MICROPHASE SEGREGATION IN SEGMENTED AMINE-CURED POLYURETHANES

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INTRODUCTION

The influence of chemical composition on microphase segregation in segmented polyurethanes based on 2,4 and 2,6 toluene diisocyanate (TDI) was investigated earlier by Schneider, Sung and co-workers (1-3). In these studies, polymers of varying degrees of phase segregation were prepared from the two types of TDI coupled to polyether or polyester soft segments and chain extended with butanediol. The extent of phase mixing was judged from infrared estimates of interurethane hydrogen bonding as well as from thermal properties, particularly the soft segment glass transition temperature Tg. In general, for 2,4 TDI-butanediol, which forms an amorphous hard segment structure, phase segregation was weak in samples with a 1000 molecular weight soft segment, but enhanced with increasing soft segment molecular weight, for the polyether as compared to the polyester soft segment, and with the use of 2,6 TDI which forms a crystalline hard segment structure.

More recent studies by Sung and co-workers (4-5) on 2,4 TDI polyurethanes, prepared by solution polymerization and cure with ethylene diamine, have shown that strong phase segregation occurs in these materials. Since the hard segment structure is amorphous, the improved phase segregation must be the result of the increased hydrogen bonding of the urea groups formed in the amine cure. The present work is directed toward understanding the structure and properties of polyurethanes based on 2,4 TDI and 80/20 mixtures of 2,4 and 2,6 TDI, cured with MOCA, which represent one of the most important commercial classes of polyurethane elastomers. These melt polymerized, amine cured polyurethanes are thermoset materials due to the formation of some biuret crosslinks. Although such
crosslinking is usually thought to play a major role in the properties, it will be seen that these materials, like those studied by Sung, are highly phase segregated. Comparisons are also made with polyurethanes cured with a non-carcinogenic replacement for MOCA.

The most direct measure of microphase segregation is offered by small angle X-ray scattering (SAXS). The quantitative application of SAXS has been recently described by several workers (6-8). The parameters used in the present work are the interface thickness \( a_I \) (assuming a sigmoidal density profile), the squared electron density fluctuation \((\Delta \rho)^2\), and the average inhomogeneity lengths \( k_H \) and \( k_S \) for hard and soft segments.

**THEORETICAL**

In the treatment of SAXS data obtained using a slit-collimated instrument, such as the Kratky camera used in the present work, one must distinguish between the experimental scattering curve \( \overline{I}(s) \) and the true scattering curve \( I(s) \), where the independent variable \( s \) is defined in terms of the X-ray wavelength \( \lambda \) and the scattering angle \( 2\theta \):

\[
s(2/\lambda) \sin \theta.
\]

In the present work, copper radiation with \( \lambda = 0.15418 \text{nm} \) was used. The data may be treated theoretically either in terms of the experimental (or slit-smeared) intensity function \( \overline{I}(s) \) or the true (or desmeared) intensity function \( I(s) \). In the present instance the true intensity function \( I(s) \) was obtained from the experimental intensity \( \overline{I}(s) \) using the iterative method of Glatter (9) to correct for distortion of the data arising from the finite length and width of X-ray beam and of the receiving slit. The correction process, known as "desmearing", can have a profound effect on the shape of the scattering curve, as shown in Figure 1. For this reason, theoretical methods have been devised to deal with the data in terms of the slit-smeared intensity function as well as in terms of the true intensity function. With the exception of the interphase thickness determination, the methods based on the true (desmeared) intensity function were used in the present work.

**Thickness of Interphase Boundaries**

For a system of two phases of finely divided particles having sharp boundaries, the SAXS intensity becomes inversely proportional to the fourth power of the angle, or of \( s \), at higher angles:

\[
\lim_{s \to \infty} [I(s)] = \frac{k_p}{s^4}.
\]

(2)