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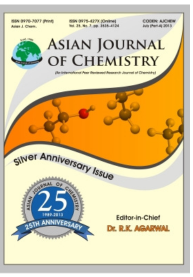

Thermal and Mechanical Properties of a Biobased Unsaturated Polyester Resin

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A biobased soybean oil monoglyceride unsaturated polyester resin (SOMGUPR) was prepared by two steps using soybean oil, glycerol, 1.2-propanediol, maleic anhydride and phthalic anhydride. FT-IR, ^{1}H NMR, DSC and DMA were employed to study the chemical structure and thermal properties of this unsaturated polyester resin. The results showed that SOMGUPR containing 30 % soybean oil monoglyceride (SOMG) exihibited optimial combination properties, where glass transition temperature (T_g), tensile strength and impact strength were 71 ºC, 7.6 Mpa and 85 KJ/m^2, respectively. The side reaction between SOMG and maleic anhydride had not occured as evidenced by ^{1}H NMR spectroscopy. The reactivity of SOMGUPR containing 30 wt % SOMG was lower than that of SOMGUPR without it. The more cotent of SOMG up to 40 wt %, the lower tensile strength. The impact strength increased with the increasing amount of SOMG content up to 30 wt % and then stabilized at nearly 100 KJ/m^2.

Key Words: Soybean oil monoglyceride, Glycerolysis, Stepwise condensation, Side reaction.

INTRODUCTION

Materials scientists have more and more interested to find the replacements for the decreasing fossil resources in recent years. Plant oil based polymers, which possess advantages of biodegradability, biocompatibility, the reduction of CO_2 emission, low toxicity, societal favorably advantages and low price[1-5], have the potential to replace some or all of petroleum based polymeric materials[6]. The global use of vegetable oil was divided into food and industrial application two types. Approximately 80 % of vegetable oil was utilized for food, while the less share was taken up by industrial sectors[7]. It is well known that the soybean oil is one of the low cost and most abundant annually renewable resources and can be developed more use for industrial applications. Therefore, it is essential and meaningful to have soybean oil use into unsaturated polyester materials, which can give more additional value for soybean oil and reduce our dependence on petroleum based products.

There are many literatures about the blends of unsaturated polyester resin/plant oil, functional plant oil/fillers, or maleic anhydride modified functional plant oil triglyceride, which combined with styrene to form polymer matrix. Miyagawa *et al.*[8] prepared a novel biobased unsaturated polyester material containing epoxidized methyl soyate. The storage modulus and heat distortion temperature decreased with the increasing amount of epoxidized methyl soyate, but the Izode impact strength was constant with the changing of epoxidized methyl soyate content. Lu *et al.*[9] prepared biobased nanocomposites with functional plant oil and layered silicate. They reported that the flexural modulus increased 30 % at only 4 vol % clay content and flexural strength, glass transition temperature and thermal stability were not significantly changed. Das *et al.*[10] prepared the blending materials of unsaturated polyester resin/styrene mix with tung oil. They reported that the impact strength, modulus and hardness increased by15, 20 and 41 % when 1 wt % tung oil was incorporated into the unsaturated polyester resin matrix. Can *et al.*[11] prepared a rigid, thermosetting liquid molding resin from the free radical copolymerization of soybean oil monoglyceride (SOMG) maleates with styrene. They reported that the T_g, flexural modulus and surface hardness were 135 ºC, 645 MPa and 72 shore(D), respectively. Though polyester derived from SOMG with phthalic anhydride and maleic anhydride is known[12], SOMG used as a diol in the synthesis of biobased unsaturated polyester resin is scarcely to our knowledge.

In our article, a bio-based soybean oil monoglyceride unsaturated polyester resin (SOMGUPR) material was prepared by two steps using soybean oil, glycerol, 1.2-propanediol, maleic and phthalic anhydride. In the first step, the soybean oil was glycerolysised to produce SOMG. Then, SOMGUPR was obtained through the stepwise condensation reaction using

1.2-propanediol, SOMG, maleic and phthalic anhydride. The synthesis schematic digrams of SOMGUPR are shown in Fig. 1. DSC and DMA were used to study the thermal properties of SOMGUPR. Mechanical properties (*i.e.*, tensile strength, impact strength) are also determined.

