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Research Article

Amidolysis of Oxirane: Effect of Protein Type, Oils, and $ZnCl_2$ on the Rheological Properties of Cross-Linked Protein and Oxirane

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Amidolysis of oxirane group of epoxidized sesame, sunflower, and cottonseed oils was achieved by reaction with primary amide of millet and gluten proteins. Gluten is a coproduct of wheat starch industry and available commercially. Millet is a major part of the staple food of the semiarid region of the tropics. Gluten is a mixture of glutenins and gliadins rich in glutamine residues; however, millet is rich in glutamine and leucine. We have taken advantage of the available primary amide of glutamine for cross-linking with the oxirane of sunflower, sesame, and cottonseed oils under controlled conditions to give a resin of amidohydroxy of gluten and millet proteins. Cross-linking gave a resin with a wide range of textural properties. The texture of the resin was dependent on the source of the oxirane, the amide group, and the amount of the catalyst ($ZnCl_2$). The thermal properties, textural, solubility, and rheological properties were determined as well as the reaction time. The data showed direct relationships between the $ZnCl_2$, nature of oil, and protein type and the properties of the final resin. Consistently, the results pointed to similarity among the outcome of the reactions between sesame and sunflower oils. Depending on the amount of $ZnCl_2$, the texture of the resin can range from viscose to rubbery. The reaction time was influenced by oxirane source, protein type, and catalyst and ranged from 30 min to 4 hr.

1. Introduction

The development and use of biodegradable plastics in packaging for environmental protection have been stimulated by public concerns and interest [1]. This has been instigated by the polluting effect of nondegradable synthetic polymers in ocean and landfills. To facilitate for faster degradation, photo-degradation is one of the methods used to degrade specific type of synthetic polymers, which is a combination of oxidation and hydrolysis catalysed by light [2, 3].

A number of packing materials, especially food packing, have been developed to meet consumer needs. Petroleum-based materials, used commonly, have many advantages such as gas permeability is easy to control, and are resilient. On the other hand, these materials are not environmentally friendly because of disposal difficulties, and generate much heat and exhaust gases when burned, thus posing a global issue of environmental pollution. Consequently, consumer demands and rising petroleum prices are inspiring the utilization of environmentally friendly packaging as an alternative to nonrenewable resources originating from agricultural sources. These materials, can be classified into three groups: (1) extracted directly from agricultural raw materials (e.g., protein, starch, or lipids); (2) produced by microorganisms (e.g., polyhydroxyalcanoates, poly-3-hydroxybutyrate); and (3) synthesized from bioderived monomers (such as polylactic acid). Wheat gluten is a biopolymer consists primarily of glutenin and gliadins [4–6]. Glutenins is the elastic portion of gluten and gliadin is the viscous part. Therefore, gluten is a viscoelastic polymer. Gluten heat denaturation reduces the viscoelastic properties of flour dough and results in low bread quality [7]. Gluten can aggregate and forms new intermolecular disulphide bonds, which changes dough rheology and gluten extractability as a result of heating [8]. Wheat gluten can be isolated from wheat flour by washing away other flour components of the dough [9]. Vital gluten is a by-product of wheat starch industry and is commercially available. Millet total protein content ranged from

11–17% dependent on variety, of which 11.3–17.2% was albumin/globulins, 6.8–11.6 prolamins, 5.9–54.4% glutelin [10, 11]. It is also rich in glutamine (26%), alanine (11%), and leucine (16%), but it is deficient in lysine. Electrophoretic analysis showed that millet proteins exhibited three albumin/globulin fractions and five prolamin and glutelin fractions, where the glutelin fraction had the highest molecular weight compared to the other fractions [12].

Despite the extensive research, thermoplastic materials obtained from plant-based materials do not have the properties that can match the properties of films made from synthetic plastics [13]. Plant-based films possess two major drawbacks, water stability and brittleness. The limitation of agricultural based materials is mainly due to their insolubility in common solvent which makes it difficult to process [14]. This can be resolved by a combination of chemical modification and specialized processes. Gliadin (one of the main wheat gluten fractions) is richer in proline, (glutamic acid + glutamine) and the mean percentage of (glutamic + aspartic) acids in the amide form is 82 for glutenin and 92 for gliadin [15].

Previously we have exploited the availability of the glutamine residues of gliadin as a reaction site to produce elastomeric products by cross-linking different oils with gliadin [16].

The reaction was on the oxirane group of the epoxydized oils which is considered as amidolysis process [17]. The oxirane group is also called epoxy group. The reaction of primary amide ($O=C\text{-}NH_2$), found in protein (gliadin or millets), with the oxirane (epoxy) group from epoxidized oils generates the secondary amide which in turn reacts with the oxirane of another epoxy group. This reaction constitutes amidolysis of oxirane which is considered to be as an addition reaction.

Unlike the previous work, this study is focused on developing epoxy resin using the entire gluten protein, not only gliadin fraction, as well as millet protein. The produced resin will constitute a reaction between epoxy groups and primary amide groups of gluten and millet proteins. The epoxydized oils include sesame oil, sunflower oil, and cottonseed oil. Gluten and millet proteins will be isolated from their respective flour. The developed resin will be characterized for its mechanical properties and the effect of the oil and the protein source will be explored.

2. Materials and Methods

2.1. Materials

2.1.1. Oils. Epoxy resin was developed by using three types of oils and two types of proteins. Sesame oil was extracted from sesame seeds purchased from the local market using a traditional press while sunflower and cottonseed oils were donated by the Arab Sudanese Vegetable Oil Company (Khartoum North, Sudan). Wheat gluten was isolated from hard red spring wheat grown locally in Saudi Arabia and millet proteins were extracted from millet grains from the local market.

2.1.2. Isolation of Wheat Gluten and Millet Proteins. Millet flour (100 g) was suspended in 1 liter of 0.1 N NaOH, pH was adjusted to 9.9, stirred for 30 minutes, and the pH was then dropped to 9 using 0.1 N HCl. The suspension was centrifuged at 10000 ×g for 30 min at 10°C where the precipitated was resuspended in NaOH and extracted twice. The pH of the combined supernatants was adjusted to 4.6 using 1.0 N HCl. The acidified dispersion was centrifuged at 10000 ×g and the precipitate was freeze dried.

Gluten was isolated from wheat flour as described by Eliasson and Larsson (1993) [18] with the exception that the isolated gluten was freeze dried instead of oven dried. Dough was formed and washed under running water to remove the starch and the water-solubles. The washing continued until no more nongluten material was observed. After washing, the result was a visco-elastic material composed of glutenins and gliadins. Glutenins are elastic part of the gluten, while gliadins are viscous.

