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Chapter

Thermal Resistance Properties of Polyurethanes and Its Composites

Javier Carlos Quagliano Amado

Abstract

The nature of starting materials and the condition of polyurethane (PU) preparation are regarded as the main general parameters that determine PU thermal resistance. The effect of structure and presence of additives were identified as the major general factors on this regard. Structural factors include phase microstructure, i.e., chemical structure, proportion, and segregation of soft and hard segments, polyol type (petrochemical or natural oil-based), isocyanate and chain extender type, and thermoplasticity of PU. In respect to the effect of additives, the incorporation of fillers is the most direct strategy to increase PU heat resistance. With respect to fiber additives, in general a positive effect is found on improving thermal resistance, although this generalization could not apply, considering the large number of different PU and environmental conditions of usage.

Keywords: polyurethane, thermal resistance, structure, additives, stability

1. Introduction

Polyurethanes (PUs) are characterized by excellent properties such as good resistance to abrasion and good oil and atmospheric resistance. Their main applications are very wide, as flexible foam in upholstered furniture and rigid foam in wall insulations, roofs, and appliances; thermoplastic PU resins in medical devices, automotive parts, and footwear industries; and last but not least their uses as coatings, adhesives, sealants, and elastomers (CASE) which are very important, for example, on floors and pipe protection and again in automotive parts.

It is not unusual that PU have to sustain very high temperatures in several uses, specially in applications such as defense [1]. For example, high-temperature resistant adhesives are required in advanced aircraft, space vehicles, missiles, and ground vehicles [2].

Thermal stability describes thermal durability as well as heat resistance. Polymers with higher thermal stability are characterized by higher melting points, softening and thermal decomposition, smaller mass loss during heating at high temperatures, and higher heat deflection temperature under load, without losing their basic properties which determine its functionality. In respect to analytical techniques, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were traditionally used to evaluate the thermal properties of several types of polyurethane and are still standard analytical techniques that are utilized. Thermal stability requirements can be summarized in the following statements: retention of mechanical properties (melting/softening point), high resistance to chemical attack, and high resistance to breakdown, specially under oxidative conditions.

The following figure introduces the general reactions involved in PU thermal decomposition:

The first reaction is fast. Flammable gases then react much faster with oxygen, producing more heat and small molecule gaseous degradation products (**Figure 1**). Finally, char reacts with oxygen but in a much slower rate, releasing heat but with a lesser rate. The first step of the degradation includes the scission of the urethane bonds to obtain the polyol and the isocyanate groups apart. In the second set reactions, dimerization gives off gaseous carbon dioxide and carbodiimide, and trimerization gives isocyanurates, while reactions with water render aromatic amines and carbon dioxide again. Heat is released in every reaction step, sustaining degradation until eventually a compact char is left.

PUs have unique properties derived from their two-phase microstructure composed of hard and soft segments. Soft segments (SS) are formed by polyols and have low glass transition temperatures, while hard segments (HS) are derived from diisocyanates and chain extenders and possess high glass transition temperature. PU can be considered as a block copolymer with alternating soft and hard segments along the macromolecule chain. The SS originates from the polyol and imparts extensibility to PU. The HS which is composed of urethane and aromatic rings aggregates into microdomains resulting from the hydrogen bonding, and the domains provide physical cross-linking points for materials [3].

Ingredients for manufacturing PU are polyisocyanate, polyester or polyether polyol, and a chain extender like a diol or diamine. The most reactive component is isocyanate due to its -NCO groups. The quality of PU obtained depends on the ratio of -NCO to -OH groups to obtain a good end product with the required properties. Insufficiency as well as an excess of -NCO groups will result in the formation of allophanate or biuret compounds, with different properties. On the other side, urea and isocyanurate linkages displayed higher thermal stability than polyurethanes [4].

