

Interpenetrating Polymer Networks Derived from Silylated Soybean Oil and Polydimethylsiloxane

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ABSTRACT: A series of interpenetrating polymer networks (IPNs) was prepared using various concentrations of silylated soybean oil and polydimethylsiloxane (PDMS) that were cross linked with inorganic silicates. This series of IPNs was prepared from emulsions of silylated soybean oil and PDMS together with colloidal silica and dioctyltin dilaurate catalyst at pH 10. Under these conditions, water soluble silicates reacted with silanols in the oil phase and formed intraparticle siloxane cross links. Upon casting films and evaporation of the water, additional interparticle cross linking were obtained between the coagulating particles to produce entangled networks of soybean oil and PDMS that were further reinforced by fine silica particles. The morphology revealed intimate mixing of the two immiscible components. The mechanical properties depended on the ratio of the soft, flexible PDMS phase and the rigid, brittle cross linked silylated soybean oil phase. These IPNs can be used as high release liners, low friction materials, or as a general protective coating. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2479–2486, 2013

KEYWORDS: cross linking; coatings; emulsion polymerization; grafting; structure-property relations

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INTRODUCTION

Incorporating triglycerides into polymeric systems in an attempt to develop natural plasticizers were generally difficult because of branching and the relatively long alkyl chains of the fatty acids, which resulted in incompatibility.¹ A more successful approach was to combine the triglycerides with a polymer matrix via an interpenetrating polymer network (IPN).^{2,3} The broad definition of IPN is a material containing two or more components that have been vulcanized (cross linked) in the presence of each other to form entangled (interpenetrated) networks.⁴ An IPN is inherently a multiphase system because the heterogeneous morphology can lead to synergistic combinations of properties that are different from the properties of the individual components or those achieved by grafting, blending, or other mixing techniques. Of particular interest are an increase in toughness and fracture resistance of thermoset polymers.⁵ Currently, products derived from IPNs find various applications such as ion-exchange resins, adhesives, high impact plastics, vibration damping materials, high temperature alloys, and medical devices.⁶

Several IPNs described in previous literatures contain plant oils and synthetic polymers. Some examples include alkyd and polyurethane IPNs (also known as uralkyds) that were prepared by solution casting followed by air vulcanization. These IPNs produced tough coatings, which displayed high abrasion and chemical resistance.^{7,8} Similarly, IPNs of alkyds and methacrylate

polymers were described⁹ and the combination of soft and flexible poly(butyl methacrylate) with the hard and brittle alkyd produced a resin, which had better physical properties than each of the individual components. IPNs of castor oil triglycerides with poly(ethylene terephthalate) (PET) exhibited a higher degree of toughness and faster crystallization rates than PET alone.¹⁰ IPNs prepared from castor oil-based polyurethanes and styrene monomers could be tailored to yield tough elastomers or reinforced plastics, depending on their compositions.^{11,12} In addition, IPNs based on castor oil with acrylics were elastomers and exhibited good mechanical properties.^{13–15} Many other IPNs have also been prepared from functionalized vernonia oil,¹⁶ lesquerella oil, crambe oil, and linseed oil (as well as their epoxidized derivatives) with polystyrene and polyacrylics.^{17–23} Most of the previous IPN work with triglycerides involved preparing a homogeneous solution of the triglycerides with the desired monomer, then polymerizing and cross linking as phase separation occurred. Thus, the morphology of the resulting IPN is generally a function of the kinetics of the phase separation. In this work, we wish to report a different approach where the IPNs are prepared from emulsions containing particles of silylated soybean oil and polydimethylsiloxane (PDMS).

There are numerous IPNs containing PDMS with a variety of synthetic polymers^{24–28} showing microphase separation and multiphase structures because of the inherent immiscibility of

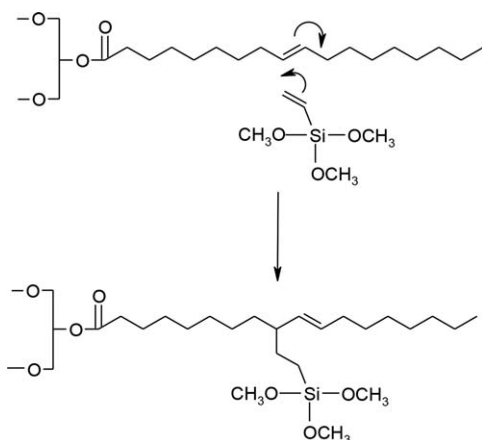


Figure 1. Silylation of unsaturated fatty acids in soy oil triglycerides with VTMS by the “Ene reaction.”

PDMS with most organic polymers. Many of these IPNs have interesting and useful properties because of the high chain flexibility, low surface energy, high thermal stability, and low T_g of the polysiloxane chain. Although there are large numbers of silicone-containing IPNs, no IPNs of silicone polymers and triglyceride oils are described in the literature.

