *n*-propoxide. The number after each abbreviation indicates the percentage of the metal oxide used.
[b]Pencil hardness determined by ASTM D522; cross-hatch adhesion, ASTM D3359; reverse impact resistance, ASTM G14; and conical mandrel flexibility, ASTM D522 (Ref. 13).

TABLE 2
Tukon Hardness and Tensile Properties of Epoxidized Soybean Oil Ceramers

Chemical composition[a]	Tukon hardness[b]	Tensile modulus[c] (MPa)	Tensile strength[c] (MPa)	Strain at break[c] (%)
Epoxidized soybean oil	0.95 ± 0.042	3.28 ± 0.37	0.54 ± 0.082	16.4 ± 1.20
TIP5	1.64 ± 0.026	14.89 ± 0.87	3.04 ± 0.30	20.52 ± 2.67
TIP10	2.02 ± 0.074	38.52 ± 2.97	4.61 ± 0.36	12 ± 0.97
TIP15	5.24 ± 0.91	33.09 ± 3.64	3.52 ± 0.44	10.6 ± 1.12
TIA5	0.89 ± 0.01	10.37 ± 1.00	1.74 ± 0.27	16.96 ± 3.24
TIA10	1 ± 0.012	24.12 ± 4.68	4.69 ± 0.57	19.72 ± 2.30
TIA15	3.24 ± 0.498	49.98 ± 11.38	4.69 ± 0.60	10 ± 3.58
ZRP5	1.57 ± 0.06	5.03 ± 0.37	0.52 ± 0.64	10.27 ± 0.89
ZRP10	1.38 ± 0.04	39.2 ± 5.80	3.05 ± 0.19	7.72 ± 0.59
ZRP15	2.81 ± 0.27	—	—	—

[a]See Table 1 for explanation of designations.
[b]Determined according to ASTM D1474-85.
[c]Determined using a model 1000 Instron Universal Tester. $n \geq 5$.

between oils and hybrid-based coatings. The least reactive sol-gel precursor (TIA) exhibited the lowest hardness, while the TIP-based coatings exhibited the greatest Tukon hardness. The difference in hardness data is not surprising. Typically, the Tukon hardness is correlated to the modulus and less sensitive for elastic films, whereas the pencil hardness normally is related to strain-at-break (14,15).

Tensile properties. Table 2 also shows the stress-strain behavior of ceramer coatings as a function of sol-gel content and type. As previously mentioned, the 15 wt% ZRP ceramer film could not be removed from the substrate without catastrophic damage to the film. As a consequence, the tensile properties of the ZRP films were only evaluated at 5 and 10 wt%. For TIA-based coatings, the tensile modulus increased with increasing TIA loading. The highest tensile modulus of 38 MPa was observed at 15 wt% TIA loading. For ZRP-based coatings, the tensile modulus followed a similar trend exhibited by TIA-based coatings. The highest tensile modulus of 38 MPa also was attained with 10 wt% ZRP. However, for TIP-based coatings, a different trend was observed. The modulus initially increased with increasing TIP concentration and then appeared to decrease at 15 wt% of sol-gel precursor loading. The difference in modulus, however, was within experimental error. The highest tensile modulus of TIA-based coatings was 50 MPa with a 15 wt% loading.

There was a systematic increase in tensile strength with increasing sol-gel precursor up to 10 wt% loading. The TIA- and TIP-based ceramers have a maximum of 46 and 47 MPa, respectively (at 10 wt% loading). The ZRP ceramer also showed an increase in tensile strength from 5 to 30 MPa when the percent loading was increased from 5 to 10 wt%. At 15 wt% loading, the tensile strength of the TIA ceramer stayed constant. The TIP ceramer, however, decreased to 35 MPa.

At 5 wt% loading, the strain-at-break of both the TIP- and TIA-based ceramers were within experimental error of the parent epoxidized soybean oil specimen. The ZRP-based ceramer, however, exhibited a decrease of strain-at-break from 17 to 12%. At 10 wt% loading, the TIP- and ZRP-based ceramer films both decreased. In contrast, the TIA-based ceramer at 10 wt% loading was within experimental error of the parent oil. As the loading was increased to 15 wt%, the strain-at-break of both TIP and TIA ceramers were in the 10–11 wt% range.