Thermal stability of PU has been extensively studied for many decades. As introduced above, three general reactions can occur during the thermal degradation of polyurethane: (i) dissociation to the original polyol and isocyanate; (ii) formation of a primary mine, alkene, and carbon dioxide; and (iii) formation of a secondary amine and carbon dioxide [5]. The tendency for a particular mechanism depends on the chemical nature of the groups, adjacent to the urethane linkage, and the environmental conditions. Polyurethane degradation usually starts with dissociation of the urethane bonds and carbon dioxide and isocyanate evaporation [6]. The general consensus, however, is that decomposition occurs in three steps at the level
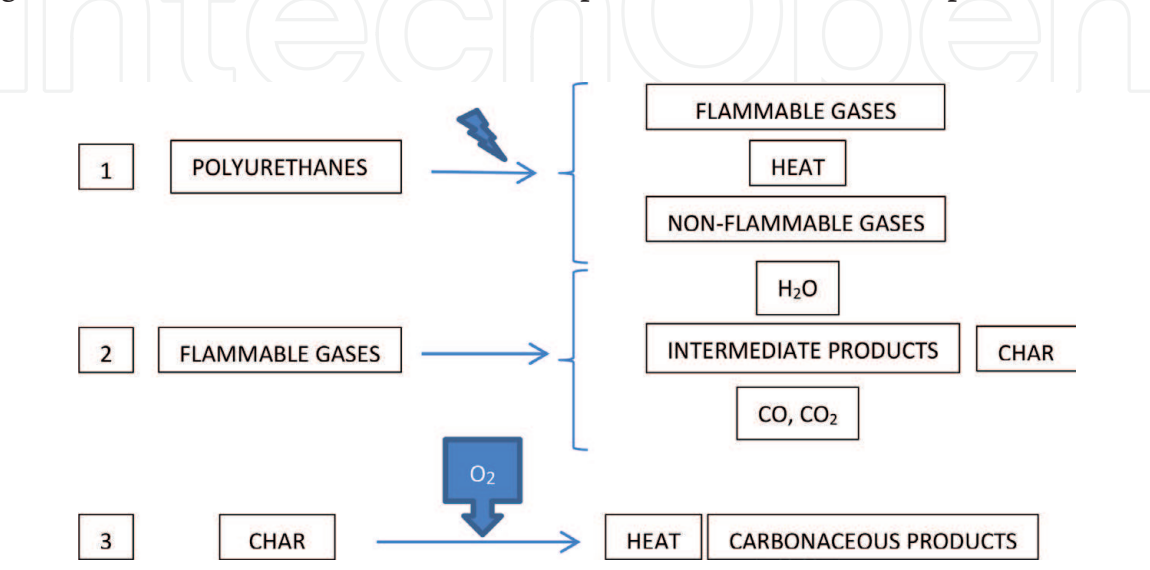

Figure 1.
General mechanism of thermal decomposition of PUs.

of the urethane group between 200 and 300°C [7]. The most important factors that determine thermal stability of PU are the nature of starting materials and the condition of polymer preparation [4].

When polyurethanes undergo thermal degradation, some potentially hazardous chemicals are released. These chemicals could not lead to visible warning. When PU is submitted to high temperatures, special health and safety precautions should be put in practice. It was early noticed that at temperatures above 600°C, cyanide is produced from PU decomposition and polyureas, giving off the so-called yellow smokes [8, 9] and emission of other toxic products [10]. The conditions of synthesis (polycondensation) and the nature of the reagents (initial prepolymers and monomers) influence the composition of the volatile compounds and residues arising from decomposition [7]. Health and safety, apart from material performance, is one of the reasons why it is important to establish heat stability ranges for materials with such a wide spectrum of utilization as PUs.

This review is intended to convey a brief compilation of research in the field of thermal resistance of non-foamed PUs and to identify strategies to augment stability to high temperatures of PUs and its composites. It is not focused in other aspects of PU which has been thoroughly covered by many other experts in reviews and books [6, 10–16]. We will concentrate on the effect of structural changes and on the effect of additives on PU thermal resistance. This contribution has in mind that the vast information about thermal properties of PU cannot be summarized in one single review but tries to present main factors that determine thermal resistance of these important polymeric materials.

