

Biobased interpenetrating polymers networks derived from oligomerized soybean oil and polydimethylsiloxane

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ABSTRACT: A series of interpenetrating polymer networks (IPNs) with different compositions were prepared from silylated oligomerized soybean oil and silanol-terminated polydimethylsiloxane. Oligomerization of soybean oil was achieved by heating it with a catalyst in a Parr reactor at elevated temperatures. Vinyltrimethoxysilane was then grafted onto the oligomerized oil. Crosslinked films were obtained from solutions as the silanol groups between the two immiscible components condensed to form stable siloxanes linkages resulting in an entangled network characterized by microphase separation typical to IPNs. The crosslink density between the dispersed phase and the continuous phase was calculated from the average particle size of the dispersed phase. The mechanical and thermal properties were also studied and were found to be directly related to the composition and the crosslink density. These IPN resins can be used as high release liners, low friction materials, soft-feel coatings or as convenient one-package protective coatings. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41709.

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INTRODUCTION

The broad definition of an interpenetrating polymer network (IPN) is a material containing two or more immiscible components that have been crosslinked in the presence of each other to form entangled (interpenetrated) networks.¹ Due to the intimate mixing and crosslinks no gross phase separation takes place and IPNs appear as homogeneous materials to the naked eye. It was found that the morphology of such intimate entanglements of the two, or more, immiscible polymeric networks can lead to interesting physical properties that cannot be achieved by grafting or blending. Currently, products derived from IPNs find applications include false teeth to ion-exchange resins, adhesives, high impact plastics, thermoplastics, vibration-damping materials (for outdoor, aircraft, and machinery applications), high temperature alloys and medical devices.² Based on the method of synthesis, IPNs can be classified into the following three categories: (A) Latex IPNs (LIPNs) whereby the formation of the interpenetrating networks is achieved by emulsion polymerization; (B) simultaneous interpenetrating networks whereby the first polymer is mixed with a monomer of a second polymer along with the initiator and a crosslinking agent allowing it to polymerize and crosslink inside the swollen first polymer; and (C) sequential IPN whereby two polymers are mixed either in a solution or in the bulk and then crosslinked in presence of each other.³

Since it is difficult to incorporate triglycerides into polymeric systems because of the inherent branch structure of the triglycerides, the relatively long chain length of the fatty acids and the inherent incompatibility of the of these bio-based materials with many synthetic polymers,⁴ an efficient approach would be to use the IPN technology.^{5,6} Indeed, several IPNs have been described in the literature that contain either plant oils or oil-based polymers. Some examples include IPNs that were derived from combining hard and brittle alkyds with soft and flexible poly(butyl methacrylate) polymers.⁷ These IPNs exhibit better physical properties than each of their individual components. Similarly, IPNs of alkyd and polyurethane (also known as uralkyds) that were prepared by solution casting followed by air vulcanization have also been reported.^{8,9} These IPNs produced tough coatings with superior abrasion and chemical resistance. Several examples of castor oil IPNs with acrylates or polyesters have also been reported and these IPNs showed better mechanical and physical properties than the individual components.^{10–15} Other IPNs have been prepared from functionalized vernonia oil,¹⁶ lesquerella oil, crambe oil, and linseed oil (as well as their epoxidized derivatives) with polystyrene and polyacrylics.^{17–22} Most of the previous IPN work with triglycerides involved preparing a homogeneous solution of the triglycerides with the desired monomer, then polymerizing and crosslinking 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 report a different approach where the IPNs are prepared from solution of silylated polymerized soybean oil and polydimethylsiloxane (PDMS).

Recently, it was shown that the incorporation of refined unsaturated vegetable oils as a bio-based feedstock is advantageous for several industrial applications such as printing inks, lubricants and general coating applications.²³ However, it was reported that for best results in these applications high viscosity oils are preferred instead of the native triglycerides. One method to increase the viscosity (and the molecular weight) of soybean oil is the ring opening process of epoxidized soybean oil with anhydrides and alcohols.^{24,25} Microwave irradiation of soybean oil has been reported to increase the viscosity of the oil and has been used to develop bio-based lubricants.²⁶ Another approach was to use air plasma to polymerize soybean oil.²⁷ Alternatively, anthraquinone has been used as a thermal catalyst for the oligomerization of soybean oil in the development of printing inks.^{28,29} In fact the bodying of triglycerides under thermal conditions is an established technique that has been studied extensively. One typical example describing the use of heat and catalysts to increase the rate of the dimerization reaction of alkene is described by Lozada *et al.*²⁹ A semicontinuous process for the bodying of drying oil has also been reported which clearly established that the triglycerides react to yield highly branched structures during this heat bodying process.³⁰ This thermal polymerization of oils and fats is characterized by increased viscosity products and the formation of high molecular weight polymers with interesting physicochemical properties.^{23,31}

Although there are numerous IPNs containing PDMS with a variety of synthetic polymers, there are no IPNs of PDMS and natural oils or fats.^{31–35} aside from our earlier work.³⁶ The published synthetic polymers-silicone IPNs display clear microphase separation and multiphase domain structures because of the inherent immiscibility of PDMS with most synthetic 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. Previously, we described an example of IPNs containing triglycerides and siloxane polymers that were prepared by the latex method and were useful for various coating applications.³⁶ The LIPN method is a convenient method for the generation of IPNs from low viscosity materials. Since it is difficult to prepare latexes from the high viscosity substances, an alternative approach is needed here if one is to use high viscosity (bodied) oils.