Instead of using organic solvents or relying on the solubility of the monomer in the triglycerides, it is also possible to prepare oil in water emulsions of immiscible components and cross link them before casting films. This method is known as “Latex IPN.”²⁹ It consists of blending together two emulsions composed of components A and B, then cross linking each independently with suitable cross linkers. Alternatively, polymer A latex is cross linked, then monomer B, initiator, and a cross linking agent are added and polymerized³⁰ to yield the desired IPN. The latter latex IPNs combine both networks in a single latex particle and, as such, their morphology is limited to the size of the latex particles. The effects of the addition sequence and the polymer composition on the inter- and the intraparticle microdomains morphology (core/shell structures) as well as the bicontinuous IPN particles structure were reviewed.³¹

In this work, we focus on latex-blending IPNs, where two emulsions of incompatible polymers are prepared separately and then combined together with a common cross linking agent. Under these conditions, the particles from both emulsions undergo intraparticle cross links while still suspended in the water phase. Upon casting, additional interparticle cross linking takes place between the coagulating particles to yield typical IPN morphology, whereby the two phases are intimately mixed and cross-linked. These IPN resins composed of silylated soybean oil and PDMS can be used as high release liners, low friction materials, or as convenient one-package protective coatings.

EXPERIMENTAL

Materials

Low-saturated soybean oil was kindly supplied by Zeeland Farm Services (Zeeland, MI, USA). Silanol-terminated dimethylsiloxane oligomers of 25 cSt viscosity and vinyl trimethoxysilane (VTMS) were purchased from Gelest Inc. (Morrisville, PA, USA). 4-

Dodecylbenzene sulfonic acid (DBSA), dibutyltin dilaurate (DBTDL), sodium dodecyl sulfate (SDS), and 2,5-Bis (*tert*-butylperoxy)-2,5-dimethylhexane (Luperox[®]101) peroxide were purchased from Sigma-Aldrich (St. Louis, MO, USA). Colloidal Silica (NALCO-1115) 15 wt % solids having particle size 4 nm was kindly supplied by Nalco Co. (Naperville, IL, USA).

Equipment and Characterization

¹H NMR spectra were recorded on a 500 MHz NMR spectrometer (Varian Inc., USA, Unity Plus 500 MHz) using the solvent peak as an internal standard. Thermogravimetric analyses (TGA, TA instruments, USA, Q500) were obtained by heating samples (~8.5 mg) from room temperature (RT) to 500°C at 10°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC, TA instruments, USA, Q2000) data were obtained by first heating a sample (~6 mg) under a nitrogen atmosphere to 200°C to erase any thermal history, then cooling to -70°C at 10°C/min followed by heating to 200°C at 10°C/min. The extent of cross linking was determined by measuring the gel and swell ratios of cast films using toluene as a solvent following ASTM D2765-11.³² In all cases, the samples were allowed to swell at RT for 120 hours before they were removed and dried at RT to a constant weight. The mechanical properties (stress-strain) were measured at RT using a Universal Testing Machine (United Calibration Corp. and United Testing Systems Inc., USA, SFM-20) according to ASTM D638.³³ The tensile tests were performed at a strain rate of 6 cm/min and in all cases at least five specimens of each sample were tested and the average value was recorded. The molecular weight was determined by a gel permeation chromatography (GPC) equipped with a refractive index detector (Shimadzu, Japan, RID-10A) using tetrahydrofuran as mobile phase. The calibration was performed with polystyrene standards.

Scanning electron microscope (SEM, Japan Electron Optics Laboratories, Japan, JEOL-6400V) was used to study the morphology of fractured surfaces. A fresh surface was obtained by fracturing the specimen in liquid nitrogen. The fractured surface was fixed with 1% osmium tetroxide (O₅O₄) solution to stain the unsaturation of the soybean oil. Each image was observed under backscatter electron detector for better resolution and contrast. Thus, the silylated soybean oil appears as a lighter shade, while the polysiloxane appears as a darker shade.

Silylated Soybean Oil Emulsion

Low-saturated soybean oil (600 g), VTMS (306 g), and Luperox[®]101 (6 g) were mixed and added to a 2L Parr reactor (Parr Instrument Company, USA, PARR 4841). The reactor was purged with nitrogen to maintain an inert atmosphere. Then the system was heated to 280°C for 12 hours to graft the VTMS onto the soybean oil by the Ene reaction³⁴ as shown in Figure 1. The grafting of VTMS onto the soybean oil was confirmed by ¹H NMR.

The silylated soybean oil (900 g) was homogenized with SDS (22.5 g) in a laboratory homogenizer (Manton-Gaulin, USA, model No. 15MR) at 53 MPa (two passes) to yield a stable emulsion containing 45% solids. Upon aging, the hydrolytically unstable methoxysilanes hydrolyzed to form silanol functional groups attached to the soybean oil.