2. Effect of structure on PU thermal resistance

The first structural factor that greatly influences thermal resistance is phase microstructure; this is the nature, proportion, and segregation of soft and hard segments (SS and HS, respectively). At the same time, microphase is determined by the chemical structure of PU (polyol, isocyanate, and chain extender type), so the effect of phase microstructure on thermal resistance often overlaps with chemical structure. Therefore, individual effects are rather complex to analyze. Thermal degradation is mainly initiated within the HS, which has normally the faster degradation stage. When it comes to SS, as this is composed by macrodiol, which is typically the weakest link in the oxidation of PU elastomers, using macrodiols that have high oxidative stability could give PUs with better thermo-oxidative stability. A lower flexibility in chains of SS domains produced a lower thermal resistance threshold (temperature where 5% sample weight is lost) as a result of lower crystallinity [17]. The structure of the HS has more influence on thermal stability rather than SS structure. Interurethane hydrogen bonding plays a significant role in the thermal stability of segmented PUs, which can be enhanced by a higher degree of phase separation between SS and HS [18]. The higher the concentration of the urethane group, the lower are both the activation energy for thermal decomposition and the thermal stability of the PU [19].

The polyester polyol-based PUs are more stable than the materials obtained with polyether macrodiols [4, 18]. For example, onset decomposition of polyether-polyurethane in air is about 245°C. This is anticipated to be about 13°C as compared with that in nitrogen atmosphere. Such anticipation suggested that polyester-polyurethane is more stable thermally than polyether-polyurethane. It also suggested that the different soft segments will influence the thermal stability of PU [20]. Polycarbonate diols, cured with MDI and chain extended with 1,4-butanediol, showed a drop-off in the weight of samples at around 290°C [21]. Krol and Pilch

Pitera [22] studied the effect of increasing polyol chain length on TDI-cured poly-oxyethyleneglycols; the heat effect of endothermic processes within 260–420°C becomes lower and lower, while the effect at 360–440°C becomes more important. They correlated this effect with the increasing share of ether-type bonds or ester-type bonds with simultaneous reduction in the number of urethane groups; poly-ether PUs from polypropylenglycol (PPG), HDI, and BDO had melting temperatures of 223°C [23]. These few examples are representative of the general trend that poly-ester polyol-based PUs are more thermally stable than polyether macrodiol-based PUs. Hydroxy-terminated polybutadiene (HTPB) are a particular telechelic polyol in which PUs are utilized as liners for composite propellants in the manufacture of rockets. When reacted with TDI and cross-linked with small molecular weight diols as chain extenders, the final stage of decomposition was at 375°C [24].

The effect of isocyanates on thermal stability was seen early. The higher the symmetry of the isocyanate, the higher the thermal stability [25]. Aliphatic isocyanates give urethanes a higher thermal stability [4]. The decomposition of polymers made with 4,4′-diphenylmethane diisocyanate (MDI) occurred above 400°C and was at least a two-step process, while the decomposition of polymers containing toluene diisocyanate (TDI) occurred below 400°C and appeared to be a one-step reaction [26]. For PUs cured with 4,4′-dibenzyl diisocyanate (DBDI), based on polytetramethylene ether glycol (PTMEG) and chain extended with butylenglycol, three main degradation processes were seen: at approximately 340°C the decomposition of urethane groups occurred, at 420°C the destruction of ether groups took place, and at 560°C the destruction of carbon chains and rings began. In general, the DBDI material had a higher thermal oxidation stability than the similar polymer achieved with MDI [14]. Polyurethanes made from polyester-based PUs cured with MDI had a better thermal stability than those based on TDI, according to their higher degree of hard segment crystallinity [26].

Natural oil-based polyurethanes generally had better initial thermal stability (below 10% weight loss) in air than the polypropylene oxide-based PU, while the latter was more stable in nitrogen at the initial stage of degradation. If a higher weight loss (50%) is taken as the criterion of thermal stability, then oil-based polyurethanes appear to be more thermally stable material [27–30]. PU prepared from formiated soybean oil polyols and TDI with different OH functionalities showed an initial weight loss process at 210°C, while maximum weight loss was at 400°C [31]. An increase in NCO index of elastomeric PU samples prepared from soybean oil-derived polyol increased hydrogen bonds and consequently thermal stability [32]. PU from TDI, polycaprolactone, butanediol, and monoglyceride of sunflower oil had the first and second maximum peaks both linked to the degradation of urethane bonds in the rigid segment of PU. The third and fourth maximum peaks were the results of degradation of the ester bonds in the soft segments, which take place from 380°C, while the composition of the aromatic compounds begins at 480°C [33]. This findings support the fact that research on oil-based PUs is increasing, considering their natural origin and good thermal resistance properties.