In this work, we wish to describe the preparation of IPNs derived from silylated oligomerized soybean oil (SOSO) and PDMS prepared from a solution containing a common crosslinking agent. Upon casting films, crosslinking takes place to yield IPNs where the two phases are intimately mixed and crosslinked. These IPN resins can be used as high release liners, low friction materials, or as convenient one-package protective coatings.

EXPERIMENTAL

Materials

LowSat® soybean oil was kindly supplied by Zeeland Farm Services (Zeeland, MI). Silanol terminated dimethylsiloxane oligomers

with a viscosity of 50,000 cSt (weight average molecular weight of 115,000 gm/mol) and vinyltrimethoxysilane (VTMS) were purchased from Gelest (Morrisville, PA). Anthraquinone, toluene, dibutyltin dilaurate (DBTDL), and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox®101) peroxide were purchased from Sigma-Aldrich (St Louis, MO).

Equipment and Characterization

Differential scanning calorimetry (DSC, TA instruments, Q20) data were obtained by first heating a sample (~5 mg) under a nitrogen atmosphere to 250°C to erase any thermal history, then cooling to -70°C at 10°C/min followed by heating to 250°C at 10°C/min.

The mechanical properties (stress-strain) were measured at the temperature range of -50 to 300°C using a dynamic mechanical analyzer (DMA, TA instruments, Q800) with a constant shear of 0.01N and frequency of 100 μm applied on the sample. The DMA sample was equilibrated for 5 min at -50°C and then ramped up to 300°C with the heating rate of 3°C/min.

The molecular weight was determined by gel permeation chromatography equipped with a refractive index detector (Shimadzu, Japan, RID-10A) using tetrahydrofuran as mobile phase. The calibration was performed with polystyrene standards.

The viscosity was measured using a Brookfield digital viscometer (Brookfield Engineering, LVDV-E) equipped with spindle LV-1 (61) suitable for a viscosity range of 15–20,000 cPs.

The extent of crosslinking was determined by measuring the gel fraction and swell ratios of cast films as described in the ASTM D2765-11.³⁸

Scanning electron microscopy (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 oligomerized soybean oil. Each image was observed under a backscatter electrons detector for better resolution and contrast. Thus, the SOSO in these images appears as lighter shade domains while the polysiloxane appears as darker shade domains.

Oligomerized Soybean Oil

In a typical synthesis of oligomerized soybean oil, low saturated soybean oil and anthraquinone catalyst were heated as described in the literature.²⁸ Briefly, 1 mol (894 g) of soybean oil was mixed with 45 g of anthraquinone (~5% w/w) in a 2-L Parr reactor. Inert atmosphere was maintained in the reactor by purging with nitrogen for 10 min. The content was then heated to 330°C under constant stirring for 3 h. Once the reactor was cooled down, the oligomerized soybean oil that was obtained was dissolved in hexane (800 g) and filtered to remove the catalyst. The filtrate was then heated to 68°C to strip the hexane.

Silylation of Oligomerized Soybean Oil (SOSO)

SOSO was accomplished grafting VTMS onto the unsaturated fatty acids in the triglycerides via the 'Ene reaction.'³⁶ In a typical reaction, 886 g of the oligomerized soybean oil was heated with 296 g of VTMS and 8.86 g (1% w/w of oil) of Luperox®101 catalyst for 3 h at 225°C under constant stirring in a Parr reactor.

Table I. IPNs Prepared from SOSO and PDMS

SOSO	PDMS	Continuous phase	Dispersed phase	Domain size of the dispersed phase (μ)		Crosslink Density ($\times 10^{-2}$ mol/cm ³)
				Mean	STD	
20	80	PDMS	SOSO	25.58	15.78	6.98
40	60	SOSO	PDMS	19.72	4.23	72.73
50	50	SOSO	PDMS	14.30	10.45	69.60
60	40	SOSO	PDMS	8.21	6.43	78.59
80	20	SOSO	PDMS	4.37	2.12	84.02

Preparation of SOSO/PDMS IPNs

In a typical experiment, SOSO and silanol terminated PDMS were dissolved in toluene to yield 50 wt % solution. A series of such solutions containing different concentrations of PDMS and SOSO were prepared (Table I). DBTDL (1% w/w) condensation catalyst and 1% w/w of water as a hydrolyzing agent were added to each solution. The solutions were stirred well for a few minutes to ensure complete mixing and then ~ 10 g of each solution were poured into Teflon-coated petri dishes. Upon evaporation of the solvent, homogeneous and dry films were obtained. All films were equilibrated at RT and 25% relative humidity for 10 days before they were analyzed.

