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Biobased polyurethane and its composite with glass fiber

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Biobased polyurethane from soy oil derived polyol and diisocyanate on reinforcement with glass fibers enables to improve the mechanical properties of the base resin significantly. The effect of variation of glass fiber loading from 15, 30 and 50-wt% on the physico-mechanical properties of the resulting composites are evaluated and analyzed. The storage modulus of virgin biobased polyurethane gets a 14-fold increase on reinforcement with 50 wt% glass fibers. The results highlight a significant enhancement in strength and modulus of virgin biobased polyurethane by more than 260 and 480% respectively for a fiber content of 50-wt%. The original notch Izod impact strength of 26 J/m of the biobased polyurethane reaches 93, 200 and 448 J/m in composites with 15, 30 and 50 wt% of glass fibers. The environmental scanning microscopy (ESEM) analysis of the impact-fractured samples shows the efficiency of wetting and the distribution of glass fibers. Thermogravimetric analysis (TGA) shows the improved thermal stability of the biobased polyurethane on reinforcement with glass fiber.

1. Introduction

There is a growing urgency to develop novel biobased products and other innovative technologies that can unhook widespread dependence on fossil fuel. Polyurethanes (PURs) made from petroleum-based polyols and isocyanates as well as glass fiber reinforced polyurethane composites have achieved wide spread applications in foam, coating and structural materials. There is a wide range of isocyanates and polyols commercially available thus leading to almost unlimited possibilities for polyurethane materials formulations. Because of the inherent versatility in polyurethane synthesis, the properties of this class of polymer can be easily engineered to their application environments. Although isocyanates are not yet made from renewable resources; the formulations of polyols from plant oils have attracted the recent attention. The interest of polyols from soybean oil is obvious since it is one of the cheapest vegetable oils and most abundant oil currently available in the United States. The last decade has seen a growing interest in the use of renewable resources for productions of polymers generally prepared from petrochemicals. Indeed, petroleum forecasted depletion and the current environmental threat have prompted researchers to find new production ways from the renewable resources. The abundant and cheap plant oils represent a major potential source of chemicals.

Polyurethane resins are widely used in various applications ranging from medical devices to automotive body panels. The success of polyurethane is due to its ability to be produced in various forms from flexible to rigid structures [1, 2]. Biobased polyurethanes are already produced from castor oil. This oil contains hydroxyl groups that can react with isocyanate groups [3]. However, one of the drawbacks of this polyol is its high price. Soybean oil represents more interesting oil from the economic standpoint since it is produced in appreciable amounts in United States (more than 70 million metric tons) [4]. Therefore, soy-based products provide an interesting alternative to petroleum based synthetic polymers used in various applications. Conversion of soybean oil and other plant oils into polyols as well as the preparation of biobased polyurethanes from such vegetable oil based polyols and isocyanates has been described in the scientific literature [5–12].

In recent years, polymeric composite materials have received a lot of attention. Indeed, there is an increasing drive towards lightweight, durable and cost effective compounds for sector such as automotive market. Glass reinforced polyurethanes have been described and continued to be of particular interest [13–17]. In 2000, more than 900,000 tons of polyurethanes were used by automotive industry [18]. Developments in reinforced reaction injection molding (RRIM) and

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structural reaction injection molded (SRIM) of glass-reinforced polymers are expected to increase the use of reinforced polyurethanes in automotives. Among the benefits of these technologies are high-volume productivity, excellent performance at minimal thickness and effective cost enabling the replacement for traditional structural materials. Owing to the versatility of polyurethanes chemistry, a broad range of properties and applications are possible for glass-reinforced composites, such as seat pans, sunshades, door panels, package trays and truck box panels. However, the adhesion between the polyurethane matrix and the glass fiber is the key parameter for improvement of mechanical performances [19–23].

In one of our ongoing research projects we are targeting to develop biobased polyurethanes using polyols derived from various vegetable/plant oils like soybean, peanut, castor, corn and linseed with various types of petroleum-derived isocyanates including aliphatic and aromatic isocyanates and their composite materials from synthetic as well as natural fibers. As a part of our investigation, this paper reports for the first time the use of a soy-based polyol in designing composite materials from glass fiber.

