# Thermal Stability of Polyurethanes from Soybean Oil as Natural Source and its Chemical Modifications

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**Abstract:** In this contribution, a summary of recent publications about the thermal stability of polyurethanes from soybean oil as natural source for polyols was made. From the review, it can be concluded that polyurethanes from natural oil-derived polyols decomposed at a temperature up to 30°C higher than petrochemically-based polyurethanes. Chemical modification of soybean oil for polyol synthesis is mainly based on epoxidation. However, we highlighted the possibility of functionalizing soybean oil by maleinization, a route that was very scarcely studied. Maleinization allows the introduction of labile reactive hydrogen to react with isocyanates for polyurethane synthesis with a broad range of properties.

**Keywords:** Polyurethanes, modified soybean oil, natural polyol, thermalproperties, maleinization.

## 1. INTRODUCTION

Polyurethanes are derived from petrochemically based raw materials, as polyols and isocyanates, as such, they are non-degradable and represent an environmental issue. Soybean oil is a readily available renewable resource. South American countries such as Brazil and Argentina are the third and fourth world producers of soybean oil, respectively; after China and the United States. Considering these reasons, it is of great relevance to find applications for natural oils such as soy oil other than edible feeding sources. One of this is its use as sources for natural-derived polyols for the manufacture of PUs in general and PU elastomers in particular.

The main components of polyurethane elastomers include polyether and polyester diols, diisocyanates and chain extenders. Polyether starting materials can be poly(oxypropylene diol)s or poly(oxytetramethylene diol)s, giving elastomeric properties with toluene diisocyanate (TDI) and amine chain extenders. Polyester PUs have very good general properties and are derived from polyester polyols. These later are required to form the soft segments and are commonly prepared from adipic acid and simple glycols.

As it is known, PUs are segmented polymers, consisting of hard (isocyanate and chain extender) and soft segments (polyols). The degree of segregation between these segments is directly related to their thermal and mechanical properties. Physical and chemical interactions within hard segments mostly determine thermal resistance [1,2]. Polyurethanes prepared from vegetable oils have numerous advantages properties due to cost, availability and facility of obtention of polyols [3] and because of the hydrophobic nature of triglycerides used in its manufacture [4].

Among the well-known methods of synthesis of bio-based polyols several can be found: epoxidation and ring opening reaction, hydrogenation, halogenation, transesterification, and also microbiological methods [5] together with more complex hydroformylation [6]. Hydroformylation is a process with high conversion of vegetable oils to polyols. The process involves reaction of hydrogen and carbon monoxide with double bonds to give aldehydes, which are then converted to alcohols by hydrogenation. Hydroformylation of soybean oil was performed and polyols were reacted with diphenylmethane diisocyanate (MDI) to obtain polyurethanes of different crosslinking density [7]. The same research group performed hydrogenation after hydroformylation of soybean oil and verified a higher reactivity respect to epoxidized and formylated polyol. PU foams obtained by reaction with a polyisocyanate were more rigid that hydroformylated/hydrogenated polyol [8].

Regarding PUs from natural oils, the first comprehensive report was published twenty years ago by leading work from Petrović group: a series of polyurethanes from polyols derived from soybean,

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corn, safflower, sunflower, peanut, olive, canola, and castor oil were prepared, and their thermal stability in air and nitrogen was examined. These authors found that PU from natural oil-derived polyols decomposed 25-30°C higher than polypropylene oxide based PUs (375 and 400-405°C, respectively). They concluded that if weight loss at a higher conversion is taken as the criterion of stability, then natural oil based polyol polyurethanes have better thermal stability, both in air and in nitrogen [9]. The same group also reported the effect of halogenation of epoxidized soybean oil (ESBO) reacted with two commercial isocyanates on PU properties, finding that PUs with brominated and chlorinated polyols had comparable glass transition and strength [10]. They have also studied the effect of OH/NCO molar ratio on properties of soy-based polyurethane networks [11].

