



TECHNOLOGY OF HIGH TEMPERATURE RESISTANT COATINGS FROM POLYURETHANE

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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.

Introduction

Polyurethanes 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 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. For example, high-temperature resistant adhesives are required in advanced aircraft, space vehicles, missiles, and ground vehicles.

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.

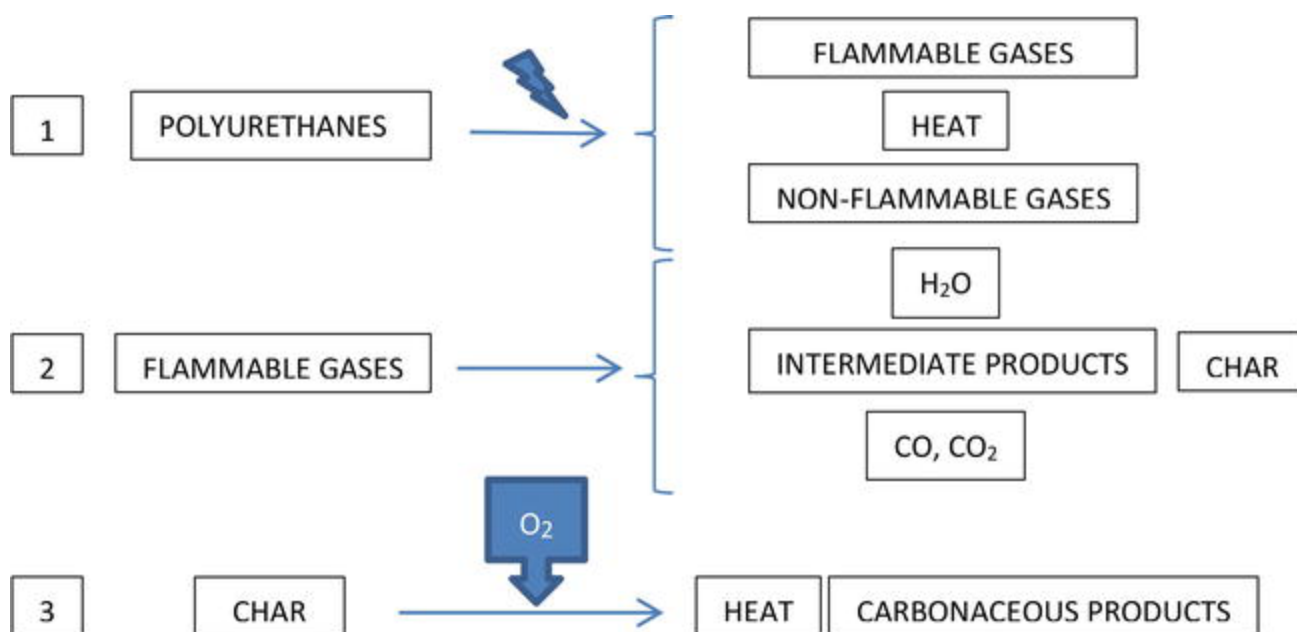


Figure 1.

General mechanism of thermal decomposition of PUs.

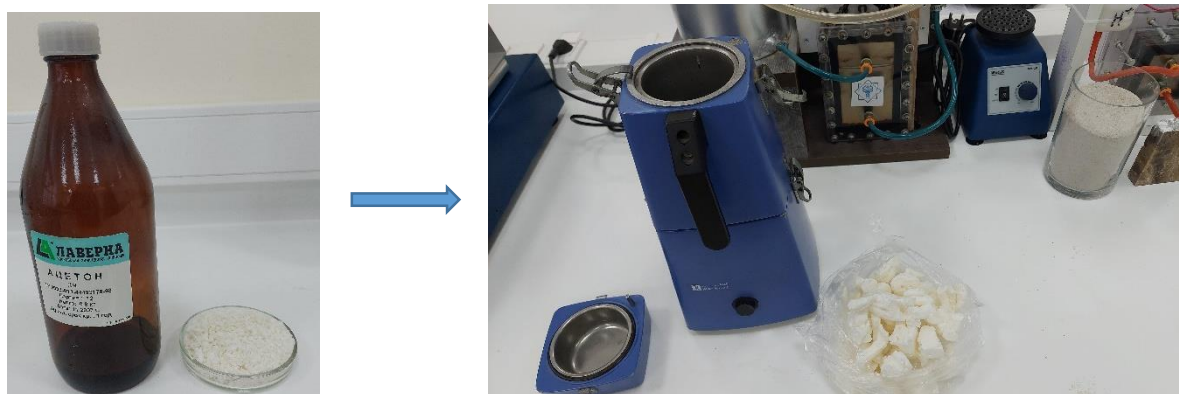
PUs have unique properties derived from their two-phase microstructure composed of hard and soft segments. Soft segments (SS) are formed by polyols and have low glass transition temperatures, while hard segments (HS) are derived from diisocyanates and chain extenders and possess high glass transition 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.

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 amine, alkene, and carbon dioxide; and (iii) formation of a secondary amine and carbon dioxide. 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. The general consensus, however, is that decomposition occurs in three steps at the level of the urethane group between 200 and 300°C. The most important factors that determine thermal stability of PU are the nature of starting materials and the condition of polymer preparation.

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 and emission of other toxic products. 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. 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.



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. 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. 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. 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. 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.

The effect of isocyanates on thermal stability was seen early. The higher the symmetry of the isocyanate, the higher the thermal stability. 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. 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. 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.

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. 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. An increase in NCO index of elastomeric PU samples prepared from soybean oil-derived polyol increased hydrogen bonds and consequently thermal stability. 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. This findings support the fact that research on oil-based PUs is increasing, considering their natural origin and good thermal resistance properties.

Thermoplastic polyurethanes are a relatively novel group of the family of PUs and have high comparative thermal resistance which allows them to being easily processed. 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. Significant thermal decomposition was observed only after 300°C.

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. 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.

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