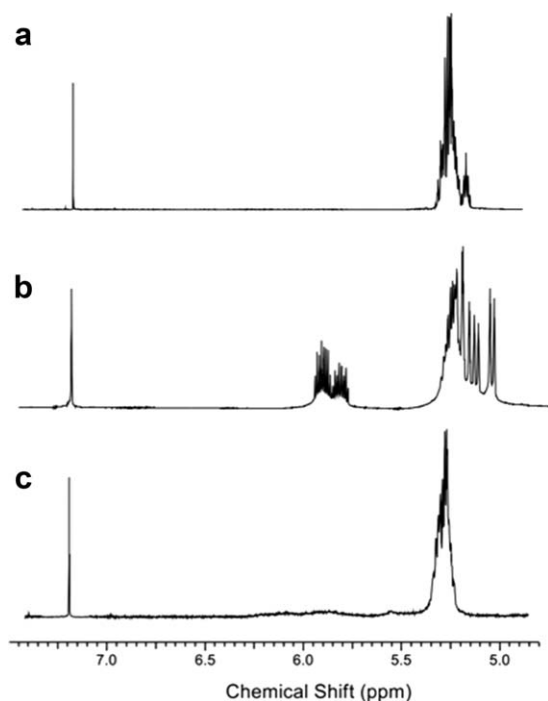


Figure 2. Partial ¹H NMR spectrum of soy oil (a), intermediate reaction with VTMS (b), and the final silylated soy oil product.

Emulsion Polymerization of Polydimethylsiloxane

The preparation of high molecular weight PDMS in emulsion is well known.^{35,36} Briefly, a stable emulsion was prepared by homogenizing 500 g of low molecular weight, silanol-terminated dimethylsiloxane oligomers (average DP = 35), 500 g distilled water, and 12.5 g DBSA in a laboratory homogenizer at 53 MPa. Two passes through the homogenizer under these conditions yielded a stable emulsion. This emulsion was then allowed to polymerize at RT and the molecular weight of the silicone oil was monitored by periodically drawing a sample, neutralizing it with 0.5 N KOH and then precipitating the polymer in methanol. At the end of the polymerization (23 hours), the pH of the emulsion polymer was adjusted to ~10 by adding potassium hydroxide (KOH) followed by addition of colloidal silica (20 g) and DBTDL (1.0 g).

Preparation of Soybean Oil-PDMS IPNs by the Emulsion Method

Various IPN compositions were prepared simply by mixing different amounts of the PDMS and the silylated soybean oil emulsions, then casting films and allowing the water to evaporate at RT. In all cases, the mixed emulsions were stable with no apparent coagulation or creaming. Similarly, no apparent gross phase separation was observed in the cast films after the water was evaporated.

RESULTS AND DISCUSSION

Emulsion Polymerization of PDMS

High molecular weight PDMS was obtained by emulsion polymerization after 23 hours at RT. GPC data indicate that the resulting PDMS were characterized by a relatively uniform

molecular weight distribution with $M_n = 66,400$ g/mol and $M_w = 92,400$ g/mol.

Silylation of Soybean Oil

A high degree of grafting of VTMS onto the soybean oil was achieved by the “Ene reaction” as observed by ¹H NMR (Figure 2). The chemical shift of the protons associated with the double bonds of the fatty acids in the soybean oil appears around 5.25 ppm [Figure 2(a)]. The partial ¹H NMR spectrum of an intermediate product from the reaction of soybean oil with VTMS is shown in Figure 2(b) where the protons of the double bond in the VTMS appear as multiple resonance peaks near 6.0 ppm. Furthermore, the complex shape of the resonance peaks related to the unsaturation of the soy oil around 5.25 ppm also changed as the reaction proceeded. The final silylated product is shown in Figure 2(c), which clearly indicates the disappearance of the resonance peak associated with the unsaturation of the VTMS near 6.0 ppm. It should be emphasized that unlike hydrosilylation reactions, the “Ene reaction” mechanism consumes the unsaturation linkages in VTMS, but the end product still contains an unsaturation. The yield of this grafting can be calculated from the initial mass ratios of the reactants and was found to be 95%.

The extent of grafting was confirmed by isothermal TGA experiments conducted at 150°C. This temperature was chosen because it is above the boiling point of VTMS (123°C) but well below the degradation temperature of soy oil. Under these conditions, all free (not grafted) VTMS will be removed and the yield of the grafting reaction can be determined from the weight loss. Indeed, it is apparent from Figure 3 that all the unreacted VTMS were removed within 10 minutes, indicating that the unreacted fraction is 3 wt % of the total mass of the sample. Therefore, knowing the initial concentration of VTMS in the sample, it was found that the yield of the grafting was 95%, in good agreement with the NMR data.