As mentioned above, other natural based oils were used for PU preparation, although the number of studies for soybean oil based PUs is higher than from other natural oils. For example, PU based on castor oil cured with toluene diisocyanate, isophorone diisocyanate or hexamethylene diisocyanate were prepared by Jadhav [12] as early as almost 35 years ago. Considering the temperature for 98% weight loss,$T_{98\%}$, TDI-cured PUs begun to degrade 30°C lower than the other systems. $T_{50\%}$ ranged from 373 to 385°C. These values are similar to those seen as a mean for soybean oil based polyols, although slightly lower.

In another example, PU from canola oil based polyols was compared to PU from soybean oil based polyol. The TGA thermographs showed two well-defined steps of degradation for these elastomers. In the first step, up to 30% weight loss was recorded, the fastest loss rate was found at 345°C for canola oil based PU, while soybean oil-based PU lost most of its weight in the second step [13].

## 2. THERMAL STABILITY OF POLYURETHANES FROM MODIFIED SOYBEAN OIL

Soybean oil has been employed extensively in polyurethane manufacturing, mainlyafter its transformation in epoxidized soybean oil (ESBO) [14, 15].

Several factors that influence the thermal stability of PU in general and particular those obtained from polyols coming from natural sources. The length of alkyl fatty acid chain in natural oil influences the elasticity of prepared or modified polymer. The content of unsaturated groups per polyol molecule influences the functionality of the obtained oil. Polyurethanes obtained from polyols with primary hydroxyls are generally more stable than those from secondary hydroxyls.

Heterogeneity of functionalities in polyols had no negative effect on properties of glassy polyurethanes, but caused low strength and elongation of rubbery PUs [16]. The functionality of these polyols increased linearly with molecular weight to very high values, resulting eventually in their high crosslinking power [17].

Degradation of PUs obtained from soybean and castor oil polyols without solvent and catalyst was observed at temperatures between 200°C and 300°C by TGA. These signals can be attributed to the decomposition of labile urethane groups, while those observed in the temperature range from 300°C to 450°C resulted from chain scission in the soybean oil [18].

PU obtained from soybean oil polyol reacted with 4,4´-diphenylmethane diisocyanate (MDI) and chain extended with ethylene glycol decomposed in four sequential steps, being the third decomposition step the one that showed maximal weight loss at values of 380-390°C, as seen by Ryszkowska group in Poland [19]. More recently, the same group determined the influence of used soybean oil based-polyol on the thermal properties of PU elastomers, with a different value of isocyanate index ($I_{NCO}$). Thermal properties, determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed that the highest $I_{NCO}$ caused an increase in hydrogen bonds in PU and a higher thermal stability. Peak at 380°C resulted from the degradation of the ester bonds in the soft segments, while the decomposition of the aromatic compounds begun at the remarkably high temperature of 480°C [20]. They have also concluded that the increasing number of isocyanate groups during the production of elastomeric PU with soybean oil derived-polyol changed the number of hydrogen bonds and degree of phase separation, improving thermal resistance properties (higher mass loss by TGA at 400°C) [21].

Another polish group obtained a PU from a mixture of petrochemically based polyol and hydroxylated soybean oil, chain extended with 1,2-bio-propanediol, which was advantageous in comparison to bio-based 1,3-propanediol,and exhibited elastomeric properties.

However, in this case, only glass transition temperatures were reported, which were reported to depend on the type of polyol mixture and chain extenders used [22].

## 3. MODIFICATION OF SOYBEAN OIL FOR POLYURETHANE OBTENTION

Polyurethanes, being hydrocarbon polymers, have limitations in terms of adhesion and compatibility with mineral fillers, as well as with polar resins such as epoxy, polyesters and polyamides. Therefore, two main approaches arise to enhance their properties: by means of additives, or by coupling new functional groups. The first approach was attempted since the start of polymer practice and is a specific area of research [23, 24] so we will focus on the second approach. The coupling of new functional groups to the hydrocarbon chains of unsaturated hydrocarbon skeleton can be done by grafting polar monomers that confer a new chemical reactivity, or by reacting the unsaturations (if present) according to the chemistry of the alkenes: this is, modifying them directly by carrying out reactions such as electrophilic addition and epoxidation.