RESULTS AND DISCUSSION

Oligomerization of the soybean oil under our experimental conditions increased the viscosity of the oil from 30 to 5760 cPs. This increase in the viscosity correlates well with a molecular weight of 60,400 g/mol described by Erhan *et al.* in Ref. 28 and obtained by identical procedure. This oil was then combined with silanol terminated PDMS in toluene at different relative concentrations. A small amount of water was added to hydrolyze the methoxy groups of the grafted silane [Figure 1(A)], and the resulting silanols were allowed to condense and form the desired network [Figure 1(B)].

It should be emphasized that, under these conditions, siloxane linkages between SOSO and PDMS can be obtained by silanol condensation as well as siloxane linkages between two SOSO molecules or two PDMS molecules. The ultimate outcome is a crosslinked network held together by siloxane crosslinks that prevents any gross phase separation of the oligomerized soybean oil and the PDMS oil.

A. Morphology

The morphology of cast IPN films composed of different compositions of SOSO and PDMS is shown in Figure 2. A typical microphase separation that is characteristic to IPNs is observed. In this series of SEM images the PDMS phase appears as dark areas and the SOSO phase containing the unsaturated fatty acids that were stained with osmium tetroxide as the bright areas. It is apparent that the overall size of the dark areas increases in direct proportion to the concentration of the PDMS in the IPN (Table I). Furthermore, the shape of the dispersed SOSO particles generally appears as elongated oval particles while the PDMS particles appear to be more symmetrical

spherical particles. This apparent difference in the shape of the dispersed phases could be related to the crosslinking process and the mechanical properties of the SOSO phase where a higher silanol concentration and a more rigid network was obtained while the solutions were stirring before casting. In contrast, the spherical shape of the PDMS dispersed phase is most likely related to the low crosslink density of this phase and the flexible nature of the PDMS polymer.

Of particular interest is the phase inversion between the continuous SOSO phase and the dispersed PDMS phase [Figure 2(E)]. It is clear from this image that a phase inversion occurred when the concentration of PDMS was increased to 80 wt %. As a result, the morphology was changed and PDMS became the continuous PDMS phase. This apparent phase inversion is also reflected in the other properties of the IPNs as discussed below.

B. Crosslink Density

The degree of crosslinking was determined by measuring swell ratio and gel fractions at different compositions [Figure 3(A,B), respectively]. In these experiments, equilibrium swell ratio (Q) was calculated using eq. 1:

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

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

The gel fraction (G) was calculated using eq. 2:

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

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

The degree of swell is related to the free chain length between crosslinks and to the interaction of the solvent with the polymer chains. Thus, low crosslink density usually indicates a high degree of swelling and a low gel fraction. However, it is apparent from our data that plots of both the swell ratio and the gel fraction are inversely proportional to the concentration of SOSO in the IPN. These observations where high swell ratio is associated with high gel fraction is highly unusual and not commonly observed in polymeric systems.³⁶ One likely explanation could be related to the nonhomogeneous structure of the IPN where the relatively high molecular weight PDMS fraction is