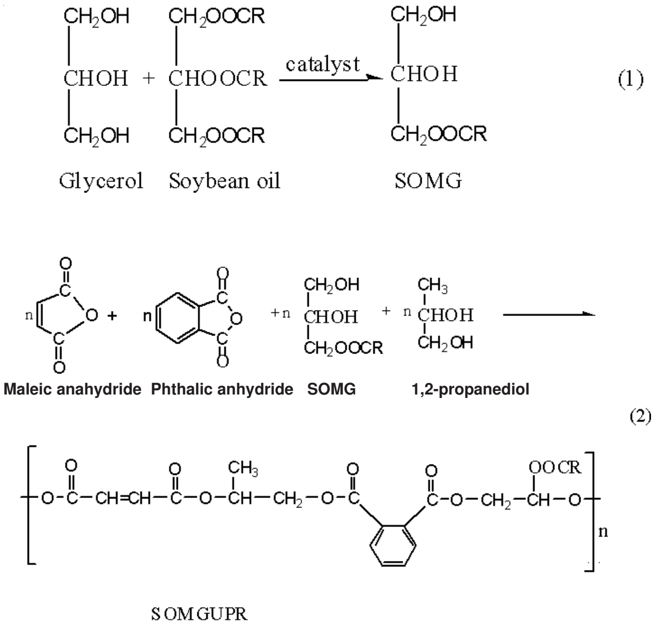


Fig. 1. Two step synthesis of soybean oil monoglyceride unsaturated polyester resin (SOMGUPR). Where R have zero to three double bonds and vary from 14 to 22 carbons in length

EXPERIMENTAL

The soybean oil was food grade and used alkali refined. The glycerol was 99.5 % pure and supplied by Shanghai Reagent Company. The lithium hydroxide, maleic anhydride, phthalic anhydride and 1,2-propanediol were 99.5 % pure and obtained from Sinopharm Chemical Reagent Ltd. Phosphoric acid and styrene were obtained from Beijing Chemical Company and used as received.

The FT-IR analysis was performed on a Thermo Nicolet Nexus FTIR spectrometer using KBr disc. ^{1}H NMR spectrum was obtained on a Bruker AV400 NMR spectrometer (Bruker Instruments) and the solutions for ^{1}H NMR analysis were prepared by dissolving the prepared compounds in $CDCl_3$. The curing process was evaluated on a Power-compensation differential scanning calorimeter in N_2 atmosphere from 50-200 ºC at the heating rate of 10 ºC/min. Dynamic mechanical analysis was performed on Perkin-Elmer PYRIS dynamic mechanical analyzer in N_2 atmosphere from-50-180 ºC, using the heating rate of 5 ºC/min at 1 Hz. Tensile strength was tested on Instron model 1341, according to chinese standrd GB/T2568-1995. Impact strength test was carried out on the XJU-22 charpy impact analyzer in accordance with Chinese standard GB/2571-1995.

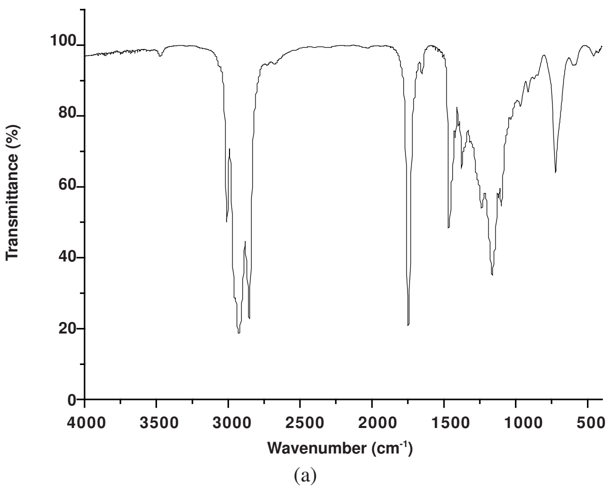
Preparation of SOMGUPR: Glycerol (57.5 g, 0.625 mol) was placed into a 500 mL three necked round-bottom flask equipped with a mechanical stirrer, a nitrogen gas inlet and a reflux condenser and heated to about 240 ºC under N_2 atmosphere. The temperature was kept in 240 ºC for 2 h to remove the residue water. Then 2 g lithium hydroxide and 220 g soybean oil were stepwisely added within 1 h. At the end of this time, a little phosphoric acid was added to the reaction flask unless the pH = 7. After agitated for 6 h, the excess glycerol stratified as a lower layer was removed when the temperature cooled to 15 ºC. SOMG was obtained as a viscous oil.

