Statistical Treatment of Allophanate Crosslinking in the Formation of Polyurethane Networks

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Summary

Crosslinking of polyurethanes by a reaction of isocyanate groups with urethane groups leading to trifunctional allophanate branch points is treated statistically using the theory of branching processes. The occurrence of gelation in the diol – diisocyanate system and its dependence on the excess of isocyanate groups and the intensity of allophanate formation is discussed.

Introduction

The formation of allophanate groups is the most important side reaction accompanying the formation of polyurethanes. Allophanate (A) groups are formed from isocyanate (I) and urethane (U) groups

\[ -\text{NHCO}^- + -\text{NCO} \xrightleftharpoons[k_1]{k_{-1}} -\text{NCO}^- + -\text{CONH}^- \]

It has been found (1) that (a) this reaction is reversible; the rate and equilibrium constants depend on the nature of the catalyst, and the stability of A decreases with increasing temperature, (b) the formation of A leads to additional crosslinking since A has a functionality of three. Allophanate formation is sometimes considered undesirable (branching and gelation in linear polyurethanes), but sometimes it has a beneficial effect as it improves the ultimate properties of polyurethane networks. Also, polyurethanes lightly crosslinked by A can be processed as thermoplastic rubbers at elevated temperatures when A groups dissociate and are re-formed at lower temperatures.

In spite of the importance of A formation, no quantitative study is available correlating the extent of A formation with branching, gelation and network formation. In this contribution, a theoretical approach to crosslink formation by A is presented, based on the theory of branching processes which was earlier applied to polyurethane networks when urethane formation was the only proceeding reaction (2-4).
Statistics of Formation of Urethane-Allophanate Networks

The hydroxyl groups (H) in the polyol and isocyanate (I) groups in diisocyanate are considered of equal and independent reactivity; cyclization is not taken into account. As is seen from Eq. (1), the urethane group is bifunctional (U = -H-I-) whereas the allophanate group is trifunctional (A = -H-II-) and is composed of two former I groups. Because the probabilities for I to be bound in A or U are different and only a single I-I bond is present in A (I-I-I-... is not allowed), one has to distinguish between reacted I-units by adopting a different notation

\[
\begin{align*}
I \text{ (in urethane)} & \rightarrow U, \\
I \text{ (in -HII- of A)} & \rightarrow X, \text{ i.e. } A = -H-X-I, \\
I \text{ (in -H- of A)} & \rightarrow Y.
\end{align*}
\]

The extent of A formation can be characterized in two ways - either by the fraction of reacted I groups in A \((X+Y)\),

\[
\alpha_A = \frac{2[(I_0 - I) - (H_0 - H)]}{I_0 - I} = \frac{2A}{I_0 - I} = \frac{2[1 - \frac{\alpha_H}{\alpha_I}]}{I_0 - I} 
\]

or by the fraction of reacted H groups in A,

\[
\alpha^* = \frac{I_0 - I - (H_0 - H)}{H_0 - H} = \frac{A}{H_0 - H} = \frac{\alpha_A/2}{1 - \alpha_A/2} 
\]

In these equations, I, H, and A are the respective molar concentrations of isocyanate, hydroxyl, and allophanate groups, the subscript 0 refers to initial concentrations. The conversions are defined as \(\alpha_I = (I_0 - I)/I_0\), \(\alpha_H = (H_0 - H)/H_0\), \(r_H\) is the initial mole fraction \(r_H = H_0/I_0\).

Probability generating functions. Let us consider the reaction of mono-, di-, and trifunctional, H-containing components in the polyol, their distribution in the mixture being characterised by the respective mole fractions \(n_{H1}, n_{H2}, n_{H3}\) \((n_{H1} + n_{H2} + n_{H3} = n_H)\), with diisocyanate \((n_{H2} = n_H)\). The probability generating functions (pgf) for the number of bonds issuing from H- and I-containing units in the root read as follows

\[
F_{OH}(\theta) = [n_{H1}(1 - \alpha_H + \alpha_H\theta) + n_{H2}(1 - \alpha_H + \alpha_H\phi)^2 + \\
+ n_{H3}(1 - \alpha_H + \alpha_H\phi)^3]/n_H
\]

\[
F_{OI}(\theta) = \{1 - \alpha_I + \alpha_I[(1 - \alpha_A)\theta_{HU} + (\alpha_A/2)(\theta_{XH}\theta_{XY} + \theta_{YX})]\}^2
\]

where \(\phi = [((1 - \alpha_A)\theta_{HU} + (\alpha_A/2)\theta_{HXY})/(1 - \alpha_A/2).\)