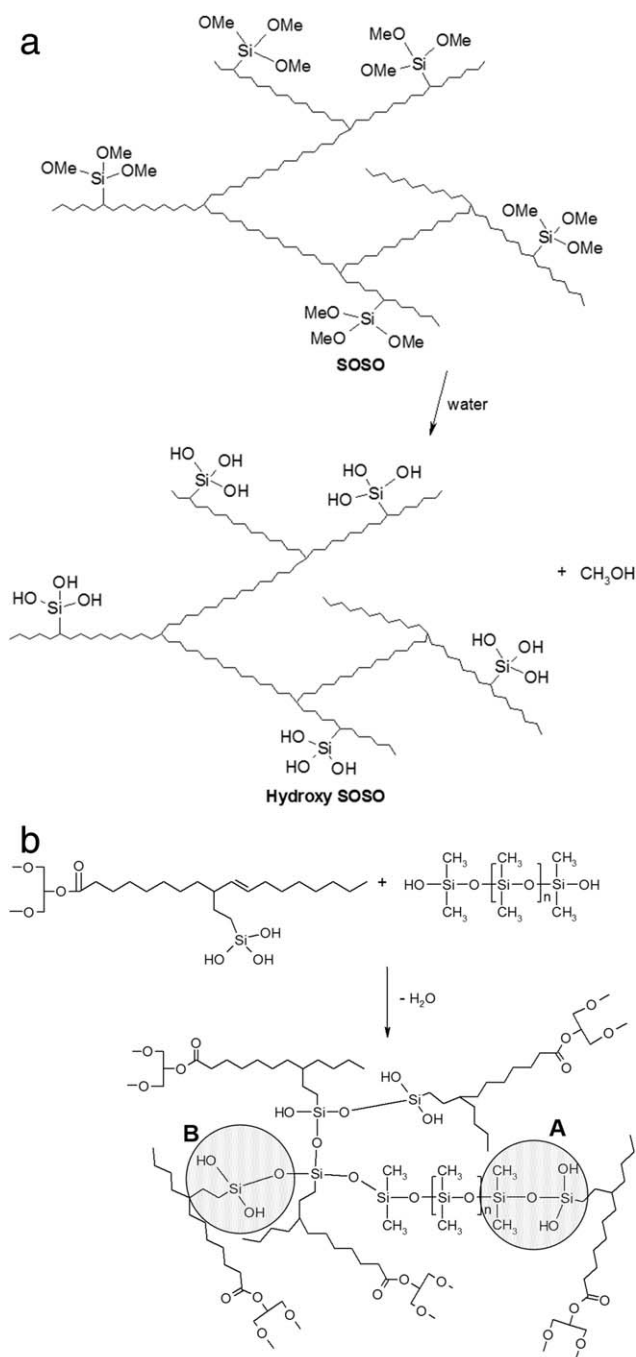


Figure 1. (A) Hydrolysis of methoxysilane groups grafted onto SOSO. (B) Condensation of silanols groups to yield siloxane crosslinks. (A): crosslinks between PDMS and SOSO, and (B): crosslinks in the SOSO phase.

lightly crosslinked (e.g., it consists of only two terminal silanol groups per polymer) whereby the SOSO fraction contains multiple crosslink sites (e.g., multiple grafted silanol per molecules). Thus, at low SOSO concentrations where the IPNs consist of primarily PDMS, a relatively loose network is obtained due to the limited number of crosslink sites. As the concentration of SOSO is increased, microphase separation containing regions of

high crosslink density are obtained next to PDMS regions that are characterized with lower crosslink density. Subsequently, both the gel fraction and the swell ratio decrease. It should further be emphasized that both components (i.e., SOSO and PDMS) are crosslinked and participate in the network. If only one of these phases was crosslinked to yield semi-IPNs the gel fraction would be directly proportional to the concentration of the crosslinked phase but the swell ratio would have been inversely proportional to the concentration of this phase.

A thermodynamic approach (eq. 3) was used to correlate the cellular domain size in IPNs with the crosslink density.^{39–41} The main variables in these derivations were the crosslink density, the molecular weight of the polymers and the interfacial energy between the two polymer phases. Since the two polymers are inherently incompatible, some microphase separation occurs even when the polymers are intimately mixed as depicted in figure:

$$n_A = \frac{W_B \left[\frac{2\gamma}{RTD_B} - \frac{1}{M_B} \right]}{\left[\frac{1}{(1-W_B)^3} - \frac{1}{2} \right]} \quad (3)$$

where n_A is the crosslinking density in mol/cm³; W_B is the weight fraction of the dispersed phase; R is the gas constant in J/mol-K; T is the temperature in K; D_B is the diameter of the dispersed phase in cm; γ is the interfacial energy between the two phases in dynes/cm. M_B is the molecular weight of polymer B (for crosslinked polymers, $M_B = \infty$).

It was concluded that, in general, the size of the cellular phase domain in IPNs is inversely proportional to the crosslink density. Although it was realized that the compositional variation is more complex than described in this semiempirical model, a reasonable agreement with the experimental data under a variety of conditions was observed.^{40,42–44} Indeed, the calculated crosslink density continuously increases in proportion to the concentration of SOSO in the IPN (Figure 4). As mentioned above, the high dependency of the crosslink density on the SOSO concentration is directly related to the relatively large number of silanol crosslink sites in this phase compared with much fewer numbers of the terminal silanols on the high molecular weight PDMS phase. Thus, this increase in the crosslink density is supported by the decrease in the swell ratio shown in Figure 3(A).

C. Thermal Properties

DSC plots (Figure 5) indicate a melting transition at -45°C independent of the IPN composition, a small melting peak around 5°C and a relatively large transition around 175°C that is clearly dependent on the IPN composition. It is apparent that the area under the low temperature peak at -45°C is directly proportional to the concentration of PDMS (Figure 5) and, undoubtedly, is therefore due to melting of the polysiloxane phase.³⁶

The magnitude of the broad melting peak that is observed at around 5°C is directly proportional to the concentration of the SOSO phase. Thus, it is most likely due to the melting of the saturated fatty acids in the triglycerides. These saturated fatty acids are not affected by the grafting reaction and are known to melt around this temperature. It was found³⁷ that completely