Then, different amount of SOMG was placed into another reactor and heated to 120 ºC. After that, 54.48 g maleic anhydride, 82.28 g phthalic anhydride and 79.7 g 1,2-propanediol were added to the flask. The reaction ending point was determined by the acid value maintaining at 40-50 mg KOH/g. When the temperature decreased to 80 ºC, 134 g styrene was added to the reactor. A transparent viscous liquid of SOMGUPR was obtained when the products cooled to room temperature. The codes SOMG-10, SOMG-15, SOMG-20, SOMG-25, SOMG-30, SOMG-35, SOMG-40 were denoted as SOMGUPR containing 0, 10, 15, 20, 25, 30, 35 and 40 wt % SOMG. If more SOMG added, there would be some oil-like SOMG floated on the mixture.

Samples for testing: Samples for testing were prepared by pouring 100 g SOMGUPR solution into the glass/iron mold containing 1 g BPO as initiator and 1 g cobalt naphthenate as promotor and then placing the glass/iron mold in ambient temperature for 24 h and followed by 120 ºC in oven for 4 h. The size of samples for FTIR, DSC and DMA analysis was 10 mm × 10 mm × 4 mm and tensile strength and impact strength testing was consistent with each Chinese standard.

RESULTS AND DISCUSSION

FT-IR analysis: FT-IR spectrum is a useful tool to study the chemical structure for polymeric materials[13]. The FT-IR spectrums of different products and some valuable absorption bands in SOMGUPR are shown in Fig. 2 and Table-1, respectively. As shown in Fig. 2(b), the band at 3390 cm^{-1} (-OH stretching vibration), which did not shown in Fig. 2(a), was clearly observed. Also, the transmittance of the peaks at 1740 and 1750 cm^{-1} (ester functional groups stretching vibration) was 32 %, as nearly one thirds as that of peaks in Fig. 2(a), suggesting the formation of SOMG instead of soybean oil diglyceride. In Fig. 2(c), there was a weak hydroxyl absorption peak at 3390 cm^{-1} due to the consumption of -OH groups in the condensation reaction. The peaks at 1680-1610 cm^{-1} were CH=CH absorption peak, showing that maleic anhydride was successfully introduced into the polyester principal chain.



(a)