2. Experimental section

2.1. Materials

Soybean phosphate ester polyol (SOPEP) (OH number = 154 mg KOH/g and viscosity of 7,500 cps at 25°C) is received from ATOFINA Chemicals, Inc. Blooming Prairie, MN. Polymeric diphenylmethane diisocyante, (pMDI) (Baydur 410 IMR) is a gift from BAYER Corporation, Pittsburg, PA. The chemical structures of SOPEP and pMDI are shown in Fig. 1. Raw glass fibers (1/4 inch) (Johns Mansville) are dried overnight in vacuum for composite fabrication.

2.2. Procedure for composite fabrication

In an air ventilated room, SOPEP and glass fibers were weighted and mixed in desired proportions in a beaker. The mixture is kept for 1 h under vacuum. Aromatic isocyanate (BAYDUR 410 IMR) is then added in to the beaker (isocyanate index = 110) containing a mixture of glass fiber and soy-based polyol (SOPEP). The mixture is then poured into mold. Sheets (thickness of 2.5 mm) were prepared by compression molding at 150°C for 10 min in a Carver Laboratory Press and then post-cured for 3 hours in an air oven at 125°C.

2.3. Testing

Specimen densities are determined by the mass to volume ratio equation. Thermogravimetric analysis (TGA) is carried out under nitrogen atmosphere with a Hi-Res. TGA 2950 Thermogravimetric Analyzer at a heating rate of 20°C/min. from 30 to 600°C. Dynamic mechanical analysis (DMA) is performed with a DMA 2980 TA instruments. The samples are tested in a three-point bending mode at fixed frequency (1 Hz) with a heating rate of 5°C/min. The three point flexural properties are measured following the ASTM D 790 standard using a United Tensile Testing (UTS) Machine. Notched Izod impact strength is measured in a TMI Impactometer as per ASTM D 256 standard. Environmental Scanning Microscopy (ESEM) micrographs of the impact fractured samples are recorded with a Philips ElectroScan model 2020 after coating with gold for 25 s.

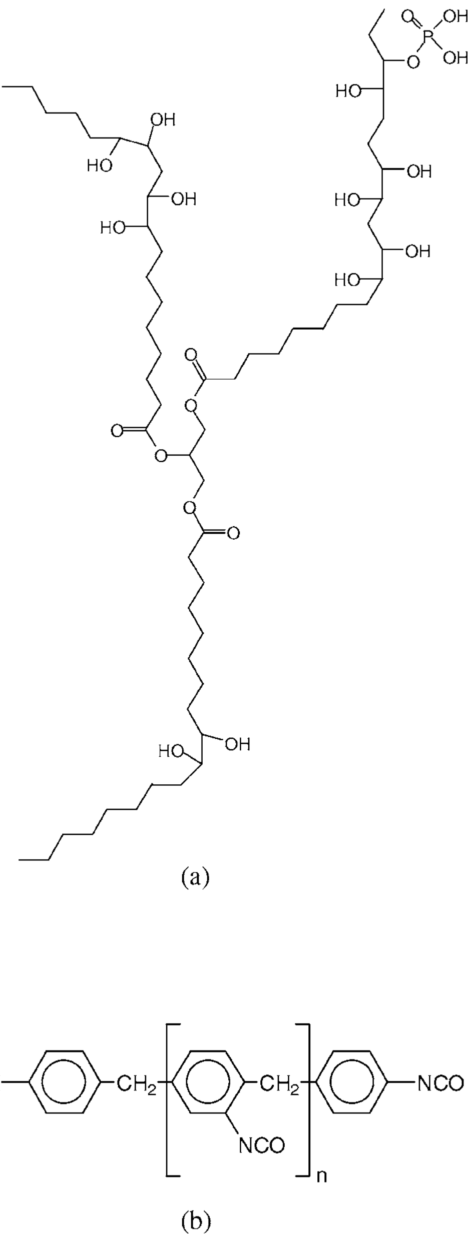


Figure 1 Chemical structure of: (a) Soybean phosphate ester polyol (SOPEP) and (b) polymeric 4,4′-diphenylmethane diisocyanate (pMDI), $n \cong 1$.