It is interesting to note that the weight loss of the silylated soy oil in this experiment continued even after all free VTMS was removed from the product. This slow degradation at elevated temperatures is due to a redistribution reaction of the methoxy group of the grafted VTMS with the carbonyl group of the triglyceride fatty acid esters³⁷ as shown in Figure 4. The methyl fatty

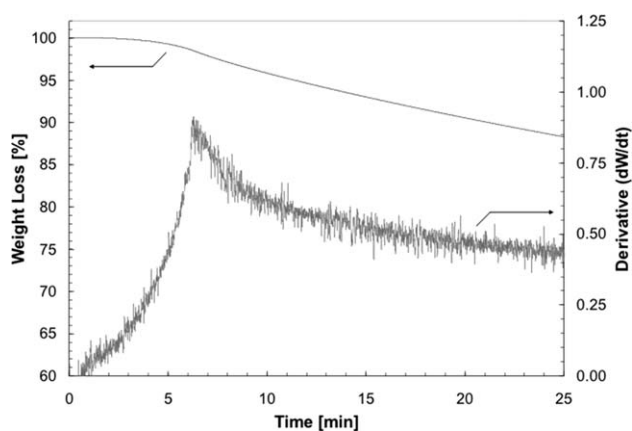


Figure 3. Isothermal TGA (150°C) of silylated soy oil.

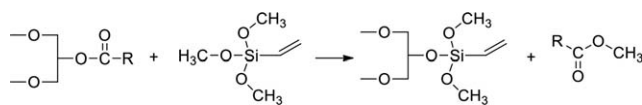


Figure 4. Redistribution side reaction between VTMS and the carbonyl group of the triglyceride.

ester products in this side reaction have lower molecular weight and are responsible for the observed weight loss.

Although it is possible to remove the unreacted fraction of VTMS by distillation, it was deemed unnecessary because upon hydrolysis and condensation to yield the IPNs all the siloxy groups, whether grafted or free, would be part of the network.

Formation of IPN

Network formation is obtained in two stages via siloxane cross links: in the first stage, silicates that were introduced via partial dissolution of colloidal silica in the alkaline pH of the mixed emulsion lead to cross linked silicone particles. As described previously,³⁸ these soluble silicate species are grafted onto the silanol chain-ends of both PDMS and the silylated soybean oil. This silanol condensation reaction is catalyzed by DBTDL leading to intraparticle cross links. In the second stage, additional interparticle cross links are obtained upon evaporation of the water phase between the coagulating emulsion particles. These interparticle cross links through additional silanol–silanol condensations further contribute to the overall network via condensation reactions between the terminal PDMS silanols, silanol-grafted soybean oil and the inorganic silicates/silica filler. The small silica particles further act as a reinforcing agent to reinforce the entangled cross linked network as shown schematically in Figure 5.

It should be noted that because all the components in this system contain terminal silanols, their condensation to yield stable siloxane linkages is the basis for the cross links of the network. These cross link linkages connect all components to the network and include siloxane linkages between the triglycerides, PDMS, and silica. Siloxane linkages between adjacent fatty acids of the same triglyceride or the formation of macrocyclic PDMS cannot be ruled out. These siloxane linkages are considered as defects and will not contribute to the network. However, because of the large number of silanols, the total number of such defects is expected to be negligible. Furthermore, as depicted in Figure 5, it is expected that not all silanols will be condensed to siloxanes and will remain as Si-OH. This residual silanols and silicates are advantageous as they act as adhesion promoters and enhance the adhesion of these IPNs to inorganic substrates such as glass, cement, concrete, brick, aluminum, and steel.

Morphology

The morphology of the IPNs is greatly affected by the relative concentrations of PDMS and silylated soybean oil as observed in the SEM micrographs [Figure 6(a–d)]. All four micrographs indicate distinct phase separation that changes with the ratio of the silylated soybean oil (component 1) and PDMS (component 2). For better distinction between these two components, the IPN samples were stained with OsO₄ prior to their examination in the SEM and the images were captured using a backscattering mode. Because OsO₄ adsorbs onto the double bonds, it stains

only the silylated soybean oil phase containing the unsaturated fatty acids and, hence, this component appears as the bright phase in the backscattering mode. As the concentration of one component is increased and the other is decreased, a dual phase morphology is observed followed by a bicontinuous morphology and then again a dual phase morphology. Thus, the IPN containing 20 wt % silylated soybean oil [Figure 6(a)] shows the PDMS-rich phase (component 2) as the continuous matrix with the silylated soybean oil phase (component 1) dispersed in it as fine globular nodules, about 5–15 μm in size. Further, increasing the concentration of the silylated soybean oil to 40 or 60 wt % (such that it is present at about the same concentration as PDMS) leads to a co-continuous morphology [Figure 6(b,c)]. The globular nature of the domains is still visible but the continuous phase is less distinct giving rise to the appearance, where all the globular domains are stuck to each other. Upon further increasing the concentration of the silylated soybean oil to 80 wt % [Figure 6(d)] leads again to dual phase morphology. However, here the continuous phase is the silylated soybean oil matrix and the dispersed phase consists of globular PDMS domains about 0.5–2 μm. Similar changes in the dual phase morphology were noted before when component 1 of an IPN was dispersed in component 2 at low concentrations and appeared as the dispersed phase. However, upon increasing the concentration of component 1, it then became the continuous phase and component 2 became the dispersed phase.⁴

The presence of phase separation and globular domain structure are influenced primarily by the extent of the miscibility between the silylated soybean oil matrix and the PDMS. However, in this case the shape of the domain is also determined by the intramolecular cross links that were induced in the emulsion phase in both particles. These cross links in each phase prevent unrestricted flow upon coagulation and film formation and restrict the shape of the domains. The cross link density of each component need not be the same because it is expected that these variations in the morphology will have significant effects on the mechanical properties.