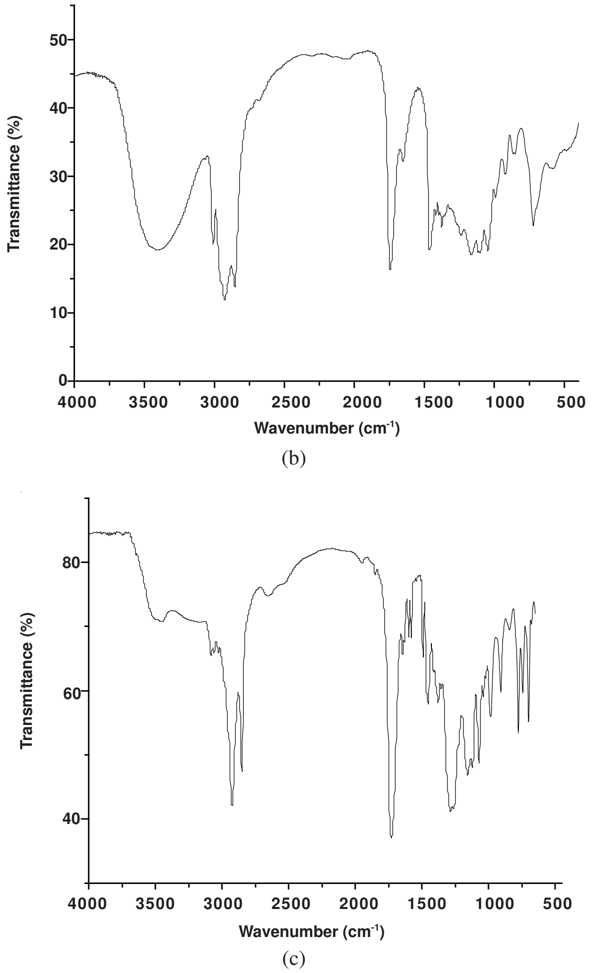


Fig. 2. FT-IR spectrum of different solution: (a) soybean oil; (b) SOMG; (c) SOMG-30

TABLE-1
KEY FTIR ABSORPTION PEAKS (cm^{-1}) IN SOMGUPR

Absorption peak (cm^{-1})	Group	Absorption peak (cm^{-1})	Group
777	$^1\gamma$-CH_2-	1610-1680	St-CH=CH
812	$^2\delta$ C-H	1730	St-C=O
1160	^{3}sys stC-O-C	1740, 1750	St-COO-
1290	^{4}st C-O	2920, 2874	St-CH_3
1450	δ-CH_2-	3390	St-OH

$^1\gamma$, $^2\delta$, ^{3}sys and ^{4}st are designated as rocking, bending, system stretching and stretching vibration.

^{1}H NMR analysis: The ^{1}H NMR of different SOMGUPR are shown in Fig. 3. Mean while, chemical shifts of different types of hydrogen nucleis in SOMG are presented in Table-2. As shown in Fig. 3(b), many sharp peaks in SOMG between 3.5 and 4.0 ppm (CH-OH and CH_2-OH protons), which didn't shown in Fig. 3(a), were clearly observed. It's thought that SOMG was successfully synthesised from glycerolysis reaction of soybean oil.

The structure of soybean oil triglyceride was complex, some fatty acids from SOMG were unsaturated and had one or more than one double bond. The active double bond may react with maleic anhydride.In order to unstand this side reaction, the ^{1}H NMR spectrums of SOMGUPR products at different SOMG content are shown in Fig. 4.