3. Results and discussion

3.1. Dynamic mechanical analysis

Polyurethane thermoset is obtained by reacting soy-based polyol (SOPEP) with polymeric diphenylmethane diisocyante (pMDI). A schematic representation of biobased polyurethane cross-linked structure is represented in Fig. 2. A general reaction scheme showing the synthesis of polyurethane from polyol and diisocyanate is represented in Scheme 1. The hydroxyl value of SOPEP (154 mg KOH/g) is not suitable for

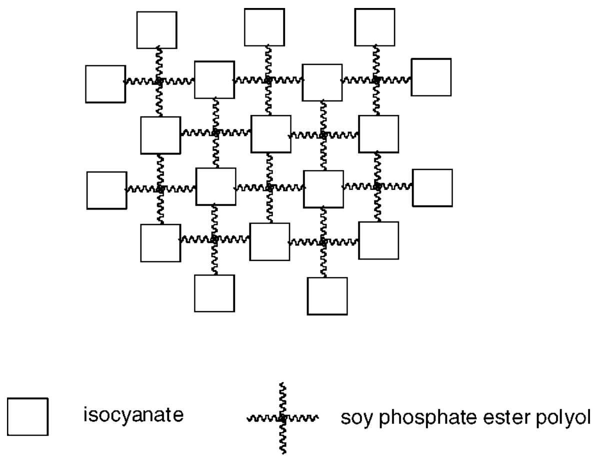


Figure 2 Schematic representation of a polyurethane thermoset prepared by reaction of soybean phosphate ester with aromatic isocyanate.

TABLE I Density, Storage modulus and T_g of glass reinforced biobased polyurethanes

Samples	Glass content (wt%)	Density (g/cm^3)	G' (MPa) at 30°C	G'_{specific} (MPa) at 30°C	T_g (°C)
A	0	0.91	165	181	66
B	15	1.08	865	801	85
C	30	1.13	1078	954	91
D	50	1.20	2296	1913	90

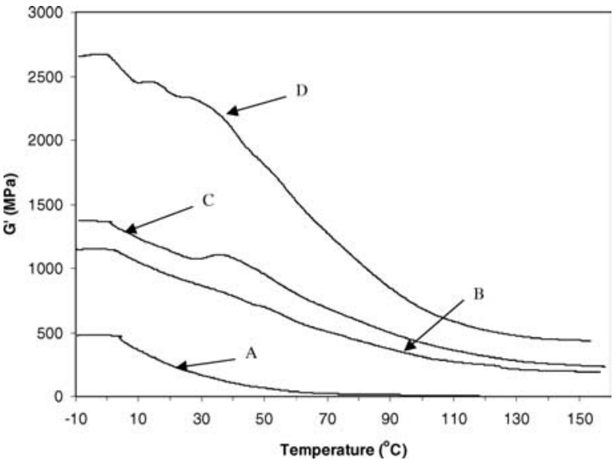
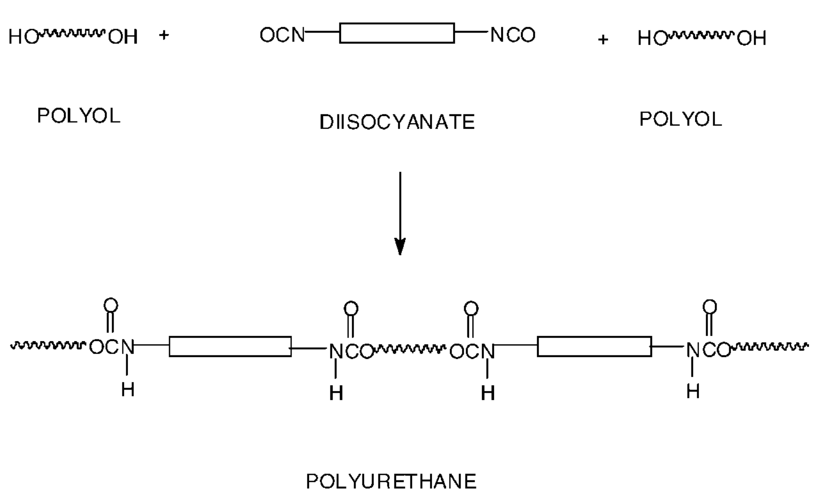


