Editorial corner – a personal view

Ideal rubber theory and internal crosslinking in polyurethane elastomer

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Ideal rubber theory assumes affine deformation of Gaussian chains where entropy retrieves deformation resulting in an equation: $G = \rho RT/M_c = NkT$ (G : plateau modulus, ρ : density, R : gas constant, T : absolute temperature, M_c : molecular weight between crosslinks or of sub-chain, N : moles of sub-chain per volume, k : Boltzmann constant). Data showing a well-defined rubbery plateau increasing with temperature indicate that the polymer system follows the theory. It is derived for homogeneous systems but proved useful for others.

Polyurethane elastomer (PUE) typically contains about 70% soft segment and 30% hard segment and shows elastomeric behavior at ambient temperature. Interchain siloxane bonding being flexible and hydrophilic, significantly enhances adhesion, stress-strain behavior, water, and solvent resistance. The modulus is easily tailored by the theory via M_c and N as described above.

To synthesize PUE, isocyanate terminated prepolymers are synthesized and chain extended to build up the molecular weight (MW). To introduce crosslinking with well-defined M_c , isocyanate termini are capped with multifunctional hydroxy acrylate or amine alkoxysilane (<https://doi.org/10.1002/polb.23359>). In this way, all chains are ideally placed within the networks leaving no dangling chains. The acrylate-containing PUE is UV cured to form networked structure, while in the silane-containing version interchain siloxane bridges form via sol-gel reaction. Both PUE types exhibit well defined rubbery plateau over a long temperature range implying networks are well defined to follow the theory.

Prepolymer of MW 3500 Da showed about two times greater modulus than that of 7000 Da due to the halved M_c or doubled N according to the equation (<https://doi.org/10.1039/c1jm10722d>). When nano-sized silica particles were covalently introduced into PUE under constant N , plateau value is further increased owing to the filler effect. It is obvious that the theory works fairly well with nanocomposites having interchain siloxane bridges. For multiple crosslinks natural polymers and biodegradable fillers are often used. These include starch (<https://doi.org/10.1016/j.carbpol.2011.09.098>), hydroxyethylcellulose (HEC) (<https://doi.org/10.3144/expresspolymlett.2018.71>), gelatin (<http://doi.org/10.1016/j.porgcoat.2014.03.011>), and β -cyclodextrine (<http://doi.org/10.1016/j.porgcoat.2017.04.039>). Acrylate capped PUE and VTMS modified filler-containing PUE are UV cured. In all cases, plateaus are well developed and their values increase with decreasing M_c , and increasing filler loadings. Thus the theory is useful to confirm internal crosslinking where G is designed by M_c and N manipulations even for nanocomposites.

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