2.2. Methods

2.2.1. Synthesis of Epoxydized Oils. The epoxy was developed by reacting sunflower, sesame oil or cottonseed oil with hydrogen peroxide in the presence of formic acid. The oil of interest (about 280 g) was placed in a three neck flask with a heating jacket and placed in water bath. On the top of the flask, a mechanical stirrer with different speed was used to maintain good mixing and stable temperature during the reaction. The initial temperature of the reaction was 40°C. After adding 25 ml formic acid and while stirring, 200 ml of 50% peroxide was added and the reactor temperature was set at 70°C. After 7–9 hours reaction time, the product was washed with saturated ethyl acetate and NaCl at pH adjusted to 7.5 and dried at 60°C in a vacuum oven

2.2.2. Analysis of Epoxidized Oils. The yield of the reaction was tested by Fourier Transform Infrared (FTIR) Attenuated total reflection (ATR) method. Bands at 824–842 cm^{-1} of the C-O-C stretching of the epoxy ring were detected by the FTIR [19]. The end of the reaction was determined by observing the size of the oxirane peak.

2.2.3. Development of Epoxy Resin. The epoxy resin preparation starts by adding epoxidized oil of choice (50 g) in a jacketed glass reactor with three openings. The reaction was carried out at 50°C or 70°C and three different amounts of catalyst (zinc chloride). When the temperature reached 50°C or 70°C, 20 g of gluten or millet protein was added slowly, followed by 1, 2 or 3 g of $ZnCl_2$ under continuous stirring at 650 rpm in the beginning for few minutes and then at 550 rpm until the reaction is completed. Under constant stirring, the material in the reactor became thick and reached the point of preventing the stirrer from turning signifying the end of the reaction. A slight nitrogen purge was applied during the reaction. In the event that the product did not reach rubbery texture, the end of the reaction was determined by the disappearance of the C-O-C bond of the oxirane at 845–824 cm^{-1} using FTIR as mentioned earlier. The reduction on the amide I at 1655 cm^{-1} and II at 1533 cm^{-1} on the IR spectrum is also another indication of the

reaction completion. Resins were also prepared by using a cell connected directly to the rheometer where data was collected automatically during resin development. Unlike the reactor method, (12.5 g) epoxidized oil, (5 g) protein of choice and 0.75 g zinc chloride were placed in the cell and stirred at 50/s shear rate. The operational gap was set at 5500 μm.

2.2.4. Testing of Epoxy Resin Product

Thermal Analysis (TGA). The reaction product was tested for its thermomechanical properties using thermogravimetric (TGA) analysis. Samples with different types of protein, oil, and amount of catalyst were tested. Thermogravimetric analysis (TGA) was performed using a 2050 TGA (TA Instruments, New Castle, DE). Each sample (~10 mg) was heated at 10°C/min to 800°C and held at an isotherm for 3 min. The furnace was purged with nitrogen throughout the testing time.

Textural Properties of Epoxy Cubes. Epoxy resin texture was determined by a TA-XT2 texture analyzer (Stable Microsystems, Surrey, UK) provided with the software *"Texture Expert."* The firmness (g) and springiness (%) of the epoxy cubes having dimensions of 1 cm width, 1 cm length, and 1 cm height was measured by P/20 cylindrical aluminum probe using 50 KG load cell. The samples were compressed to 20% of their original thicknesses at a cross-head speed of 1 mm/sec and held for 30 seconds.

Solubility. Resin solubility was administered by cutting resin cubes with similar dimensions (10 mm wide × 10 mm long × 3.5 mm thickness) [20] and immersing for 72 hr in 1.0 M or 0.5 M HCl and 1.0 M or 0.5 M NaOH. Samples were then rinsed with distilled water and dried under vacuum for 24 hr. The difference in weight before and after immersion was recorded as present weight loss.

Reaction Time. The time needed for the reaction to end was measured from the time of adding the epoxidized oil and the protein up to the formation of the rubber-like resin which was determined by the complete stop of the stirrer. However, when reactions did not result in rubbery material, FTIR was used to determine the depletion of the epoxy group which signifies the end of the reaction.

Rheological Properties of Epoxy Resin Samples. Steady shear and dynamic shear rheological data were obtained with Discovery HR-1 rheometer (TA Instruments, New Castle, USA). Rheological properties were carried out in two different ways. The first was done on a resin developed in the reactor and then transferred into the rheometer, while in the second it was developed using the rheometer cell.

Rheological Measurements of Epoxy Cured Directly Using the Rheometer. Monitoring the resin development was carried out directly during reaction in the cell connected to the rheometer. The data was recorded in 7 steps. In the first five steps, samples were held for 20 minutes at each step starting at 30°C with an increment of 10°C. In the sixth step, the sample was cooled down from 70°C to 30°C at 5°C/minute and data was plotted to get the effect of cooling on the viscosity (Pa·s)

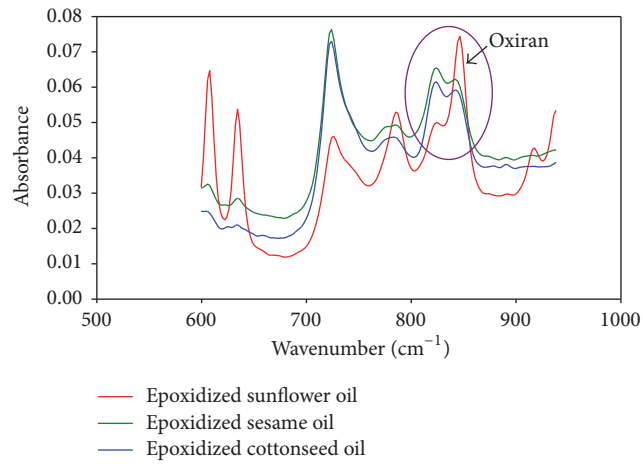


Figure 1: FTIR spectra of epoxidized sunflower, sesame, and cottonseed oils.

buildup of the developed epoxy resin and to obtain values for the elastic (G') and loss moduli (G'') as well as the complex viscosity.

Dynamic Rheological Measurements of the Resin Cured in the Reactor. Resin samples were transferred from the reactor during the cross-linking reaction done in the water bath. Dynamic rheological measurements were performed by taking samples during reaction progress at different time intervals (10, 20, 30, 40, 50, 60, 90, 120, 180, and 240 minutes). Epoxy resin was placed in 40 mm diameter plate with cone plate angle of 2.002° and the temperature was set at 50°C. The gap between the plates was set at 200 μm and dynamic shear data was obtained at frequency sweeps ranging from 0.1 to 100 rad/s at 5% strain. Experimental data was processed to obtain storage modulus (G') and loss modulus (G'').