Figure 3 The temperature dependence of the storage modulus (G') of biobased polyurethanes: (A) No fiber, (B) 15 wt%, (C) 30 wt% and (D) 50 wt% glass fiber.

preparation of rigid polyurethanes. Indeed, OH number higher than 250 mg KOH/g is recommended to achieve a high degree of crosslinking [2]. Therefore, under the present investigations; the polyurethane prepared from SOPEP and pMDI is expected to be a low modulus material and should exhibit a flexible to semi-flexible behavior. Dynamic mechanical analysis (DMA) supports our above-mentioned explanation. Indeed, the specific storage modulus ($G'_{\text{specific}} = G'/\text{density}$) of polyurethane prepared from SOPEP and pMDI is evaluated to be 181 MPa at 30°C (Table I). Addition of glass fiber to such biobased polyurethane matrix results in increased values of modulus (G') as well as specific storage modulus (G'_{specific}) at 30°C (Table I). Increase of glass fiber contents from 15 to 50 wt% exhibits a regular trend in storage modulus increase of the resulting composite materials. A significant achievement of the present studies is that with 50 wt% glass fiber reinforcement, the storage modulus of the virgin biobased polyurethane gets around 14-fold enhancement. The effect of variation of temperature from −10 to 150°C on the storage modulus of biobased polyurethane and its composites is represented in Fig. 3. It is observed that with increase of temperature the modulus data drop. Glass fibers reinforce the matrix by allowing a greater stress transfer at the matrix-fiber interface, therefore increasing the stiffness of the overall material. Glass transition temperatures (T_g) are determined from the peak of the tan delta (ratio of loss modulus, G'' to storage modulus, G'') curves. With fiber loading; T_g of biobased polyurethane (66°C) is shifted to higher values and is measured at 90°C for a fiber loading of 50-wt% (Table I). Moreover, the intensity of tan delta is reduced with addition of glass fiber (Fig. 4). The restricted chain mobility accounts for higher T_g for the composites.

3.2. Flexural and impact properties

The effect of glass fiber reinforcement on flexural strength and modulus of biobased polyurethane is



Scheme 1 General reaction scheme of polyurethane synthesis from polyol and diisocyanate.

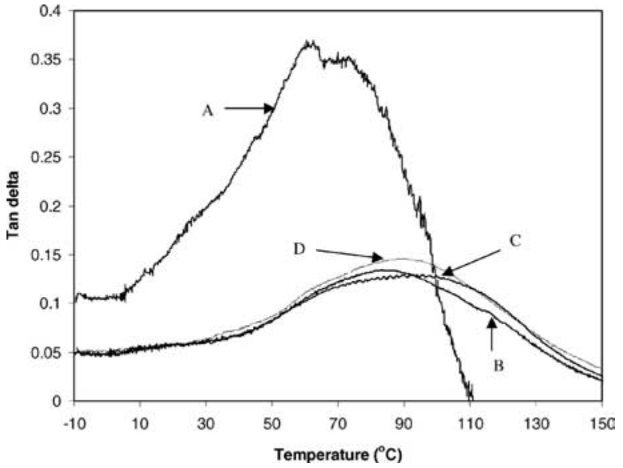


Figure 4 The temperature dependence of tan δ (damping parameter) of biobased polyurethanes: (A) No fiber, (B) 15 wt%, (C) 30 wt% and (D) 50 wt% glass fiber.