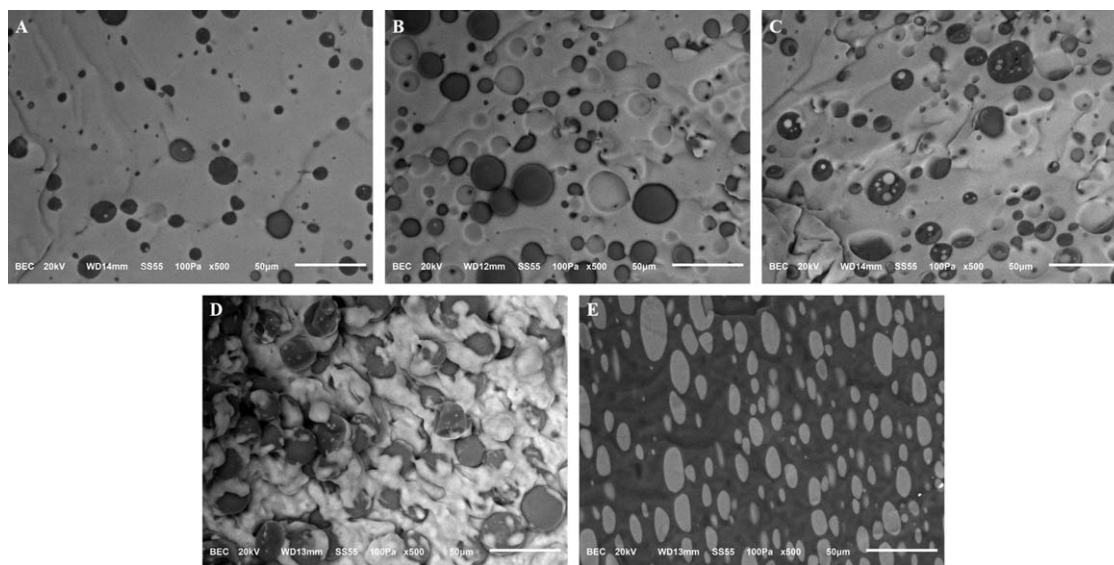


Figure 2. SEM images of IPNs with different ratio of SOSO/PDMS. The bright areas correspond to SOSO and the dark areas correspond to PDMS. (A) 80/20; (B) 60/40; (C) 50/50; (D) 40/60 and (E) 20/80.

saturated triglyceride containing only stearic acids melts at 73.5°C but the melting point of the triglycerides is decreased by replacing the saturated stearic acid with unsaturated fatty acid like oleic acid. Thus, introducing only one oleic acid reduces

the melting point 44.1°C and even lower when two oleic acids are introduced. Furthermore, it was observed that the introduction of oleic acid to form symmetrical triacylglycerols lowered the melting point of the triglycerides by about 30°C.” Unlike these melting transitions of the saturated fatty acids and PDMS, additional thermal transition is observed around 175°C. The area under this peak is relatively large and is directly proportional to the SOSO concentration in the IPN (Figure 6). Further analyses of this transition indicate that it is related to the curing reaction in these IPNs as it is not present upon repeated heating/cooling cycles.

Thus, upon heating a sample above this transition and then cooling it down, no apparent peak is observed (Figure 7). No traces of this peak were observed after subsequent heating and cooling cycles even when the sample was allowed to equilibrate for a substantial period of time between these cycles. It was therefore concluded that this transition could not have been related to melting or crystallization and is simply due to an incomplete cure when the IPN samples are allowed to cure at room temperature.

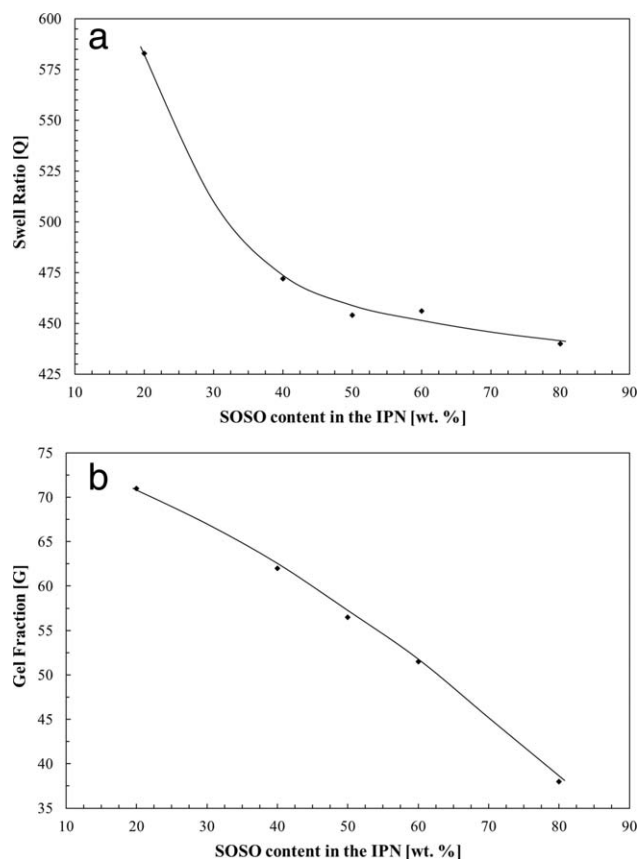


Figure 3. (A) Swell ratio [Q] of IPNs composed of different concentrations of SOSO and PDMS. (B) Gel fractions [G] of IPNs composed of different concentrations of SOSO and PDMS.