3. Results and Discussion

3.1. Analysis of Epoxidized Oils. The analysis of the epoxidized oils showed that sunflower oil exhibited the highest number of oxirane groups (epoxy groups) as displayed by the FTIR scan of the three oils followed by the sesame oil and cottonseed oil (Figure 1). The high number of oxirane is expected to influence the reaction time during resin preparation, as well as the texture of the final product.

3.2. Thermogravimetric Test (TGA). The TGA thermal degradation of the resins in nitrogen environment showed three peaks ranging from 190°C to 447°C depending on the protein type and the level of zinc chloride. Although resins containing 3 g zinc chloride should be more tolerating to heat degradation elicited by cross-linking, that was not true for millet protein resin, where the 2 g zinc chloride started degrading at higher temperature. In general, resins with gluten protein exhibited higher degradation temperature compared to millet protein. The weight loss associated with these transitions appeared to depend on zinc chloride content in the blend and the type of protein and less with the type

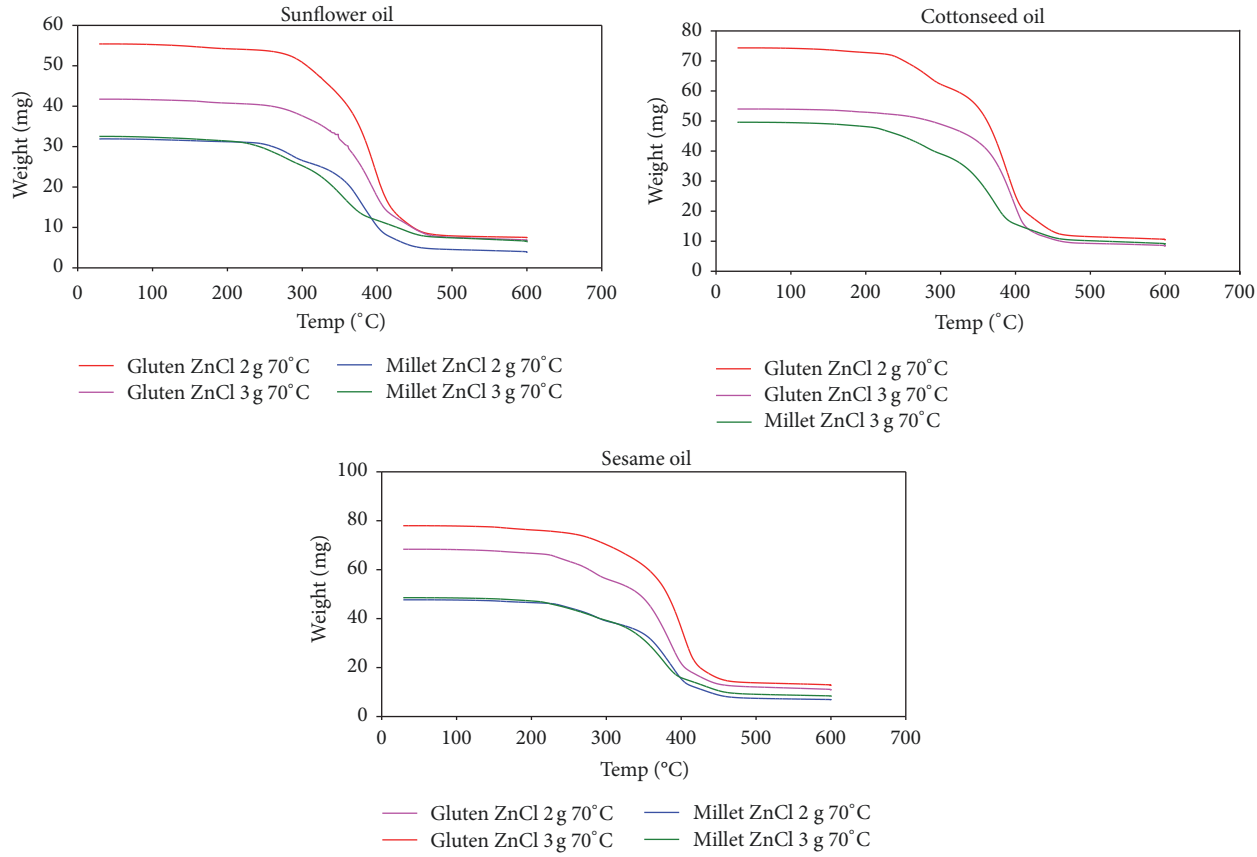
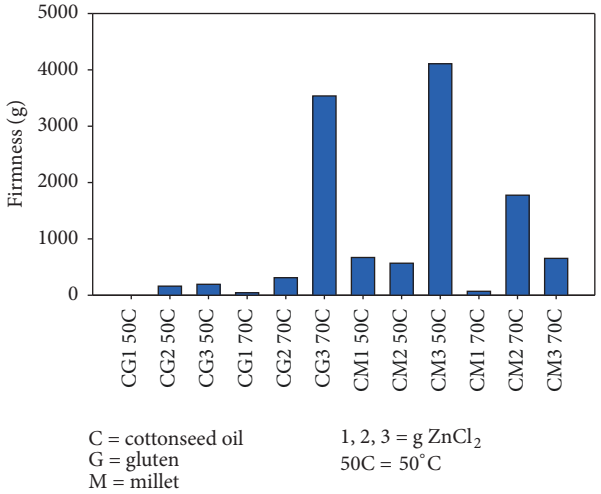


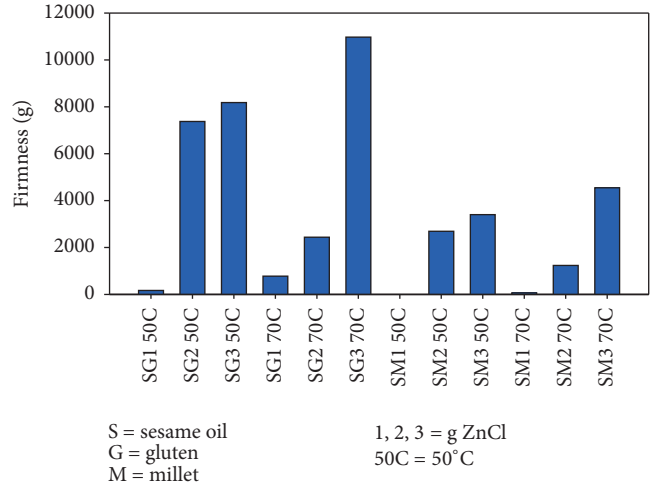
Figure 2: TGA degradation kinetics of epoxy resins.