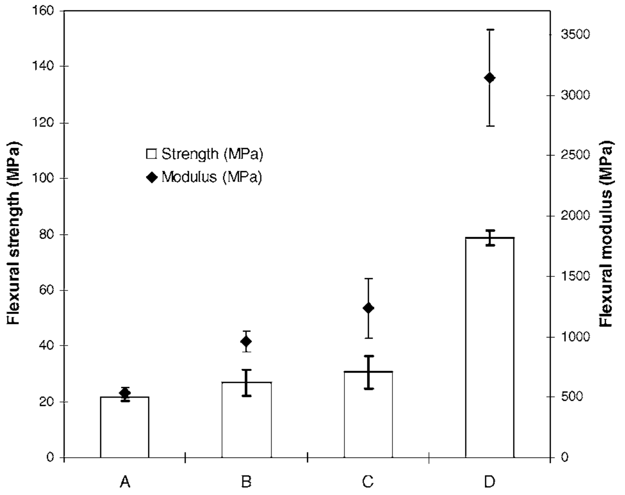


Figure 5 Comparison of flexural strength and modulus of biobased polyurethanes: (A) No fiber; (B) 15 wt%; (C) 30 wt% and (D) 50 wt% glass fiber.

represented in Fig. 5. A linear increase of flexural strength (FS) and flexural modulus (Modulus of Elasticity, MOE) is observed with increase of fiber content from 15 up to 30-wt%. The FS and flexural modulus of virgin biobased polyurethane on reinforcement with 15 wt% glass fibers enhance by 25 and 78% respectively as contrast to 42 and 129% for 30 wt% glass fiber reinforcements. The results highlight a significant enhancement in strength and modulus of virgin biobased polyurethane by more than 260 and 480% respectively particularly for a fiber content of 50-wt%. It suggests a very effective reinforcement effect for such high fiber loading compared to other composite samples with 15 and 30 wt% loading. Conversely, the extensibility is reduced with such high fiber loading as depicted from the stress and strain (displacement) curves (Fig. 6). Except the biobased polyurethane, all the composites break during flexural tests.

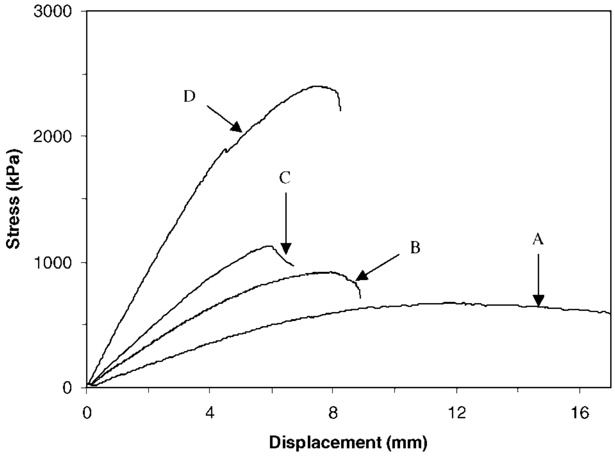


Figure 6 Stress-displacement curves of biobased polyurethanes: (A) No fiber, (B) 15 wt%, (C) 30 wt% and (D) 50 wt% glass fiber.

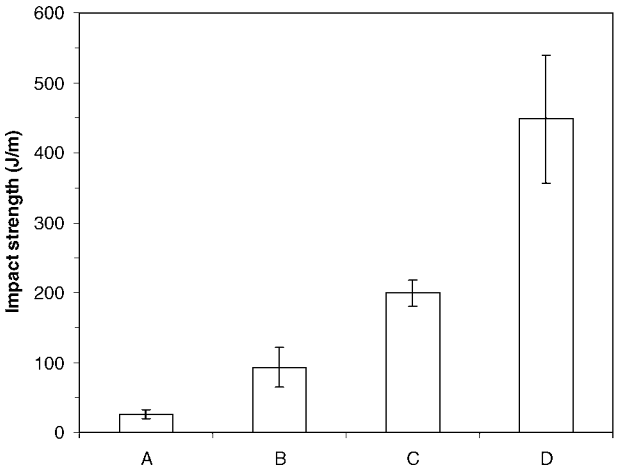


Figure 7 Notch Izod impact strength of biobased polyurethanes: (A) No fiber, (B) 15 wt%, (C) 30 wt% and (D) 50 wt% glass fiber.