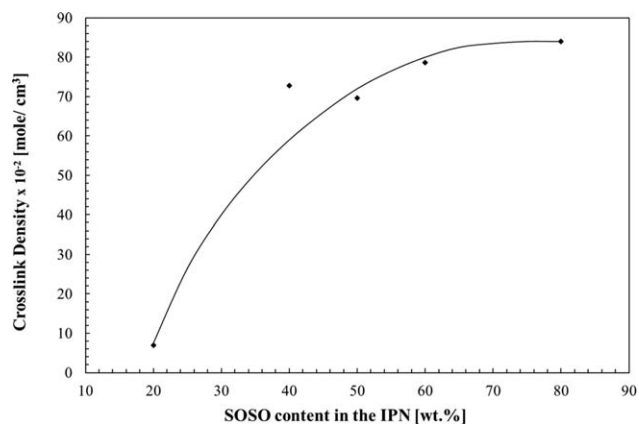


Figure 4. Crosslink density as calculated from eq. 3 as a function of SOSO concentration in the IPN.

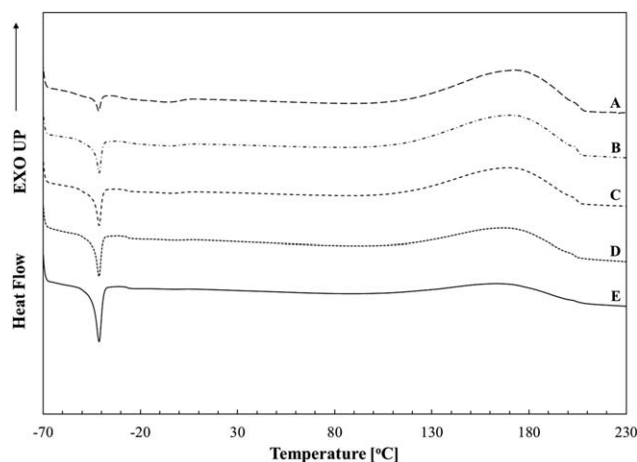


Figure 5. DSC curves of IPNs with different ratio of SOSO/PDMS. (A) 80/20; (B) 60/40; (C) 50/50; (D) 40/60; and (E) 20/80.

D. Mechanical Properties

DMA curves of IPNs prepared with different concentrations of SOSO and high molecular weight silanol terminated PDMS are shown in Figure 8. The data indicate the presence of two transitions; a major peak below 0°C ($\tan \delta_1$) and a smaller peak at around 125°C ($\tan \delta_2$). The low temperature transition appears as a multiple peak consisting of one maximum just below 0°C and another maximum that is inversely proportional to the SOSO concentration in the IPNs (Figure 9). It is apparent that at low SOSO concentration (20 wt %) in the IPN, a symmetric peak is observed. However, at high SOSO concentration (80 wt %) or in films prepared from just SOSO, this peak is much broader and uneven. It is therefore most likely associated with

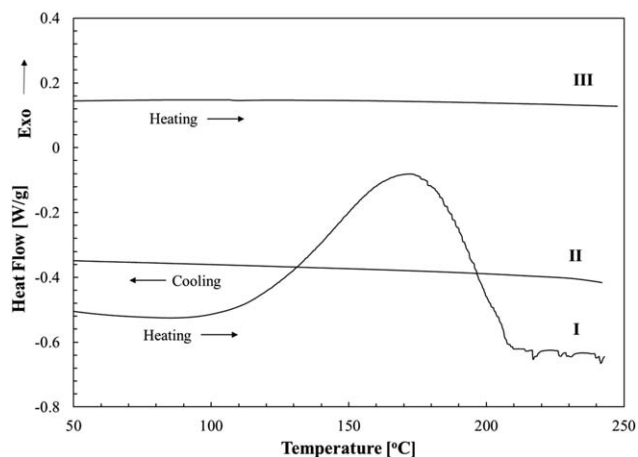


Figure 7. Representative DSC plots of IPN (SOSO/PDMS 80/20) indicating the disappearance of the peak near 175°C upon repeated heating/cooling cycles.

the crystal transition of the saturated fatty acids in the SOSO that did not participate in the silane grafting reaction and are free to crystallize around this temperature range.