of oil. The exact effect of the oil type and catalyst level on the degradation profile of these resins is clear on the shape of the profile (Figure 2), that is, whether the degradation profile is comprised of more than one peak or whether the resin starts degrading at a lower or higher temperature relative to other resins. Like most proteins, gluten protein thermal degradation starts around 210–215°C [20]. This data showed comparable onset degradation of gluten-containing resin compared with the neat gluten reported in the literature. Overall, samples comprising gluten appeared to degrade at higher temperature and faster rate than millet samples and that was obvious on the TGA profile shape and the way it drops as sample loses weight (Figure 2). Gradual drop in weight loss beyond degradation onset, as in millet samples, could indicate the presence of a material resulting from the reaction of millet protein resin and the positive effect of the catalyst on the cross-linking progression. This behavior is more obvious in millet samples than gluten regardless of oil type (Figure 2). Although the TGA results appear to indicate some degree of thermal stability occurring in some resins, this change is an indication of the effect of the cross-linking reaction resulting in favourable thermal stability of the blend.

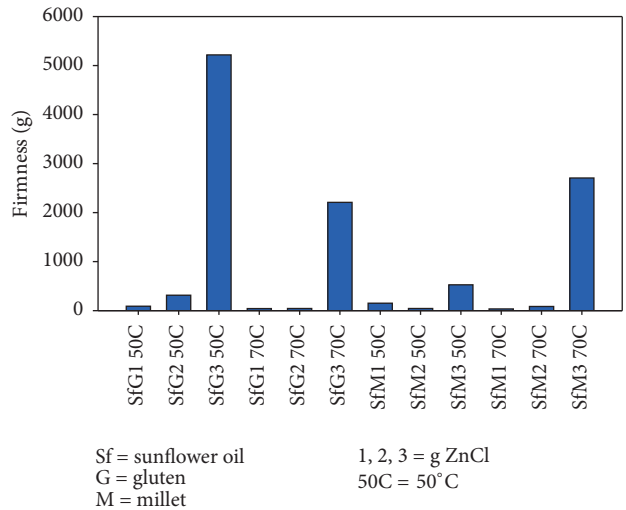
3.3. Resin Texture. Firmness is the force required to compress a material and defined as the force necessary to attain a given deformation. Texture was performed on samples prepared in the reactor, after being allowed to take room temperature, where samples were collected at 50°C and 70°C. The firmness of the cross-linked material depended on the type of protein, oil, catalyst, or reaction temperature as shown in Figures 3(a), 3(b), and 3(c). In general, samples with 3 g zinc chloride and 70°C exhibited the highest firmness indicating maximum cross-linking. Sesame oil-gluten resin sample at 70°C and 3 g zinc chloride exceeded the firmness of other samples by twofold firmness (Figure 3(a)), while cottonseed oil resin exhibited the least firmness at the same cross-linking conditions (Figures 3(a), 3(b), and 3(c)). Contrary to the overall firmness trend of other resins within cottonseed oil, millet protein exhibited the highest firmness at 50°C and 3 g zinc chloride compared to gluten resin at the same cross-linking conditions (Figure 3(b)). However, sunflower oil-gluten resin exhibited the highest firmness at 50°C and 3 g zinc chloride (Figure 3(c)). This data showed the direct effect of the oil source as well as the protein type and the processing conditions on the resin firmness, where 50°C was more effective in producing firmer resin from sunflower and cottonseed oils than 70°C and the opposite was true for sesame oil. Therefore, these results mean that epoxidized sesame oil generated more cross-linking sites which resulted in more coherent and firmer material. These observations are in line with the effect of cross-linking conditions on the reaction time. Although cottonseed oil data showed longer reaction time especially with gluten, it generated the least firm product except for gluten and millet resins at 70°C and 50°C,



(a) Effect of cottonseed oil, temperature, and zinc chloride on the firmness of gluten or millet resin prepared in water bath at 50°C and 70°C



(b) Effect of sesame oil, temperature, and zinc chloride on the firmness of gluten or millet resin prepared in water bath at 50°C and 70°C

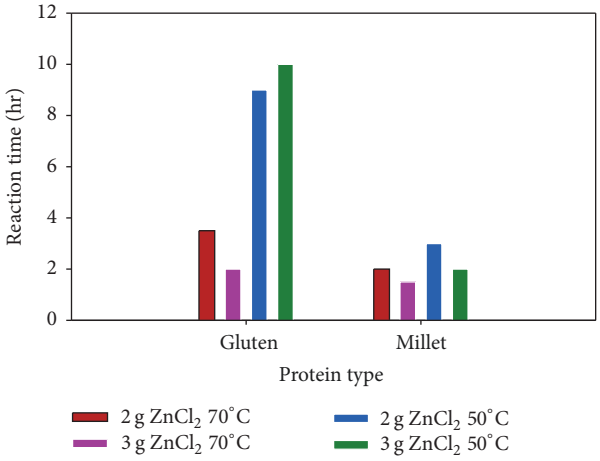


(c) Effect of sunflower oil, temperature, and zinc chloride on the firmness of gluten or millet resin prepared in water bath at 50°C and 70°C

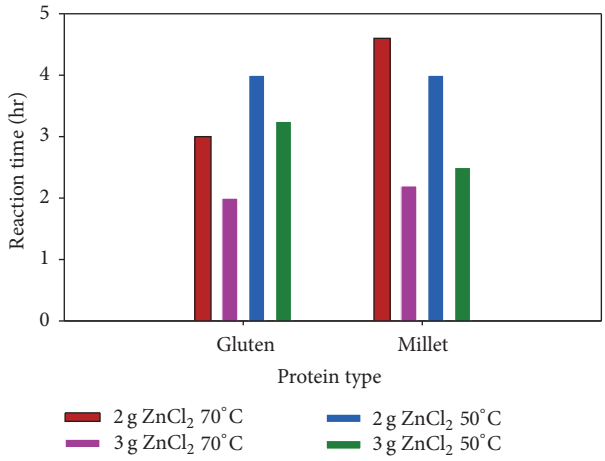
Figure 3

respectively (Figure 3(b)). Springiness represents the ratio of the highest point at which the sample springs back after the first compression compared to the maximum deformation. Despite the clear difference between all three oils in terms of firmness, springiness data did not show clear difference between the samples regardless of the composition of the material.