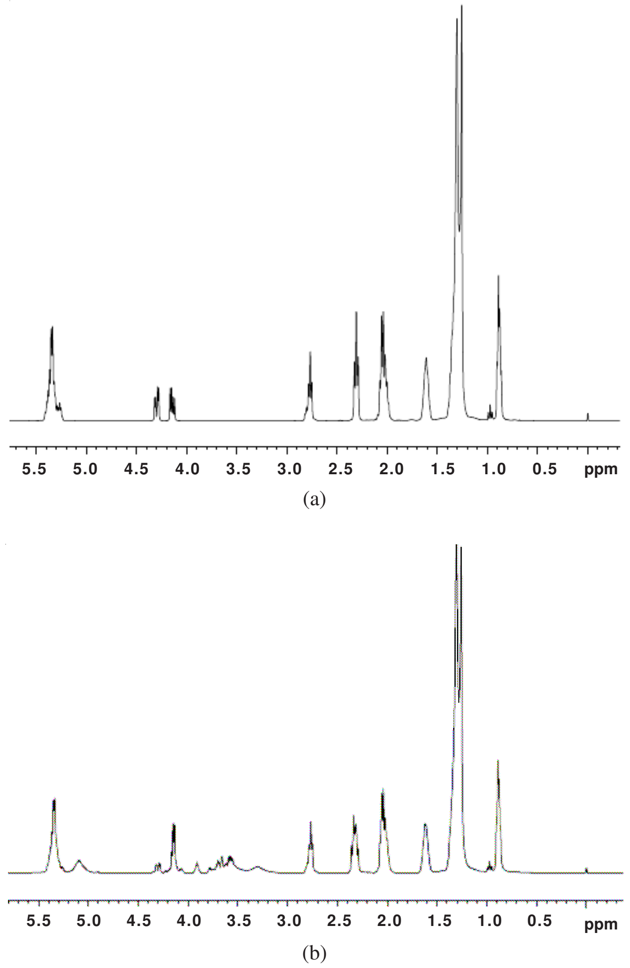
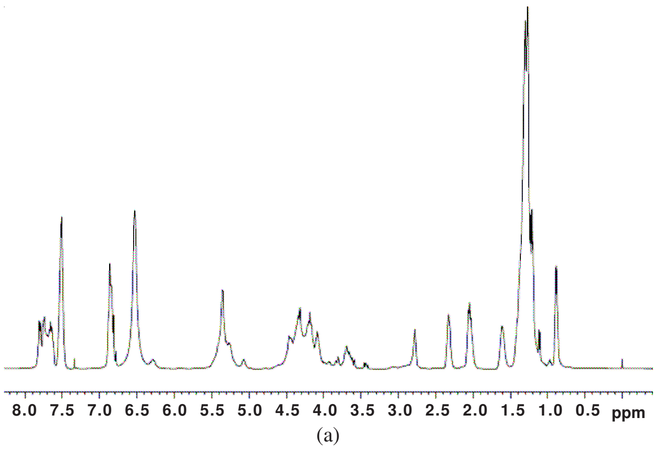
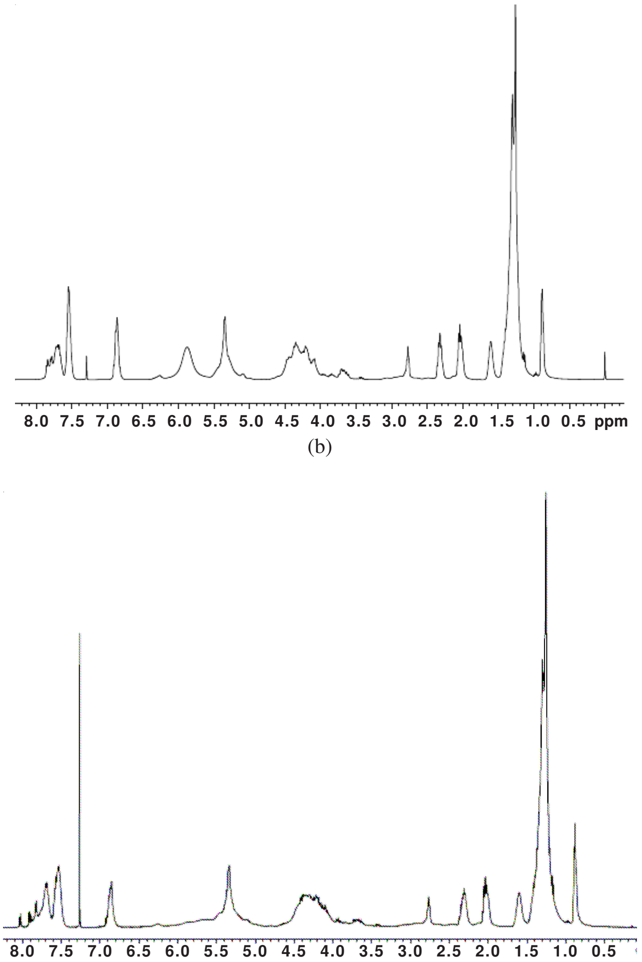


Fig. 3. ^{1}H NMR of different solution: (a) soybean oil; (b) SOMG

TABLE-2
CHEMICAL SHIFTS OF DIFFERENT TYPES OF HYDROGEN NUCLEI IN SOMG

Types of hydrogen nuclei	Chemical shifts (ppm)
-CH_3	0.9
-CH_2-	1.3
-CH_2-CH=CH-	2.0
-CH_2-COO-	2.3
-CH=CH-CH_2-CH=CH-	2.8
-CH_2-OH,-CH-OH	3.5-4.0
-CH_2-OOC-$(CH_2)_n$-	4.2
-CH-OOC-$(CH_2)_n$-	5.1
-CH=CH-	5.3





(b)

(c)

Fig. 4. ^{1}H NMR spectrum of SOMGUPR: (a) SOMGUPR-10; (b) SOMGUPR-30; (c) SOMGUPR-40

As can be seen in Fig. 4, with the increasing addition of SOMG, the intensity of peaks at 3.5-4.0 ppm region (CH-OH and CH_2-OH protons) decreased gradually and the intensity of peaks at 5.3 ppm which are an indicative of CH=CH protons is invariable. These analysis implied that side reaction between maleic anhydride and SOMG had not occurred.