The effect of variation of glass fiber amount on the impact properties (notched Izod impact strength) of the resulting composites is represented in Fig. 7. The energy transferred to the matrix before its break is substantially increased upon reinforcement of the matrix with glass fiber [24]. From 26 J/m impact strength of virgin biobased polyurethane (PUR); it is evaluated to be 93, 200 and 448 J/m with addition of 15, 30 and 50-wt% of fibers, i.e., improvements from neat PUR resin by about 258, 669 and 1623% respectively. Such increase of impact strength with glass fiber loading has also been described and studied by Yosomi and Morimoto [25]. Partial break is observed for fiber loading of 50-wt% suggesting that the glass fiber introduces new dissipation mechanisms not observed in the neat biobased polyurethane. The exact mechanism of impact fracture of composites is complex. However, increased of the impact strength during the Izod impact test may be explained by considering the crack propagation. Basically, the crack propagates freely in the neat biobased polyurethane. In the case of composites, crack occurs first and then peeling takes place from the cracked surface along the fibers, followed by cutting of the fibers or by pulling out of the fibers from the matrix thus increasing the absorbed energy by glass reinforced biobased polyurethane composites during notch impact test. Therefore, the impact strength of composites takes into account the fracture energies of the matrix, the fiber and the energy required to pull out the fiber from the matrix.

Environmental Scanning Electron Microscopy (ESEM) was used to study the impact fracture surfaces