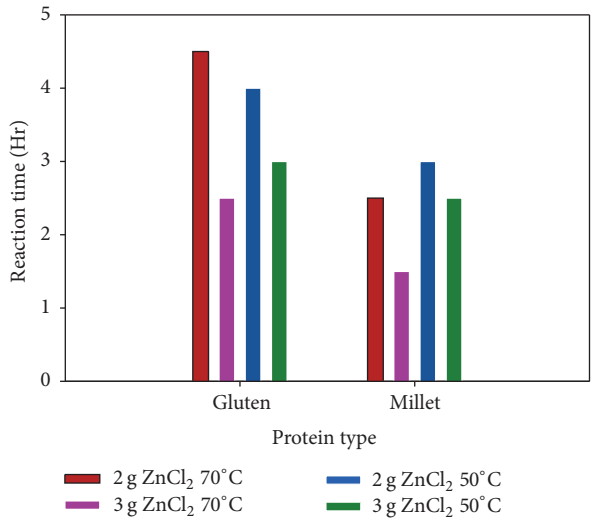
3.4. Resin Solubility. The resin prepared with millet protein and epoxidized oils was tested for its solubility in alkaline or acid solutions with different pH. All samples regardless of oil or protein types gained weight after immersion in solutions, but some samples maintained the gained weight and other lost weight after longer time in solution. The lost weight indicates that the sample started dissolving in the solution. Cottonseed-millet protein resin gained about 3.6% in acidic environment regardless of HCl molarity, whereas it gained 36% and 17.8% in 1 M and 0.5 M NaOH, respectively. After 72 hr the sample lost weight in alkaline solution which indicates that some part of the sample started degrading, but the gained weight remained in acidic environment. This sample was more stable in acid environment than alkaline. The sesame oil resin followed the same trend as cottonseed oil but with less weight gain in alkaline environment. The sunflower oil sample was the most stable of all in both acidic and alkaline environment because it maintained weight with minimal variation through the 72 hr. The most weight was gained by cottonseed oil resin indicating less cross-linking sits due to fewer epoxy rings, while the least weight gain was by sunflower oil resin. The resin prepared from gluten protein exhibited similar trend with respect to interaction with acidic and alkaline solutions where samples gained more weight in alkaline environment compared to acidic and specifically more weight gain in 1 M NaOH for cottonseed oil and less



(a) Reaction time of gluten and millet proteins interaction with cottonseed oil epoxy a a function of zinc chloride



(b) Reaction time of gluten and millet proteins interaction with sunflower oil epoxy as a function of zinc chloride



(c) Reaction time of gluten and millet proteins interaction with sesame oil epoxy as a function of zinc chloride

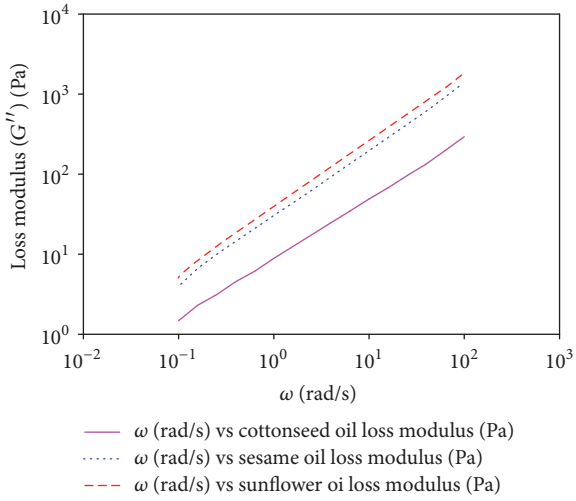
Figure 4

weight gain in the 0.5 M NaOH. All three oils performed the same way regarding weight increase after 72 hr. the most weight was gained by sesame oil resin in 0.5 M NaOH and the least was by sunflower at 1 M HCl indicating stability of the resin due to the presence of more epoxy rings leading to more cross-linking sites.

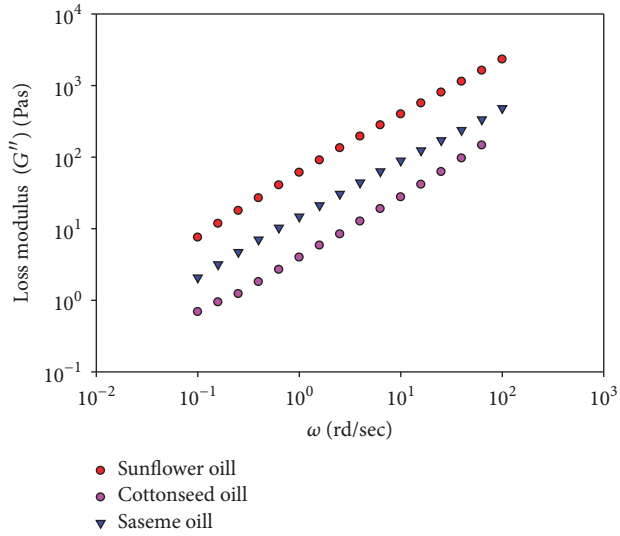
3.5. Reaction Time. The time needed to complete the cross-linking reaction was dependent on the, protein type, oil type, temperature, and amount of zinc chloride catalyst (Figures 4(a), 4(b), and 4(c)). Some reactions did not develop rubbery material at the reaction temperature except when removed from the reactor to take room temperature, but other resins were rubbery at reaction temperature. It is apparent that more catalyst at higher temperature and millet protein presented the least time needed for reaction completion, while gluten protein, 50°C, and cottonseed oil required the longest time. Sunflower oil in terms of reaction time was the best compared to the other oils. The least reaction time is directly related to the number of epoxy rings found in the epoxidized oil, which is in turn correlated with the number of the double bonds of the oil.

As mentioned above, sunflower oil exhibited the highest stability (least solubility) in different pH compared to the other oils.