DSC analysis: The reactivity of curing process is evaluated by the polymerization heat outputing. The higher heating produced in curing process, the higher reactivity of the SOMGUPR[14]. Fig. 5 shows the DSC curve of SOMGUPR-0 and SOMGUPR-30. As can be observed in Fig. 5, the heat outputing of SOMG-0 and SOMG-30 were -164.681 and -100.326 J/g, respectively. It is clearly observed that the incorporation of 30 wt % SOMG reduced the reactivity of curing process in this system. If exothermic temperature was too high, there would be some negative effects for unsaturated polyester materials, such as warping and cracking. These materials' curing exothermic temperature were ranged from100-150 °C, which can avoid these drawbacks above.

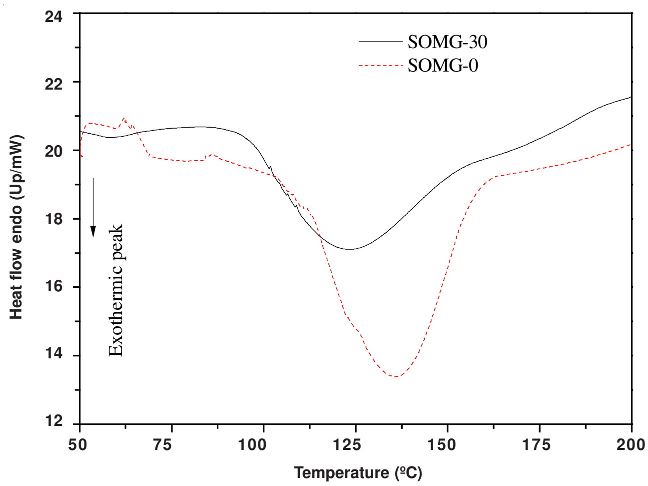
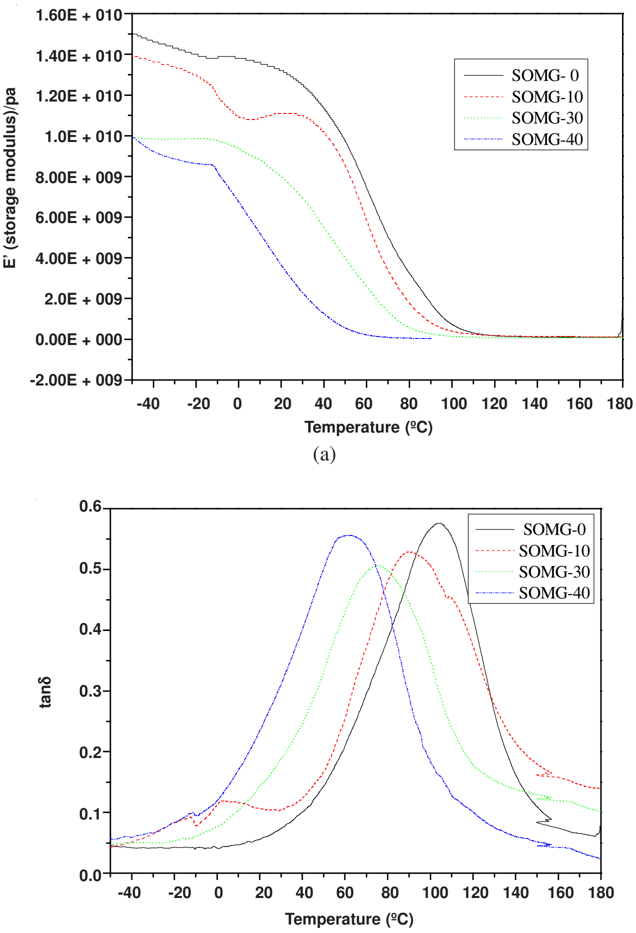