Surprisingly, the area under this $\tan \delta$ transition indicates that it reaches a maximum value in IPNs containing 60 wt % SOSO (Figure 10). This unexpected maximum is directly related to the phase inversion observed in the morphology (Figure 2) where at low SOSO concentration the continuous phase is the low modulus PDMS. In comparison, the morphology of IPNs composed of more than 50 wt % SOSO is characterized by high modulus due to the high crosslinked density in the SOSO phase continuous phase. The low modulus, lightly crosslinked PDMS phase of

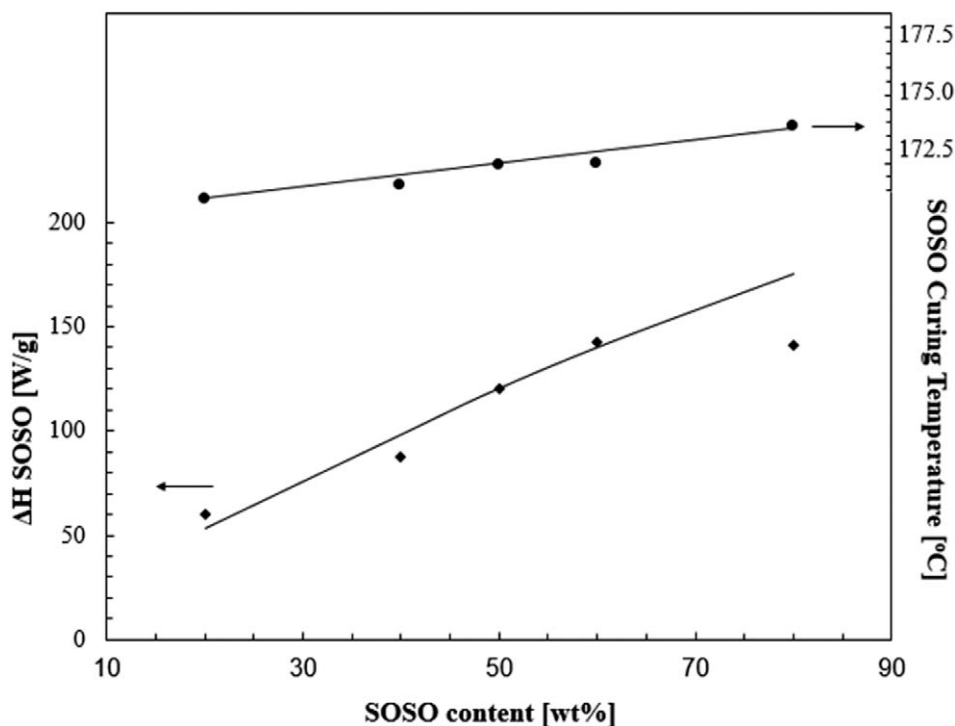


Figure 6. Curing of SOSO in IPNs as a function of their composition.

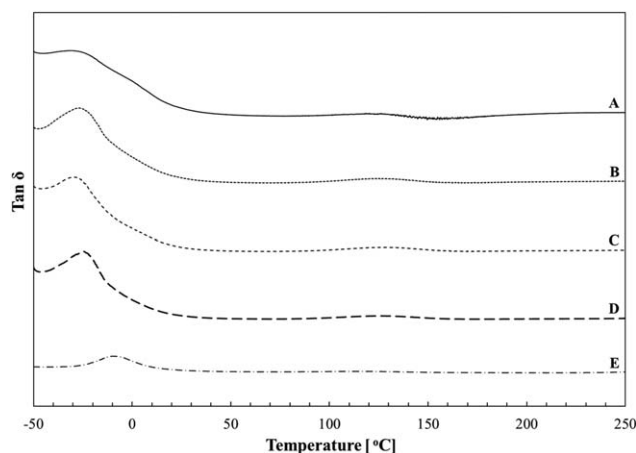


Figure 8. Tan δ observed as a function of temperature for different ratio of SOSO/PDMS (A) 80/20; (B) 60/40; (C) 50/50; (D) 40/60; and (E) 20/80.

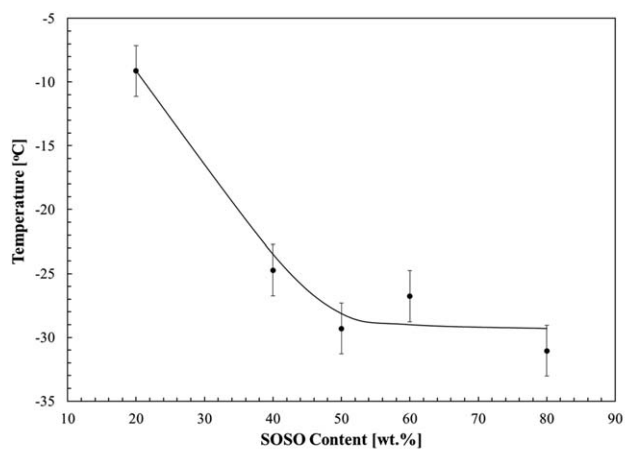


Figure 9. Maximum tan δ_1 as a function of IPN composition.

these IPNs is present as discontinuous particles suspended in the SOSO matrix.