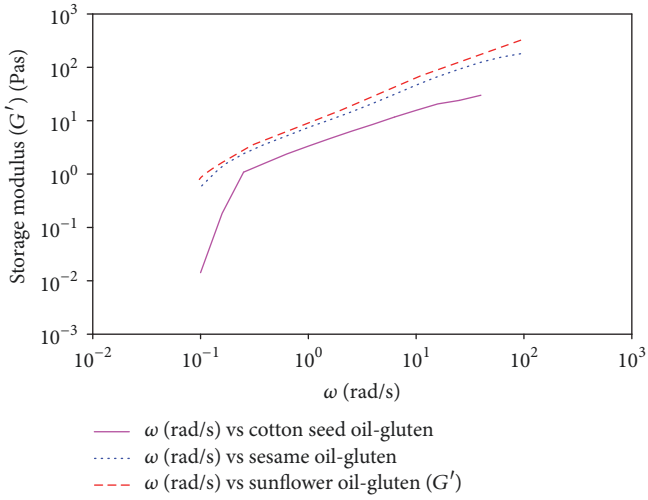
3.6. Rheological Properties. Linear viscoelastic measurements were conducted for the various cross-linked epoxidized, sesame, cottonseed, and sunflower oils with gluten or millet proteins. So as to ensure that all the measurements were made within the linear viscoelastic range, a strain-sweep experiment was performed initially. Applied shear strain in the linear range was adopted (0.1%) for the other viscoelastic property measurements for the same material. Linear viscoelasticity indicates that the measured parameters are independent of applied shear strain. Oscillatory shear tests



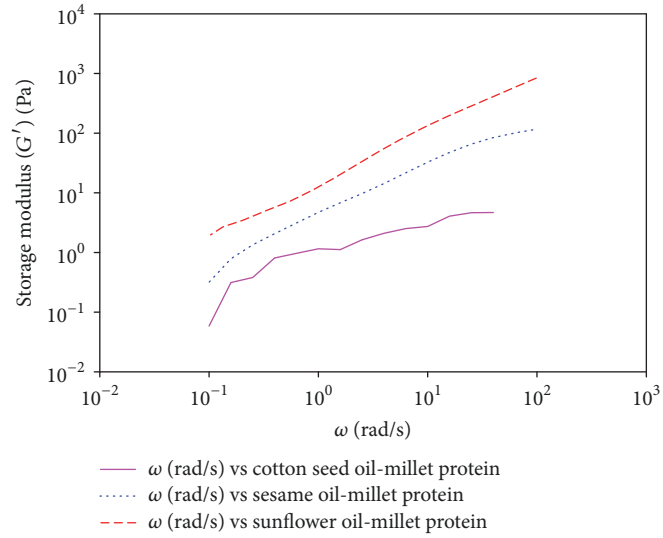
(a) The loss modulus (G'') of cottonseed, sesame, sunflower epoxidized-cross-linked oils with gluten protein as a function of frequency



(b) Viscous properties (G'') of cottonseed, sesame, and sunflower epoxidized-cross-linked oils with millet flour as a function of frequency



(c) The storage modulus (G') of cottonseed, sesame, sunflower epoxidized-cross-linked oils with gluten protein as a function of frequency

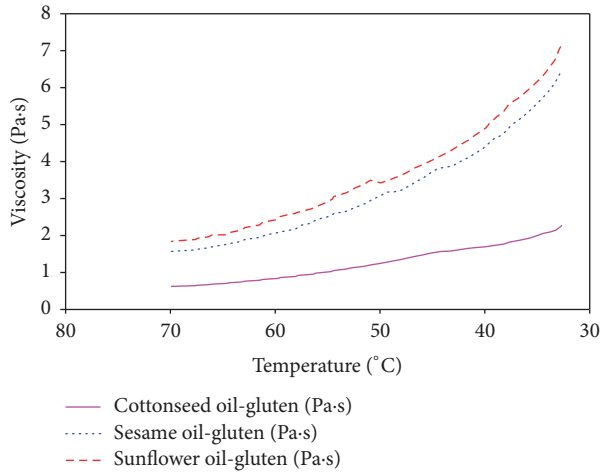


(d) The storage modulus (G') of cottonseed, sesame, sunflower epoxidized-cross-linked oils with millet protein as a function of frequency

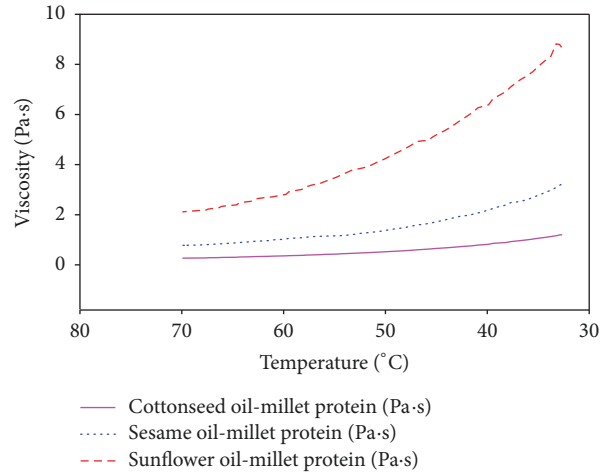
Figure 5

were conducted over a frequency (ω) range of 0.1–100 rad/s, yielding the shear storage (G') and loss (G'') moduli. The storage modulus represents the nondissipative (elastic) component of mechanical properties. The elastic or "rubber-like" behavior is suggested if the G' profile is independent of frequency and greater than the loss modulus over a certain range of frequency. The loss modulus (viscous) represents the dissipative component of the mechanical properties and is characteristic of viscous flow.

3.7. Rheological Measurements of Epoxy Cured Directly Using the Rheometer. As described above, the stepwise heating-cooling during resin development created a typical viscous fluid, where G'' of all samples exceeded G' across the frequency range investigated. Cottonseed oil exhibited the lowest G'' value (293 Pas) compared to the other oils, while sesame and sunflower oils exhibited 1395 and 1760 Pas, respectively (Figure 5(a)). This fact makes cottonseed oil less effective as a binding material relative to the other oils. Cross-linking epoxidized oil (EPO) with millet protein exhibited viscous properties as well (Figure 5(b)), but the G'' of the three oils showed significant difference in the magnitude of the viscosity as indicated by the regression slope of sunflower oil, sesame, and cottonseed oil, where 0.83, 0.78, and 0.82 slope and intercept as 0.44, 1.49, and 1.75, respectively. Compared to gluten protein, millet protein performed better by producing a resin more viscous; however, sunflower oil was the most effective of the three oils (Figures 5(a) and 5(b)). The



(a) Change in epoxidized oil-gluten protein resin viscosity as a function of Temperature ramp down from 70°C to 30°C



(b) Change in epoxidized oil-millet protein resin viscosity as a function of temperature ramp down from 70°C to 30°C

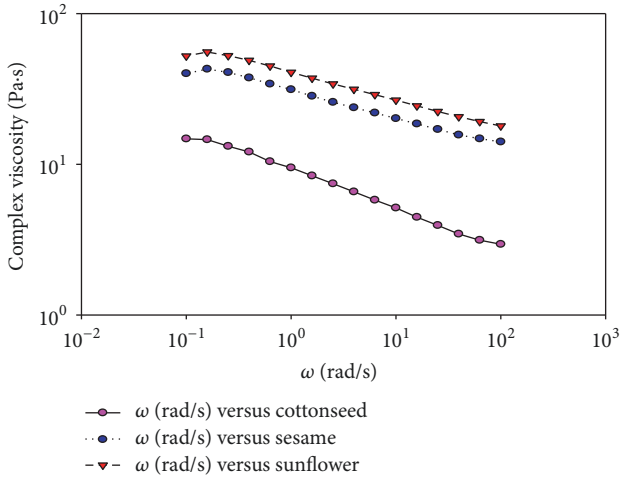
Figure 6

continuous increase of the storage and the loss moduli as a function of frequency indicates frequency dependence. It is apparent that millet protein has more primary amide groups which is the main group involved in the cross-linking process with the oxirane of the oil to generate amidohydroxy product. The elastic modulus was lower than the loss modulus and followed the same trend (Figures 5(c) and 5(d)).