Discussion. The ceramers based on epoxidized oil with sol-gel precursors can be depicted as the model (16) shown in Figure 1. The continuous phase is the organic phase, and the discontinuous phase is the inorganic phase. Three curing mechanisms are responsible for ceramer film formation: (i) polymerization of the organic phase (Scheme 2); (ii) sol-gel reactions of the inorganic phase (Scheme 3); and (iii) chemical bond formation between the organic and organic phases.

The role of rigid pre-ceramic clusters in ceramers can be viewed as that of pigment in coatings, or carbon black in rubber (17,18). Carbon black and rubber blends have been widely studied. Crack resistance of these blends depended on a number of variables, including: type, shape, aggregation, and state of dispersion of the carbon black. In addition, the thickness of the interface between rubber and carbon black is also a critical factor in determining crack propagation. The simplest morphology is depicted in Figure 2A, where the rubber is the continuous phase surrounding the carbon black particles. Other morphologies of carbon black-filled rubber are depicted in Figures 2B and C. In Figure 2B, carbon black aggregates to form semicontinuous rods throughout the continuous rubber phase. In Figure 2C, a core-shell arrangement is depicted, where the carbon black forms continuous layers surrounded by the rubber phase inside and out. Of these three modes, the only one that has been related to the ceramer concept is Figure 2A.

For alkyd ceramers, low sol-gel loading (5 wt%) resulted in a decrease in both tensile properties and hardness (11,12). It was surmised that the level of sol-gel precursors was too low to form a continuous phase, yet high enough to disrupt the organic phase. However, for our system, the interaction between inorganic and organic phases may suppress any discontinuity of the continuous organic phase.
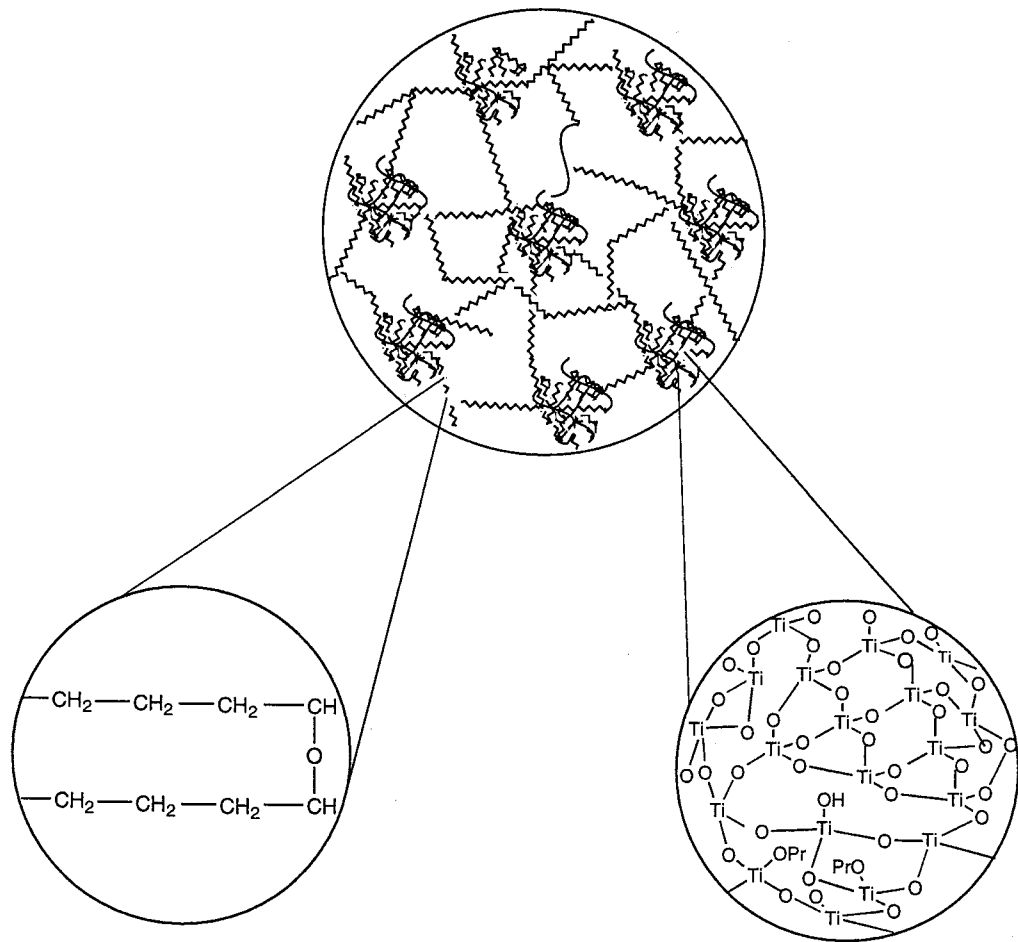
FIG. 1. Ceramer model.