A recent thorough and comprehensive review work summarized that a variety of new structures suitable for PU synthesis are available nowadays, as follows: (a) polyether polyols accessible via ring-opening polymerization of epoxy fatty acids and subsequent reduction of ester groups, (b) polyester polyols, that can be obtained from ω-hydroxy fatty esters via poly condensation or by ring-opening of epoxidized oils with a variety of nucleophiles, (c) diols of different chain lengths, accessible from fatty acids via metathesis or ozonolysis reactions followed by reduction of ester groups, (d) aromatic polyols prepared using transition-metal catalyzed cyclotrimerization of alkyne fatty acid derivatives and (e) silicon containing polyols prepared through hydrosylilation coupling [25]. Among these routes, modifications of fatty acids seem to us as the most attractive, at least in terms of costs.

Following this synthetic strategy, vegetable oils are the most obvious source of fatty acids. Vegetable oils are considered non-reactive raw materials and in order to make them reactive, functional groups have to be introduced. Among ways to functionalize vegetable oils, grafting with a polar monomer such as maleic anhydride is a well-known and old approach, although very efficient and utilized [26]. This is a type of reaction in which the π electrons of the double bond are not rearranged to form a new single bond (or sigma bond) with an electronegative atom that changes position in the molecule. The monomer to graft interacts with a simple C-H bond located in an allylic position, that is, neighboring an unsaturation. Therefore, an Alder-ene reaction like maleinization, unlike a Diels-Alder reaction, requires more drastic conditions, not only a strong dienophile as maleic anhydride but temperatures above 160°C and often longer residence times.

Maleinization process can be done by thermal initiation. This consists of heating the reaction mixture at 150 to 250°C but preferably between 180 and 230°C under nitrogen for a couple of hours. A gel inhibitor such as organic copper salt must be added to avoid premature gelation and further solidification [27].

After maleinization, the maleinized soybean oil (SOMA) together with ESBO can be used to obtain non-isocyanate PU with good properties [28]. SOMA can be also polymerized with diols to obtain soft, flexible solids or viscous oily polymers [29] which could be a route to novel natural-based PU, labile hydrogens are available to react with isocyanates.

Finally, for setting a standard parameter, high temperature resistance was defined as the ability of a polymer, after first being exposed to moisture and then temperatures of from 163°C to 218°C for about 1 hour, to retain more of its physical properties. High temperature resistance was further was expanded to include the ability of a polymer to display surface defects, such as blistering when subjected to heat and moisture [29]. Following these definitions, we can conclude that PUs derived from natural oils as resistant to high temperatures in comparison to conventional polyurethanes.

## CONCLUSIONS

As a result of this short review in the subject of thermal properties of natural based PUs, the main driven conclusion is that natural oil-based polyol polyurethanes have better thermal stability than conventional PUs from polyether and polyester polyols. As a general rule of thumb, PU from natural oil-derived polyols decompose temperature up to 30°C higher than petrochemically-based PUs. These findings clearly justifies a continued research in this area, specially when a change towards sustainable materials is foreseen in next years to come.

Thermal and mechanical results reviewed showed that the natural based PUs exhibited higher glass transition temperatures, better mechanical properties and higher thermal stability. These facts can be attributed mainly to the higher degree of cross-linking in the natural polyols.

Lastly, respect to among chemical modification routes of soybean oil for PU manufacture, epoxidation emerges as the most followed one. On the other side, maleinization of soybean oil has been only very scarcely studied, although being a straightforward chemical route, possibly because of harsher reaction conditions than epoxidation, which limits now its industrial applications.

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