Fig. 5. DSC curve of different SOMGUPR



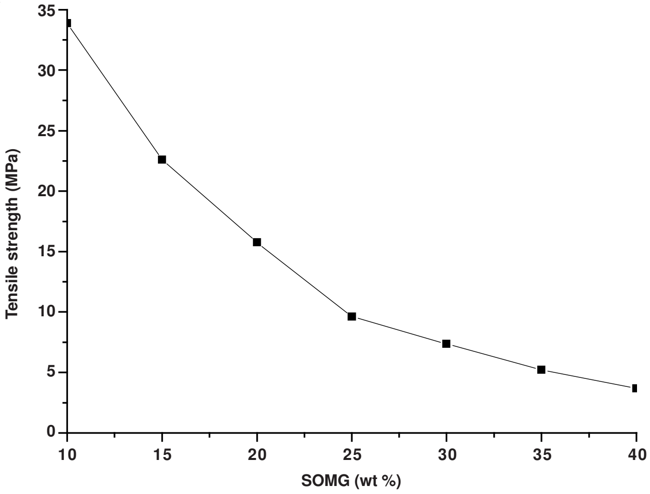
(a)

(b)

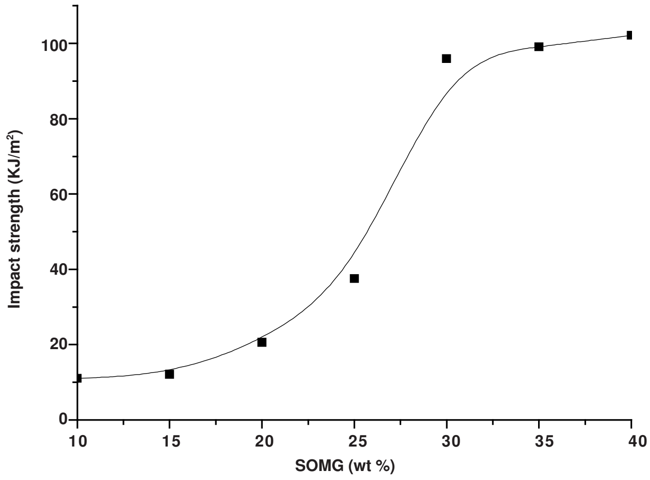
Fig. 6. (a) Storage modulus and (b) loss factor of different SOMGUPR as a function of temperature

DMA analysis: The effect of content of SOMG on the viscoelastic properties of this unsatured polyester resin are shown in Fig. 6. As shown in Fig. 6(a), the storage modulus decreased with the increasing amount of SOMG, which is attributed to the occurence of glass transition. Meanwhile, an increasing in content of SOMG produced an decreased of T_g, which determined from the loss factor curve in Fig. 6(b). That was attributed to the reduction of cross-linking density. The more long fatty R group was incorporated with the increasing amount of SOMG and R had a steric hinderance on the cross-linking reaction between SOMGUPR and styrene. In other words, more addition of SOMG could resulted in a low cross-linking density.

Mechanical properties: The change in tensile strength and impact strength for different content of SOMG are shown in Fig. 7. As shown in Fig. 7(a), the tensile strength decreased with the increasing addition of SOMG, which was ascribed to the low cross-linking density.The impact strength increased up to 30 wt % at first time and then stabilized at nearly 100 KJ/m^2. The reason is still unknown and more detailed studies should be conducted on this aspect.



(a)



(b)

Fig. 7. (a) The tensile strength and (b) impact strength with different content of SOMG

Conclusion

A bio-based unsaturated polyester resin was successfully synthesized using glycerol, soybean oil, 1.2-propanediol, maleic anhydride and phthalic anhydride. Glycerolysis of soybean oil and the concomitant condensation reaction has testified to be an alternative method for the preparation of unsaturated polyester resin. The results of FT-IR and ^{1}H NMR spectrums showed that the preparation of unsaturated polyester resin was consistented with the prospective schemes of synthesis and no side reaction between maleic anhydride and SOMG had appeared. The reactivity of SOMGUPR containing 30 wt % SOMG was lower than that of SOMGUPR without it. An increased in content of SOMG produced an decreased in T_g, which attributed to the steric hinderance of pendant groups in SOMG.The more cotent of SOMG up to 40 wt %, the lower tensile strength. The impact strength increased with the increasing amount of SOMG content up to 30 wt % and then stabilized at about 100 KJ/m^2.

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