We propose that there is an interaction between organic and inorganic phases. The epoxidized soybean oil based ceramer dried faster than blown or bodied soybean oil-based coatings at the same level of sol-gel precursor loading (19). Therefore, the sol-gel precursors are probably more reactive with epoxidized oil. In addition to the hydrolysis and condensation reactions, sol-gel precursors can also react with hydroxyl or epoxide groups as shown in Scheme 4. The reaction of sol-gel precursors and epoxide leads to the formation of hydroxyl groups. The sol-gel precursors can further react with these resulting hydroxyl groups. Moreover, the sol-gel precursors probably have catalyzed the homopolymerization of epoxidized oil (20,21).

The improvement of tensile modulus, strength, and hardness of ceramers with the inclusion of sol-gel can be attributed to either the formation of rigid clusters or the increase of cross-linking density that is due to the catalytic effect of the sol-gel precursor phase. As cross-link density increases, the coatings become more rigid. Rigid coatings have higher tensile strength and modulus, and less extension in terms of
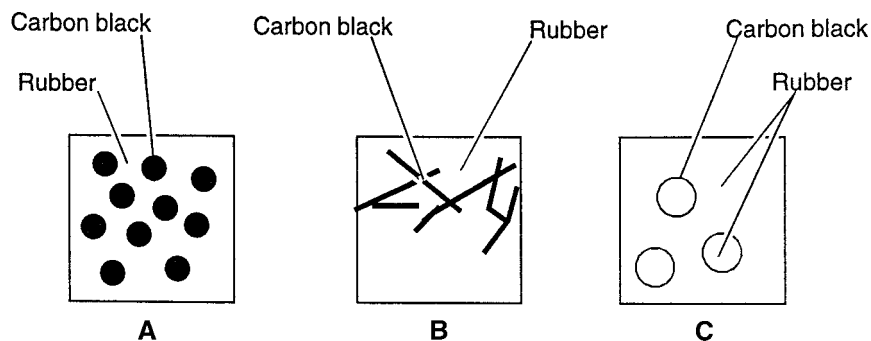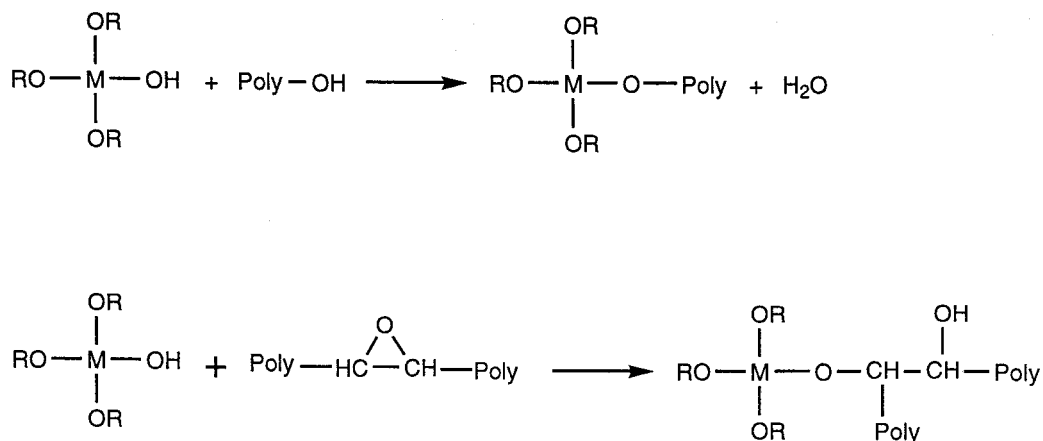