PUs synthesized with the use of oligomeric α,ω-dihydroxy(ethylene-butylene adipate) (dHEBA) polyol, aliphatic 1,6-hexamethylene diisocyanate (HDI), and 1,4-butanediol (BDO) were stable until 428°C. Ten percent of initial mass was lost at 344°C [32] which is a higher temperature than TDI or other conventional polyether polyols such as polytetramethylene ether glycol-derived PUs [33]. A TPU made from polycaprolactone polyol cured with polymeric diphenyl diisocyanate prepolymer displayed a 5% weight loss at about 260°C [34]. The thermo-oxidative degradation of phosphorus-containing polyurethane based in polypropylene glycol, TDI, and 1,4-butanediol incorporating phenylbis(hydroxyethyl) phosphonate was studied by using TGA. The onset of thermal degradation is lowered to 360°C due

to the lower thermal stability of phosphorous chain extender [35]. Although being cured with TDI, thermal resistance is much higher than for other TDI-cured PUs. Phosphonate PU displayed high thermal resistance: during the thermal degradation, the phosphorous molecules form a protective layer on the polymer surface, increasing the polyurethane thermal stability [36].

Regarding chemical structure, biuret and allophanate linkages are the thermally weakest chemical entities in PU networks. Dissociation of both types generally takes place above about 110°C and is completed by about 170°C [37]. These linkages appear when unbalanced ratios of NCO and OH groups are present in reactants and are not normally desired regarding improvement of physical properties. An increase in cross-link density, type of cross-linking, and introduction of isocyanurate ring structures in the polymer chain backbone also has a strong beneficial effect on the thermal stability of polyurethanes [4].

Finally, thermoplastic polyurethanes (TPU) are a relatively novel group of the family of PUs and have high comparative thermal resistance [38] which allows them to being easily processed. TPU were introduced by DuPont in 1954 and developed through the 1950s and 1960 [39]. In general, polyurethanes have no pronounced melting point endothermic peak on differential thermograms, which is characteristic of noncrystalline polymers. On the other side, TPU have a distinct behavior compared to conventional PU, exhibiting thermal patterns like thermoplastics. For example, TPUs synthesized from novel fatty acid-based diisocyanates were reported to display considerable thermal stability without any significant loss of weight at temperatures below 235°C [40]. Significant thermal decomposition was observed only after 300°C [41].

3. Effect of additives on PU thermal resistance

In studying the complex structure and morphology of polymers modified by mineral fillers, some problems may arise concerning the character and extent of interaction at the polymer-filler interface, the homogeneity of filler distribution, the filler orientation in the case of filler anisometric particles, and the polymer-filler adhesion [42]. Polyurethanes do not get aside from this general rules. Thermal stability of PU has been reported to be improved via hybrid formation such as the incorporation of fillers, e.g., nanosilica, Fe_2O_3, and TiO_2, silica grafting, nanocomposite formation using organically modified layered silicates (nanoclays), incorporation of Si-O-Si cross-linked structures via sol-gel processes, and the incorporation of polyhedral oligomeric silsesquioxane (POSS) structures into the PU backbone or side chain [43].

Nanoclays confer high barrier performance and improved thermal stability in composites with plastics, which make these compounds suitable for many applications [44, 45]. In a PU made from HTPB, PTMEG, and TDI, TGA results revealed that the thermal stability of PU was improved by nanoclay sepiolite, and the onset decomposition temperature for PU nanocomposites with a sepiolite content of 3 wt% was about 20°C higher than that for pure PU. Initial degradation temperature for nanocomposites was around 300°C [46] and when Cloisite was utilized with PTMEG-TDI-BDO PU, an exotherm at 370–375°C in differential scanning calorimetry studies [47].

