Increasing dynamical correlations near the glass transitions of polyurea and nanoparticle–elastomer composites

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Abstract
Using DMA (dynamic mechanical analysis) we study the glass transition behaviour of polyurea and polyurea-nanotube composites. Analyzing the real part $E'(T)$ of the complex Young’s modulus $E^*=E'+iE''$ using the approach of Berthier, et al. [1] we determine the size of a dynamically correlated region, which increases when approaching the glass transition $T_g$.

Polyurea Elastomers
Superior properties: Extreme resistance to abrasion and chemicals. Service temperatures from -60 to +200°C. Good biocompatibility and excellent mechanical properties. Two glass transitions were observed [2]. According to EHM model only possible, if distance between nanoparticles is of the order of the correlation length at $T_g$.

What is the size of dynamical correlations in polyurea at $T_g$?

Determination of $\xi(T)$ using $V(T) = (R/p\Delta C_p)(T_{maxE'/dT})^2$

Polyurea

Polyurea-MoS$_2$

Temperature and frequency dependence of $E'$ of polyurea (PU) and PU filled with MoS$_2$

Temperature and frequency dependence of $\tan\delta = E''/E'$

T$_g$ is due to loosely bound polymer chains attached to the hard segments.

From M. Vacatello, Macromolecules 2001

Fit to data with two Havriliak-Negami relaxations

$E^*(\omega) = E_c + \frac{\Delta E_1}{[1 + (i\omega\tau_1)^\beta]^\gamma}$

$E^*(\omega) = E_c + \frac{\Delta E_2}{[1 + (i\omega\tau_2)^\beta]^\gamma}$

References

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But most probably cooperative motion is stringlike

→ $\xi(T_g)=V(T_g)/r^2\kappa = 5.5$ nm

For $r=0.8$ nm