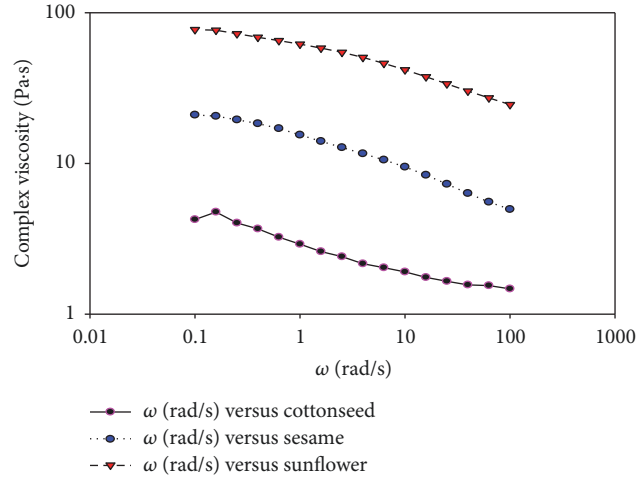
At the end of the cross-linking using the cell and after holding for 20 min at 70°C, the sample was cooled down to 30°C and the change in the viscosity was monitored. The data showed increase in the viscosity as a function of drop in the temperature (Figures 6(a) and 6(b)). Once again, sunflower oil exhibited significantly higher viscosity followed by the sesame oil. The rate of the viscosity increase was not the same for all oils where the regression slopes were 0.04, 0.12, and 0.13 for gluten and cottonseed, sesame, and sunflower oil, respectively. The low slope indicates slow buildup of viscosity (Figure 6(a)). Millet protein reaction showed the same trend of increase in viscosity upon cooling but with significantly different rates among oils. The slopes of cottonseed, sesame, and sunflower oils were 0.02, 0.06, and 0.18, respectively (Figure 6(b)). Once more, the resin containing sunflower oil exhibited the highest viscosity. The effect of protein type was obvious in Figure 6, where gluten protein profile showed that the viscosity of sesame and sunflower was closer, but millet protein indicated sesame and cottonseed oils closer in viscosity and far less than sunflower oil. The performance of sunflower oil stands out most of the time but sometimes it was closer to sesame oil rather than cottonseed oil.

The complex viscosity (η^*) which is frequency-dependent viscosity is the complex modulus divided by angular frequency and represents the overall resistance to deformation of a material, regardless of whether that deformation is recoverable (elastic) or nonrecoverable (viscous). The η^* of the gluten-sunflower oil resin was higher than the other two resins but sesame resin was closer to sunflower oil resin (Figure 7(a)). Millet protein resin exhibited η^* with clear difference between the three oils according to the following ranking, sunflower oil resin > sesame > cottonseed, despite the fact that all three resins were far apart. The magnitude of η^* of the gluten resin was higher compared to millet protein resin (Figures 7(a) and 7(b)). Unlike millet protein resin, the η^* of gluten resin as a function of temperature of sunflower and sesame was similar (Figure 6(a)), but cottonseed oil resin exhibited lower complex viscosity. As a function of time, η^* increased exponentially (Figure 7(c)) indicating the different behavior of cottonseed oil resin compared to the other two. Once again, cottonseed oxirane is different from the other oils. One can speculate that this η^* profile of the resins can be confirmed by the steady shear rheological behavior of the resins.

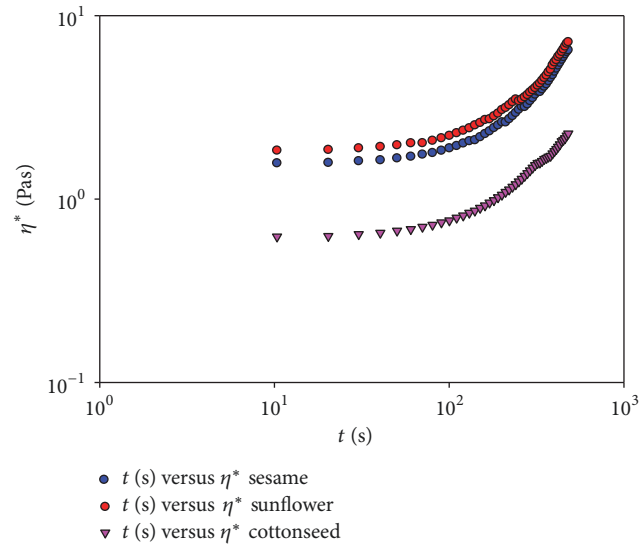
As it was mentioned above, the progress of resins formation prepared in water bath at steady 70°C was monitored by pulling a sample at specific time during reaction so as to test for the level (degree) of cross-linking as a function of time. This test included resins made from sesame and cottonseed oils. The G', G'', and $\tan\delta(G'/G'')$ were used to determine the phase of the resin texture development as the reaction time. Higher $\tan\delta$ indicates viscous properties which are due to low degree of cross-linking. The $\tan\delta$ was time and zinc chloride dependent since in some cases samples start showing elastic properties in the first 15 min and others need more than 40 min, which can be attributed to the type of protein and the availability of the amide groups. Samples with 2 g zinc chloride exhibited inconsistent behavior, where at the beginning of the test samples exhibited higher G'', due to low cross-linking, and after one hour converted abruptly to higher G'. Wheat gluten samples containing cottonseed oil had unusual profile, because for a small drop in G' the sample exhibited exponential increase in $\tan\delta$ as well as in G''. The $\tan\delta$ profiles of gluten and millet with sesame oil signified longer reaction time and the millet protein reaction became more frequency-dependent (Figure 8(a)); however, gluten protein exhibited more frequency dependency than



(a) Complex viscosity of epoxidized cottonseed, sesame and sunflower oils cross-linked with gluten as function of frequency



(b) Complex viscosity of epoxidized cottonseed, sesame, and sunflower oils cross-linked with millet as a function of frequency