Small amounts of nanoclays as modifier to polyurethane matrix led to an increase in degradation temperature. The clay plates acted as barrier to oxygen transfer causing the degradation temperature to move to higher temperatures [48]. Stefanovic and coworkers [49] have shown that that polyurethane nanocomposite (PUNC) began to degrade at a temperature 20–40°C higher than pure PU copolymers. PUNC were

prepared from α,ω-dihydroxy-poly(propyleneoxide)-b-poly(dimethylsiloxane)-b-poly(propylene oxide) (PPO-PDMS-PPO) and organo-montmorillonite nanoclay (Cloisite 30B®) and cured with diphenylmethane diisocyanate.

Rubbery modulus for PU based on PTMEG as soft segment, isophorone diisocyanate as diisocyanate, and 1,4-butanediol as chain extender reinforced with nanosilica increased to higher temperatures, enhancing mechanical and thermal properties [50].

For thermoplastic PU composites filled with huntite and hydromagnesite mineral fillers, thermal decomposition occurred through double step with maximum rates at 347 and 411°C, and two shoulders are seen at 300 and 466°C, leaving 1.3 wt% carbonaceous char [51]. The TGA analysis of synthetic silico-metallic mineral particles (SSMMP) based on talc added to PU made from polycaprolactone and hexamethylene diisocyanate showed a significant increase in the onset temperature of the nanocomposites evidencing that the thermal resistance increased with the increase in the amount of filler added. The degradation temperature of the pure PU was the lowest, with a value of 301°C, and the degradation temperature for nanocomposites with 3 wt% of SSMMP was the highest, with values of 337–340°C [52]. Polyester-type PU filled with talc produced a 7°C increase in temperature for 5% weight loss [53].

Silsesquioxane cage structure-like hybrid molecules produce nanostructured organic-inorganic hybrid polymers called polyhedral oligomeric silsesquioxane. The POSS chains act like nanoscale reinforcing fibers, producing extraordinary gains in heat resistance. Octaaminophenyl POSS was used as a cross-linking agent together with 4,4′-methylenebis-(2-chloroaniline) to prepare PU networks containing POSS. TGA results showed the thermal stability was improved with incorporation of POSS into the system. The results can be ascribed to the significant nanoscale reinforcement effect of POSS cages on the polyurethane matrix [54].

Together with fillers, fibers generally impart heat resistance to PU, or at least do not produce a deterioration effect. Thermoplastic PU elastomer nanocomposites (TPUC) filled with 15% carbon nanofiber submitted to the torch of the oxyacetylene test resisted up to 210°C for 5 seconds, while non-filled TPU resisted only up to 175°C [55]. Composites of PU made from HTPB and TDI with coir and sisal fiber showed a principal degradation peak at around 400°C. PU from HTPB and TDI displayed the same general behavior [56]. However, there are reports that stated that fiber loading decreased thermal stability of composites with TPU: main temperature peak of complicated decomposition of a TPU was around 363°C. At the TPU/Kenaf 20% fiber loading, the first peak occurred between 246 and 369°C, with a threshold at 346°C [57]. TPUs have been reinforced with synthetic fibers such as glass [58], aramid [59], and carbon fiber [60].

Flame retardants delay decomposition temperature of PU. A study of the effect of ammonium polyphosphate (APP) on the thermal stability of some N-H and N-substituted polyurethanes showed that degradation mechanism could differ markedly [61]. Phosphorus flame retardants augment thermal resistance of PU. In pure PU, the specimen surface gradually degrades to volatile oligomers, monomer, and some molecules, whereas the presence of phosphorous flame retardant additive causes delay in degradation of polymer matrix. Phosphorus flame retardant additive compounds have low thermal stability, are decomposed earlier, and protect underlying PU matrix [20, 62]. Also, a range of stabilizers, including both organic and inorganic additives for better stability against different types of degradation, are available, with a focus on their efficacy and mechanisms of action [18].