FIG. 2. Morphological models for carbon black-filled rubber. (A) Rubber is continuous phase. (B) Rod-like carbon black structure. (C) Core-shell structure.

SCHEME 4

strain-at-break. It has also been reported (16,17) that, when the preceramic metal-oxo clusters are linked to the organic phase *via* chemical bonds, a synergistic effect between the phases results (11,12). This is manifested by an additional increase in tensile properties.

In comparison to the linseed and sunflower oil-based coatings, the epoxidized soybean oil-based coatings exhibited improved flexibility and impact resistance, while retaining good hardness. It has been proposed that the epoxidization of drying oil suppresses chain scission (β-scission) shown in Scheme 5. This suppression typically occurs during the curing process, leading to an organic phase consisting of higher molecular weight polymers (22). Such longer aliphatic chains are expected to allow for higher flexibility.

The properties of epoxidized soybean oil-based coatings are also similar to the ceramer coatings based on blown soybean oil (19). Modification of soybean oil by either blowing or epoxidizing the soybean oil resulted in high-performance seed oil-based ceramer coatings. We surmised that the modification enhanced the reactivity of the soybean oil in both film formation of the organic phase and toward the metal-oxo cluster of the organic phase. This leads to a synergy between the organic and inorganic phases within the ceramer coatings. For these two types of modified soybean oil-based coatings, some differences in general film properties and tensile properties were observed, depending on the type and content of sol-gel precursors. At high sol-gel precursor content (10–15

wt%), the impact resistance of the epoxidized oil-based ceramers was higher than for blown soybean oil-based ceramers. The tensile properties are quite similar except for TIA-based ceramer. At low- to medium-TIA loading (5–10 wt%), the tensile modulus for epoxidized oil ceramers was lower than for blown oil-based ceramers. However, at 15 wt% loading, the tensile modulus of both epoxidized and blown soybean oil was approximately 50 MPa.

For both epoxidized and blown oils, the TIP precursor was more reactive than the TIA precursor as evidenced by better film properties at 10 wt% loading. Not surprisingly, ZRP is more reactive than other types of precursors for epoxidized soybean oil-based coatings. This behavior may be due in part to the increase in the rate of hydrolysis of sol-gel precursors, ZRP > TIP, and the self-condensation of ZRP occurring at a faster rate than condensation with the organic phase. Among all epoxidized soybean oil-based coatings, the 10 wt% TIP-based coatings seem to be most attractive in general properties and tensile properties. The TIA-based coating with a 15 wt% loading was similar in properties to the TIP (10 wt%); however, the 10 wt% TIP-based film was slightly better in hardness.

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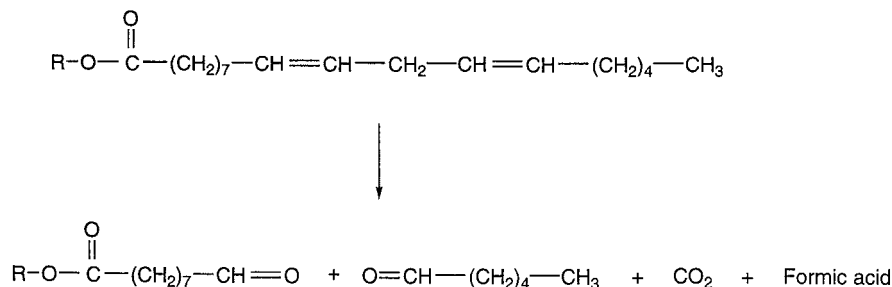
SCHEME 5

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