It is also important to note that no cracks, voids, or other defects are observed along the interface between the globular domains and the matrix. Thus, the intimate interface between

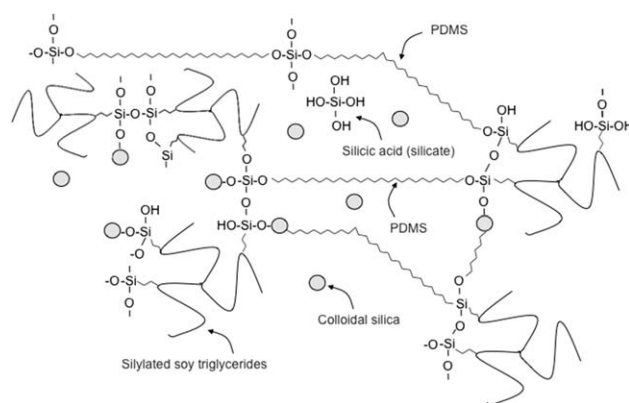


Figure 5. Schematic representation of IPNs composed of siloxane cross-links between high MW PDMS, silylated soy oil, and silica filler particles.

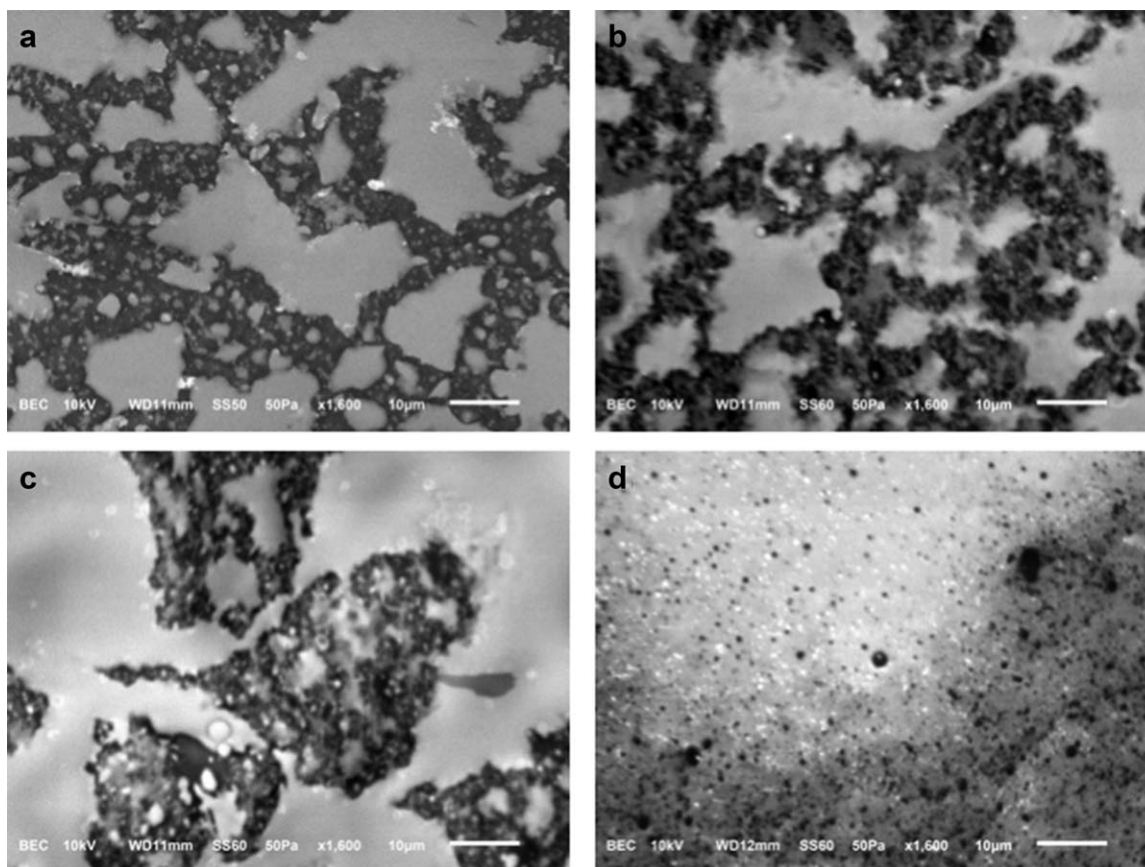


Figure 6. SEM images of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 20/80, (b) 40/60, (c) 60/40, and (d) 80/20.

the soy phase and the PDMS phase is expected to minimize any gross phase separation.