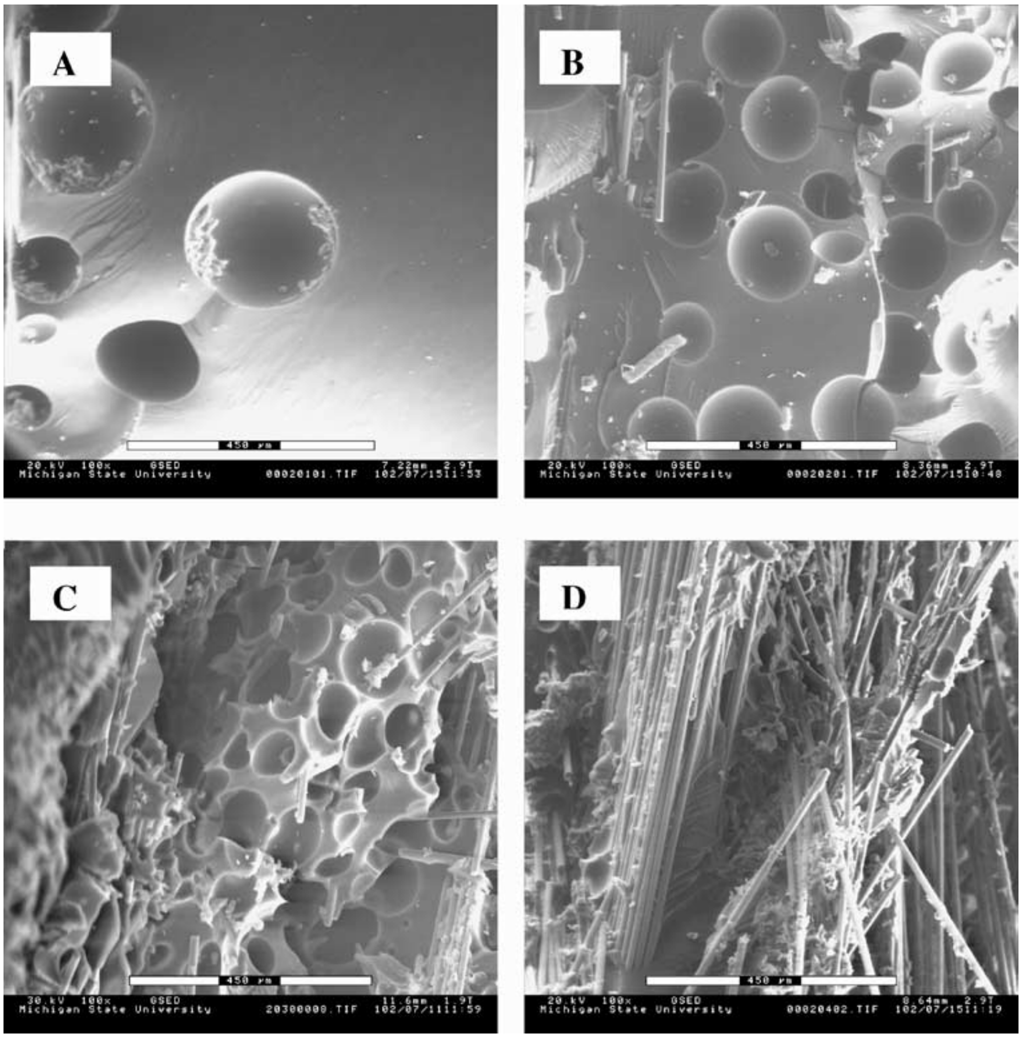


Figure 8 ESEM micrographs of glass reinforced biobased polyurethanes (magnification of 100×): (A) No fiber, (B) 15 wt%, (C) 30 wt% and (D) 50 wt%.

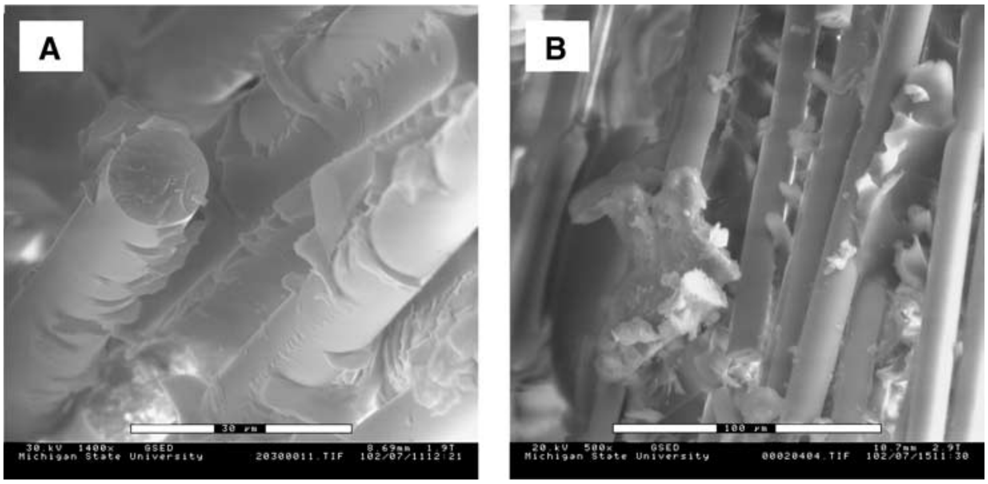


Figure 9 ESEM micrographs of glass reinforced biobased polyurethanes: (A) 30 wt% (1400×) and (B) 50 wt% (500×).

of the polyurethanes samples. ESEM micrographs of the impact fracture surfaces of neat biobased polyurethane and its composites are shown in Fig. 8. Pores can be seen on these micrographs. The residual water content in the polyol (0.05%) reacts with isocyanate resulting in evolution of carbon dioxide and thus pores are expected [2]. The pores are well visualized in the ESEM micrograph of the virgin biobased polyurethane (Fig. 8A). The requirements to obtain a composite with improved mechanical performances are good dispersion of the fibers in the matrix, wetting of the fibers by matrix and a good adhesion at the fiber-matrix interface. Glass fibers disperse well into the polyurethane matrix (Fig. 8B to D). The increase of fiber amount leads to better dispersion throughout the matrix, thus allowing enhancement of mechanical properties. Wetting of the fiber can be seen in Fig. 9A and B. Fibers are covered by matrix material that has been pulled out together with the fibers in the course of crack propagation. The exact nature of adhesion between the glass fiber and the polyurethane matrix is not clearly determined. However, a study carried out in our laboratory on the nature of interfacial interactions between polyurethane and glass interphase showed that the contribution of chemical bonding, covalent or ionic, is not important. Formation of an interphase region in which hydrogen bonding plays a key role is more likely to occur in glass reinforced polyurethanes [23]. Therefore, the enhancement in mechanical performances observed in glass reinforced biobased polyurethanes comes from an effective wetting and good dispersion of the fibers into the matrix.