Blending with other polymers is another strategy to augment thermal resistance of PU. Thermal decomposition of blends of a polyester urethane and polyether sulfone with or without poly(urethane sulfone), taken as a compatibilizing agent, was studied by TGA under dynamic conditions. Polyester-urethane has a temperature for

5% mass loss of 328°C and poly(ethersulfone) was 500°C, while among blends the one with 80/20 poly(ether sulfone)/polyester urethane had the higher value of 360°C [63]. Thermal resistance of styrene-butadiene-styrene rubber (SBS) was improved before and after thermal aging as the amount of added TPU was increased in rubber blends obtained via melt blending [64]. Thermal stability of a polyether-based TPU was found to be improved as a result of the incorporation of 5% polypropylene-graft-maleic anhydride (PP-g-MA) and 40% wollastonite: temperature for 50% weight loss increased from 380 to 416°C for composite compared to TPU [65]. From thermal degradation of polypropylene/TPU and ammonium polyphosphate blends, carbodiimide was generated, which, because of its unstability, also reacted with water to give urea. These several cross-linking reactions stabilize the urethane bonds until 400°C [66]. PP/TPU blends with fire retardants formed an intumescent char residue protecting the matrix which prevented first peak of thermal degradation up to 200°C [67]. Thermoplastic elastomers can be prepared by creating blends of an elastic polymer with a dimensional stabilizing polymer [68] and enhance thermal/mechanical properties. Also stabilization of PU elastomers against thermal degradation by polymer modification could be achieved by introducing natural derived polymeric materials such as lignin in HTPB macrodiol [18].

Finally, the following figure is designed to summarize the main factors that affect thermal resistance of PU (**Figure 2**):
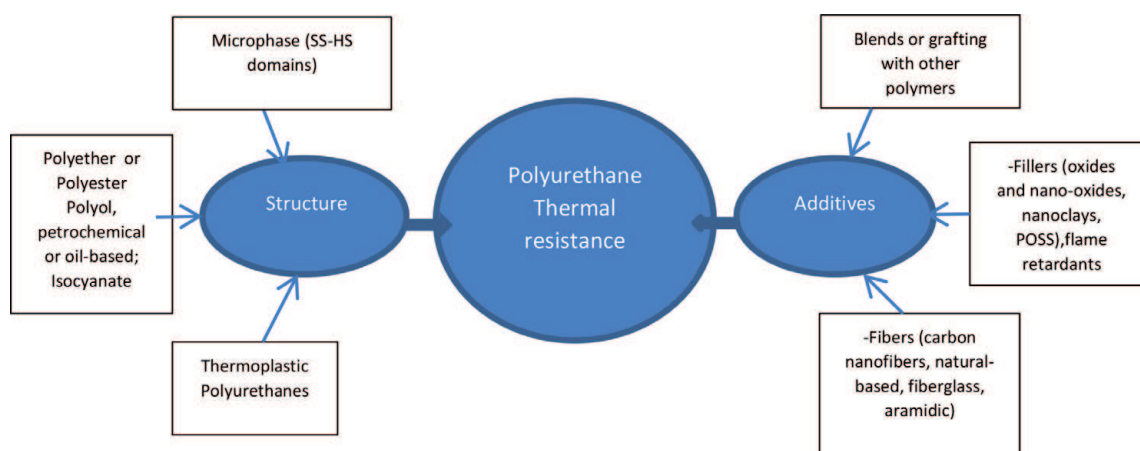

Figure 2.
Main factors that determine polyurethane thermal resistance.

4. Conclusion

As a result of this review compilation, it was concluded that the two main general factors that determine thermal resistance of PUs are its structure from one side and the presence of additives on the other side. The structural factors that influence thermal stability of PUs are the chemical nature and composition of hard (isocyanate plus chain extender) and soft (macrodiol) segments, its segregation, and PU thermoplasticity (derived from characteristic of TPU's stable linear structure). The additives that have a marked effect on augmenting thermal stability of PUs are mineral fillers (e.g., nano-oxides, nanoclays, talcs) and specific modifiers like POSS, flame retardants (both as additive and as polyol modifier), and fibers (natural or synthetic). Also, blending and grafting with other polymers are strategies that are utilized for increasing thermal resistance of PU, both for improving processing in manufacture and for high demanding applications. However, it is necessary to state that this review did not attempt to cover all particular factors that need to be taken into account when studying thermal stability of PU. Complex PU structures will

potentially have several weak chemical links, variable intermolecular forces, different relevant properties such as thermal conductivities, and even environmental factors that may cause decomposition (i.e., hydrolysis by moisture, acidity, oxidative or non-oxidative atmosphere) will contribute to only predict thermal stability in more or less broad temperature ranges.

Conflict of interest

The author declares no conflict of interest for this publication.

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