Gel-Swell Analysis

The degree of swell and the gel fraction were measured as a function of composition of the IPNs (Figure 7). The equilibrium swell ratio (Q) was calculated using the following equation:

$$Q = \frac{W_{P0}/d_p + W_s/d_s}{W_{P0}/d_p} \quad (1)$$

where W_{P0} is the initial weight of the sample, W_s is the weight of the swollen sample at equilibrium, d_p the density of the sample, and d_s is the density of the solvent.

The gel fraction (G) was calculated using the following equation:

$$G = \frac{W_p}{W_{P0}} \times 100 \quad (2)$$

where W_p is the weight of the dried sample after all the extractable sol was removed while swelling.

The degree of swell is related to the free chain length between cross links and to the interaction of the solvent with the polymer chains. Thus, low cross link density leads to high degree of swell and usually low gel fraction. However, it is apparent that the cross linked homopolymer PDMS gel exhibited relatively high

swell and high gel fraction while the sample containing cross linked silylated soybean oil exhibited low gel fraction and relatively low swelling. This combination is highly unusual and not commonly observed in polymeric systems. One possible explanation could be related to a variation in the interactions of the solvent with each component of the IPN. In the extreme case, the toluene solvent is a “good” solvent for PDMS but a poor solvent for the soy component. Under this condition the

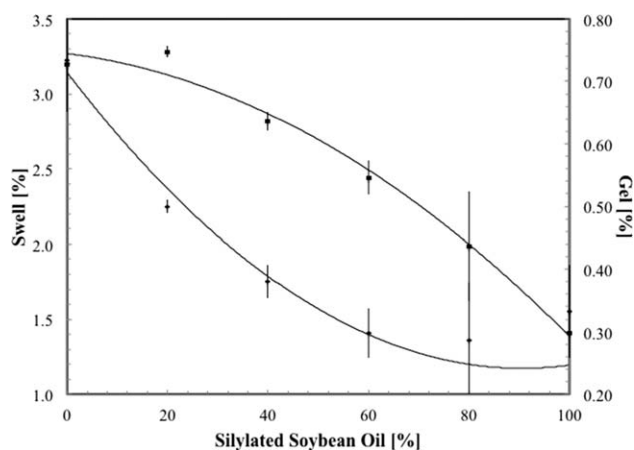


Figure 7. Gel and swell fractions of IPNs composed of different concentrations of silylated soybean oil/PDMS.

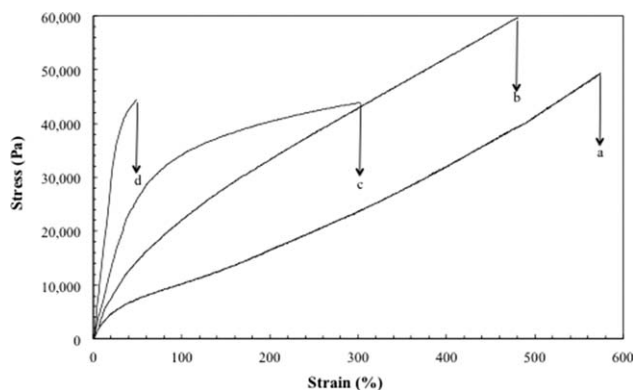


Figure 8. Stress–strain of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 0/100, (b) 20/80, (c) 40/60, and (d) 60/40.

soy oil component will not swell and will show high gel fraction even if it is not cross linked. However, this is not the case here because toluene is a “good” solvent for both the PDMS and the soy components. Apparently, the network in these IPNs is non-uniform and the silylated soybean oil phase contains a high density of localized cross links (e.g., tight network), leading to low swelling of these regions. However, other regions contain no cross links and therefore do not contribute to the gel content. Thus, the data indicate that only about 30 wt % of the silylated soybean oil sample is cross linked (70 wt % is soluble in toluene), but these cross linked regions contain a relatively high density of cross links leading to a low swell ratio of these regions. In comparison, the cured PDMS sample (containing no silylated soybean oil) exhibits a fairly high degree of swelling and also a high gel fraction. Thus, the network in this sample is more uniform and complete, leading to high gel content but the overall cross link density is low resulting in a high degree of swelling.

The cross linking reaction in both components is identical and is based on the formation of siloxane linkages by silanol condensation because the gel and swell fractions of each IPN are observed to be between these two extremes and depend on the composition of the sample. In general, it is observed that the gel content and the swell ratio are inversely proportional to the concentration of the silylated soybean oil content. Conversely, increasing the concentration of PDMS in the IPN leads to a more uniform cross link structure and a higher gel fraction. However, because of the relatively low degree of cross linking, it also leads to a higher swell ratio.

It should further be emphasized that although the network is not uniform, both phases (e.g., the silylated soybean oil and PDMS) are participating in the network. If only one of these phases was cured, semi-IPNs would have been formed where one component is interlocked (but not covalently linked) to the other component. Obviously, the identical cure reactions in this case lead to full IPNs.