3.3. Thermogravimetric analysis

The effect of glass fiber loadings on the thermal stability of these biobased polyurethane composites is evaluated by thermogravimetric analysis (TGA) under nitrogen atmosphere. Basically, the shape of the curve remains unchanged with fiber loading (Fig. 10). The first downturn is observed above 200°C. The residual weight is correlated to the amount of glass fibers added. Derivative TGA curve corresponding to neat polyurethane (no fiber) reveals four maximum peaks (350, 390, 478 and 502°C) suggesting at least four main degradation processes (Fig. 11, curve A). The same peaks are observed in the composite with 15-wt% of glass fibers while three peaks (350, 395 and 490°C) are seen for the two other composites (30 and 50 wt% of fibers loadings). Derivative curves of glass-reinforced composites are less intense and less resolved, because of the reduction of volume fraction of the polyurethane matrix. However, they show the same pattern (Fig. 11, curves A to D). Decomposition of urethane bonds starts around 200°C [26–29]. The polyol component contributes to degradation at higher temperature [9]. From these results, we conclude that glass fibers do not influence the basic mechanisms of the biobased polyurethane thermal degradation but on the other hand improve the thermal stability of the composites.

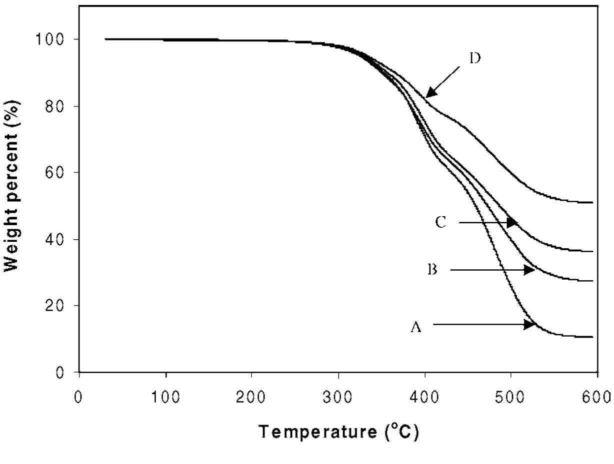


Figure 10 TGA curves recorded under nitrogen at 20°C/min of biobased polyurethane composites: (A) No fiber, (B) 15 wt%, (C) 30 wt % and (D) 50 wt% glass fiber.

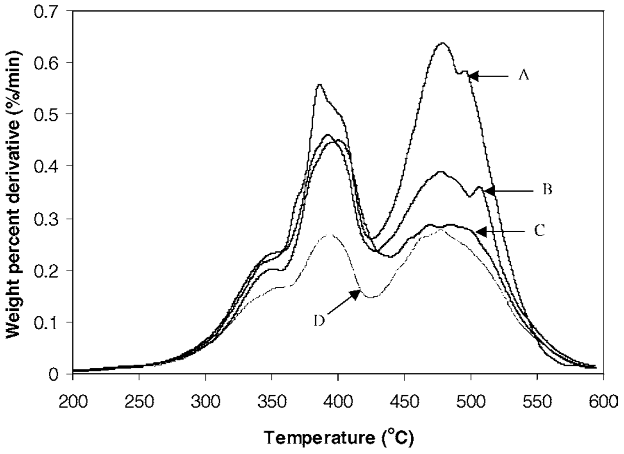


Figure 11 Derivative TGA curves of biobased polyurethane composites under nitrogen at 20°C/min: (A) No fiber, (B) 15 wt%, (C) 30 wt% and (D) 50 wt% glass fiber.

4. Conclusions

Soy phosphate ester polyol made by hydrolysis of epoxidized soybean oil has been successfully used as polyol source for preparation of low modulus polyurethane with aromatic isocyanate. Reinforcement of this biobased polyurethane with glass fiber leads to composites with improved mechanical properties (flexural strength, modulus of elasticity and impact energy). The storage modulus of the virgin biobased polyurethane gets around 14-fold enhancement through reinforcement with 50 wt% glass fibers. Impact test shows a reduction of the brittleness character of the composites. ESEM analysis of the impact-fractured sample suggests the good distribution of the fiber, the efficient wetting and the efficient interfacial interaction of the glass fiber and biobased polyurethane matrix. Thermal analysis reveals a good thermal stability (under nitrogen) of these biobased polyurethane composites.

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