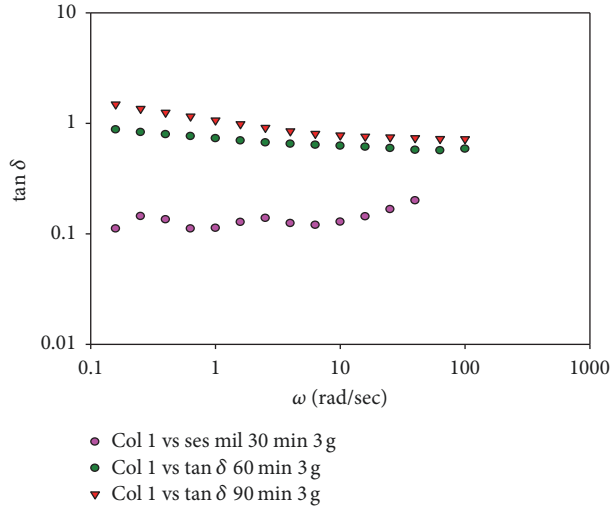
(c) Complex viscosity as a function of time of gluten-sunflower, sesame, and cottonseed oils composites during cooling from 70 to 30°C

Figure 7

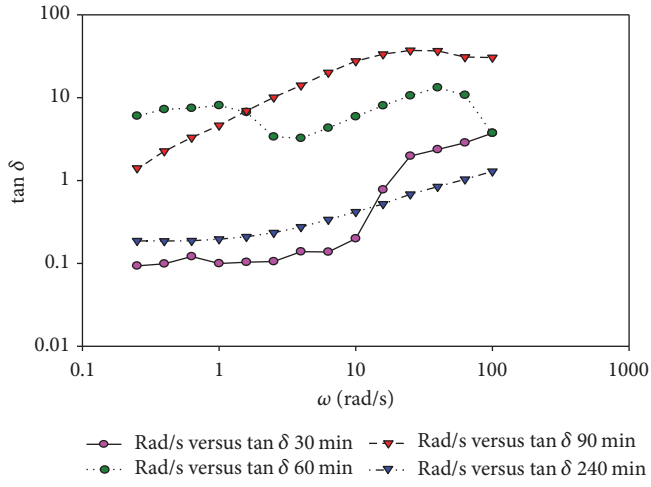
millet protein (Figure 8(b)). The relationship between G', G'', and $\tan\delta$ is illustrated in Figures 9(a) and 9(b), where the material after 45 min was not fully cross-linked but it was showing signs of becoming more elastic due to the increase in G'. Cottonseed oil profile was consistently moving from more viscose to more elastic as indicated by the increase of $\tan\delta$ at higher frequencies. The same behavior was observed for the sesame oil resin but around 10 rad/sec the resin changed to a more elastic resin (Figure 9(b)). For the samples prepared at steady 70°C, the $\tan\delta$ values were in the range of 0.07–4.30, 0.44–1.35 for cottonseed-gluten resin and cottonseed resin-millet protein, respectively, indicating a more elastic gluten resin. However, for the sesame resin, the range was 0.19–5.70, and 0.11–3.38 for gluten and millet, respectively indicating more elastic millet protein resins. The $\tan\delta$ for samples prepared in the rheometer cell exhibited higher $\tan\delta$ signifying less elastic resin (low cross-linking). The conditions of the resin made in the cell can be used for preparing viscose material good for adhesive application, whereas the other method is for rubber-like application. By cooking millet-sesame resin in 3 g $ZnCl_2$, the G' was 1.1×10^3 P which can be considered lightly cross-linked Hevea rubber (7.0×10^5 Pas) [21–23].

4. Conclusions

It is possible to produce biodegradable resins with a wide range textural property by reacting oxirane with available amide. The reaction is dependent on source of oxirane and proteins and the amount of catalyst. Sunflower oil exhibited textural and thermal properties better than sesame and cottonseed oils elicited by the higher amounts of oxirane

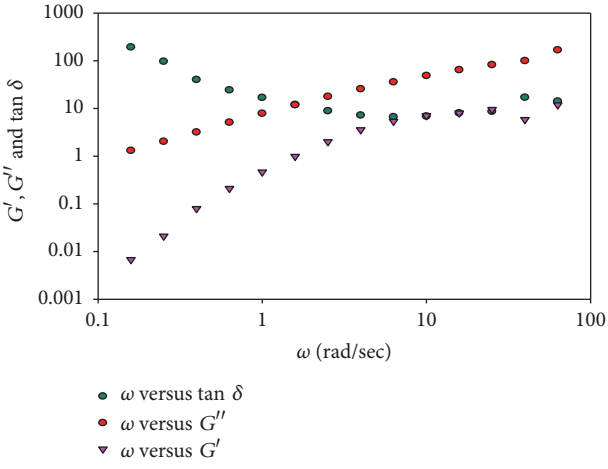


(a) Linear dynamic of sesame-millet resin prepared in water bath at 50°C with 1.0% starin. tan δ as a function of frequency

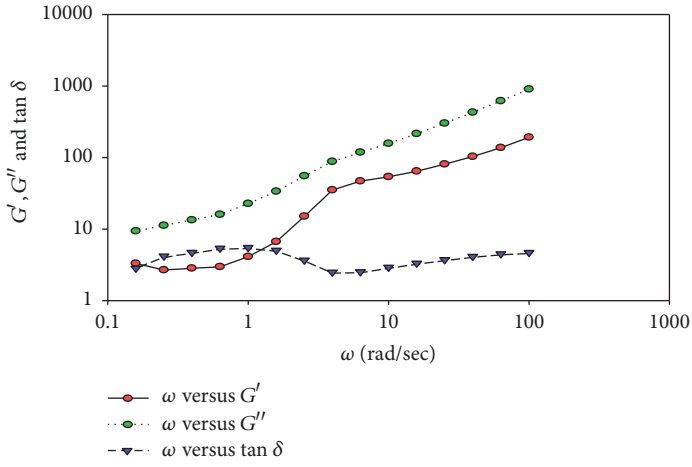


(b) Linear dynamic of sesame-gluten resin repared in water bath at 50°C with 1.0% starin. tan δ as a function of frequency

Figure 8



(a) Cottonseed-gluten resin water bath at 45°C



(b) Sasame-gluten resin water bath at 45°C 3 g ZnCl

Figure 9

as shown by the FTIR scan. Millet protein gave superior performance than gluten with respect to the reaction time and rheological properties. The texture of the millet-sesame oil oxirane resin was similar to a lightly cross-linked synthetic rubber.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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