Mechanical Properties

The effects of composition on the mechanical properties of the IPNs are shown in Figure 8 and the main properties are presented in Table I. As indicated from the gel–swell measurements, the sample containing 80 wt % silylated soybean oil and

the sample composed of only cured silylated soybean oil (no PDMS) had a high degree of cross links and thus were too brittle to accurately determine the tensile properties. The sample composed of cured PDMS (no silylated soybean oil) was found to have similar elastomeric properties to those previously reported in the literature.³⁹

The tensile strength and the initial modulus increased as the concentration of the silylated soybean oil fraction in the IPN increased while the elongation at break decreased. These changes were undoubtedly related to the high cross link density of the silylated soybean oil matrix as described earlier. It is interesting to note that, generally, the elongation at break of semi-IPNs does not decrease drastically as the cross link density is increased when compared to full IPNs.⁹ This trend is simply due to the fact that the uncross linked phase in the semi-IPN acts as a plasticizer or a polymeric filler and exhibits higher mobility compared to full IPNs, where the cross linking of both phases restrict the mobility of the network. In the current silylated soybean oil/PDMS IPNs, the elongation at break is drastically reduced as the silylated soybean oil concentration is increased, clearly indicating that this phase is an integral part of the network. Similarly, as the concentration of the soft PDMS phase is decreased, the modulus and the tensile strength of the sample are higher.

It follows from the mechanical properties that the cross linked silylated soybean oil acts as a high modulus resin-like component and the lightly cross linked PDMS as a ductile matrix. Apparently, the relatively low molecular weight of the triglycerides before cross linking (e.g., roughly 900) contains roughly one silyl group per fatty acid residue that leads to a free chain length of ~ 300 between cross links. Furthermore, each grafted silane contains three silanols and each of these silanol is available to form short disiloxane cross links because the distance between cross links is very short resulting in a rigid matrix with very low elongation. In contrast, the PDMS phase is composed of high molecular weight linear polymers that are well above the T_g and the polymer chains are tied to the network only at the chain-ends. This type of structure is expected to lead to a matrix that is highly flexible and elastomeric. Thus, useful compositions in this series are IPNs composed of high concentrations of PDMS, as the continuous phase leaves the rigid silylated soybean oil as a discontinuous, dispersed phase.

Table I. Mechanical Properties of IPNs Composed of Different Concentrations of Silylated Soybean Oil/PDMS

Soy/PDMS (wt./wt.)	E (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
0/100	2.5 ± 0.3	0.03 ± 0.01	656 ± 0.3
20/80	4.2 ± 0.4	0.03 ± 0.01	496 ± 0.4
40/60	3.8 ± 0.2	0.05 ± 0.01	302 ± 0.2
60/40	10.3 ± 0.2	0.04 ± 0.01	5 ± 0.2
80/20 ^a	–	–	–

^aFilms too rigid to determine mechanical properties

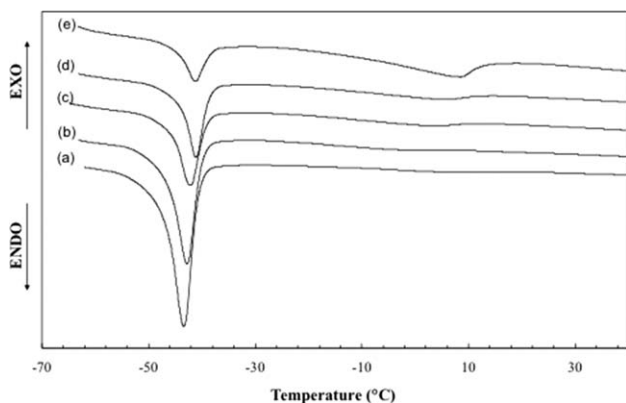


Figure 9. DSC of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 0/100, (b) 20/80, (c) 40/60, (d) 60/40, and (e) 80/20.

Thermal Properties

The thermal properties of the cast IPN films were investigated by DSC (Figure 9). The melting temperature of PDMS (T_{m1}) was observed at -43°C and slightly increased as the concentration of the silylated soybean oil was increased. The enthalpy of this melting transition was inversely proportional to the concentration of the silylated oil and decreased from 16.53 J/g for PDMS to 3.18 J/g for the sample composed of only 20% PDMS, respectively (Table II). This increase in the melting point and decrease of the enthalpy indicate a lower organization of the PDMS chains because of the formation of the network. Furthermore, a small but noticeable melting temperature (T_{m2}) was observed related to the saturated fatty acid in the soybean oil triglycerides. The melting temperature was not affected by the composition of the IPN but the enthalpy of this melting transition was directly proportional to the concentration of the silylated soybean oil in the IPN. Apparently, the saturated fatty acids do not participate in the network because the grafting of the silane only occurs onto the double bonds of the unsaturated fatty acids. Consequently, the saturated fatty acids act as “dangling ends” and are free to crystallize. This general phenomenon has been observed previously in various other IPNs where a net decrease in the chain’s mobility was noted because of close interactions (e.g. physical cross links and chain entanglements) between the phases in the microdomains.^{10,28}