The position of the peak at 125°C (tan δ_2) appears to be independent of the IPN composition. However, the area under this peak

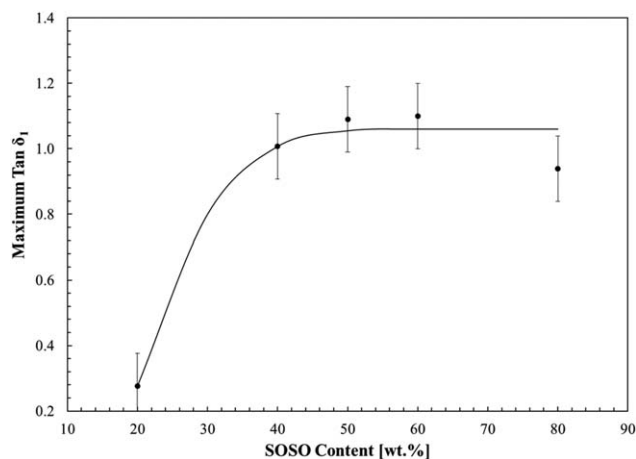


Figure 10. The maximum of tan δ value observed at the initial peak.

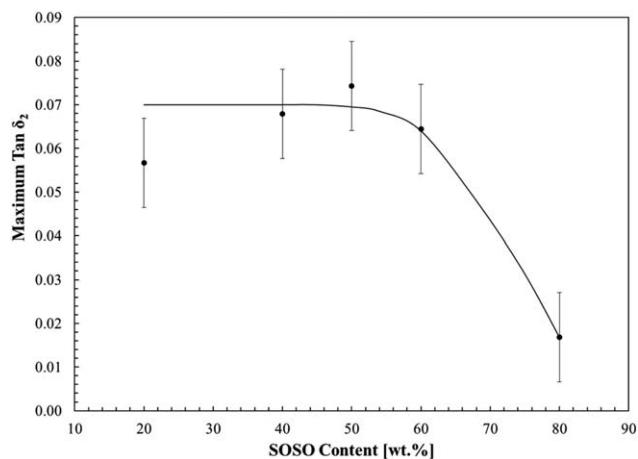


Figure 11. Tan δ_2 as a function of IPN composition.

depends on the composition of the IPN (Figure 11), and the maximum area appears to be related to the phase inversion observed earlier. As expected, increasing the concentration of the high modulus SOSO phase led to an increase in the storage modulus of the sample when the SOSO phase was dispersed in the “soft” continuous PDMS phase (Figure 12). After the phase inversion (when the SOSO phase became the continuous phase and the PDMS the dispersed phase) the storage modulus remained high and did not change much. Apparently, here again the change from a relatively “soft” continuous PDMS matrix to a more “rigid” continuous SOSO phase corresponds to this change in the mechanical properties.

CONCLUSIONS

A series of IPNs was prepared by crosslinking high molecular weight silanol terminated PDMS and SOSO from toluene solution. The crosslinks in these IPNs are derived from condensation reactions of the silanols in both phases that form siloxane linkages. These siloxanes crosslinks lead to a network that consists of siloxanes linkages between PDMS and SOSO as well as siloxanes linkages within each of these components. The morphology of these IPNs appears to be homogeneous to the naked eye but consists of “sea-island” microphase separation whereby

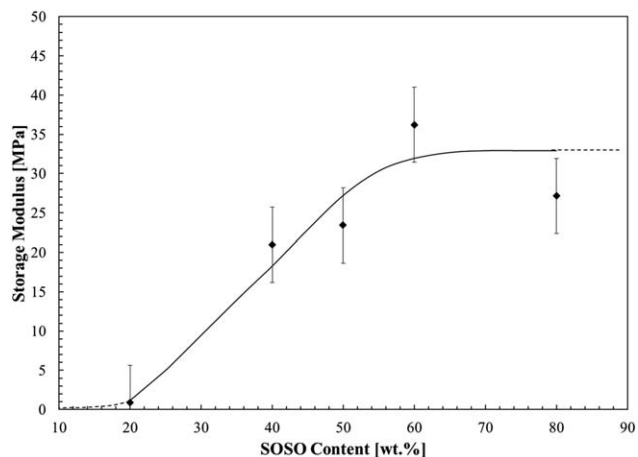


Figure 12. Storage modulus near -50°C as a function of IPN composition.

one phase is suspended as small particles in the other continuous phase. Phase inversion is observed when the concentration of the suspended phase (PDMS) is increased to 80 wt %. Due to the difference in the concentration of silanols in each of the IPN components, the network is not homogeneous and each phase consists of different crosslink densities. The SOSO phase is characterized by a low gel fraction and a low swell ratio due to the relatively high concentration of silanols and high numbers of crosslinks. The PDMS phase is characterized by a much lower crosslink density since this high molecular weight polymer contains only terminal silanols and thus relatively long chain lengths between crosslinks.

The thermal and mechanical properties of cast films were affected by the composition and the morphology of these IPNs with a major shift around the phase inversion point. The incorporation of silanol functional groups on the oligomerized soybean oil provides a convenient approach to prepare new compositions from inherently incompatible components. Similar to other IPNs, these partial bio-based compositions could be useful as protective coatings.

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