The siloxane linkages are well known for their high bond strength and thermal stability to homolytic cleavage because it was interesting to evaluate the thermal stabilities of the IPNs as a function of the siloxane content. It was surprising to note from the TGA

Table II. Thermal Properties Thermal Properties of IPNs Composed of Different Concentrations of Silylated Soybean Oil/PDMS

Soy/PDMS (wt./wt.)	T_{m1} ($^{\circ}\text{C}$)	ΔH_1 (J/g)	T_{m2} ($^{\circ}\text{C}$)	ΔH_2 (J/g)
0/100	-47.3	16.53	-	-
20/80	-46.9	12.27	-6.19	1.671
40/60	-46.0	8.98	2.83	1.572
60/40	-44.2	7.36	4.99	2.454
80/20	-44.9	3.18	8.14	4.848

data (Figure 10) that the onset temperature of degradation of the PDMS network (containing no silylated oil) was only 315°C , much lower than one would expect from a cross linked PDMS rubber. Apparently, the presence of DBTDL, which is a known reversible condensation catalyst, caused premature degradation via rearrangement of a ring-chain equilibrium.⁴⁰ It was also unexpected to note that the silylated soybean oil thermogram (Figure 10, trace f) consists of two degradation modes, the first at 131°C and the second at 374°C . The higher degradation temperature is a typical degradation temperature of soybean oil. Presumably, the lower degradation temperature is related to the redistribution reaction that results in free fatty acid methyl esters at elevated temperatures.

It is important to note that the degradation of simple blends (no IPN) of PDMS and soy oil does not depend on the relative concentration of each component in the blend. Thus, the degradation temperature of each component in the blend will not be affected by the other component in the blend. The TGA results (Figure 10) indicate that extensive grafting, cross linking, and interpenetration are responsible for the observed thermal behavior of the IPNs.

CONCLUSIONS

A series of IPNs were prepared by combining and curing latexes of silylated soybean oil and PDMS. The oil phase of both latex particles contained terminal silanol groups that were used as a common cross linking mechanism based on the condensation of silanols and silicates to form siloxane cross links. Some cross links were induced while in emulsion (e.g., intraparticle cross links) and led to partially cross linked oil particles while still suspended in emulsion. Upon evaporation of the water phase and casting films, additional interparticle cross links took place, which interlocked the two phases together and prevented gross phase separation.

The properties of the IPNs were affected by the relative concentration of each phase, however, no gross phase separation was observed and the silylated soybean oil matrix was intimately mixed with the PDMS phase at all concentrations. The morphology was examined by SEM and appeared as a dispersion of

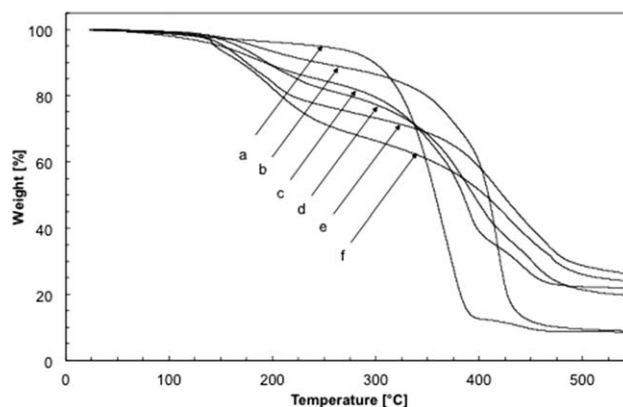


Figure 10. TGA of IPNs composed of different concentrations of silylated soybean oil/PDMS. (a) 0/100, (b) 20/80, (c) 40/60, (d) 60/40, (e) 80/20, and (f) 100/0.

the minor component in the continuous matrix of the major component when the concentration of each phase was radically different. However, when the concentrations of the silylated soybean oil and the PDMS were roughly similar, bicontinuous morphology was observed. In these cases, diffused particles that closely adhere to each other were observed.

Although both phases were cross linked to form full IPNs, the cross link density of each phase was different. The silylated soybean oil component was characterized by a low gel fraction and a low swell ratio indicating regions of high cross links but other regions contain no cross links. The PDMS component was characterized by a high gel ratio and high degree of swelling indicating a more uniform cross link structure because of the relative long chain lengths between cross links. This uneven morphology and cross link distribution affected the mechanical properties of the cast films. At low concentrations of silylated soybean oil (high PDMS content), the films were elastomeric with relatively high elongation and moderate tensile strength. Conversely, at high concentration of silylated soybean oil (low PDMS content), the cast films were resin-like materials with high modulus and low elongation at break.

DSC and TGA results indicate that extensive grafting, cross linking, and interpenetration affect the thermal properties of these IPNs. However, the thermal decomposition temperatures of the IPNs were lower than soybean oil or typical silicone rubber. Because of lower degradation stability, the DBTDL redistribution catalysts are left in the system, which causes transesterification and formation of free fatty acid methyl esters.

These new IPNs provide convenient, one-package, cross linked water-based coatings derived from PDMS and soybean oil. The coating can be used as high release liners, low friction materials, or as a general protective coating.

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