Chemical/Mechanical Analyses of Anhydride-Cured Thermosetting Epoxys: DGEBA/NMA/BDMA

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ABSTRACT:

The chemical state of cure in a thermosetting resin was used to predict the resin's equilibrium modulus. High performance liquid chromatography analyses of the sol fraction yielded molar dynamics for monomeric, oligomeric, and polymeric molecules. Their population density distributions were compared with theoretical predictions based on a chain-growth polymerization mechanism. The resulting chemical estimates of the state of cure were integrated into calculations yielding concentrations of network structures within the gel that contribute to the density of elastically active strands and junctions. The theory of rubber elasticity was then used to predict the equilibrium modulus. Measurements incorporated dynamic mechanical analysis. A comprehensive understanding of the polymerization mechanism and cure history are required for accurate simulations of contributions from branch nodes and chain links. Deterministic models based solely on chemical reaction analysis were used to estimate chain connectivity with the gel. Results were interpreted using stochastic-based reasoning.

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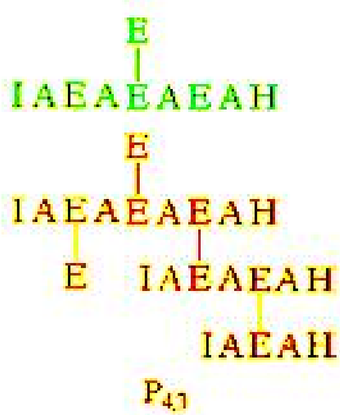

Figure 1. Representative molecule P_{41} for the resin DGEBA/NMA/BDMA.

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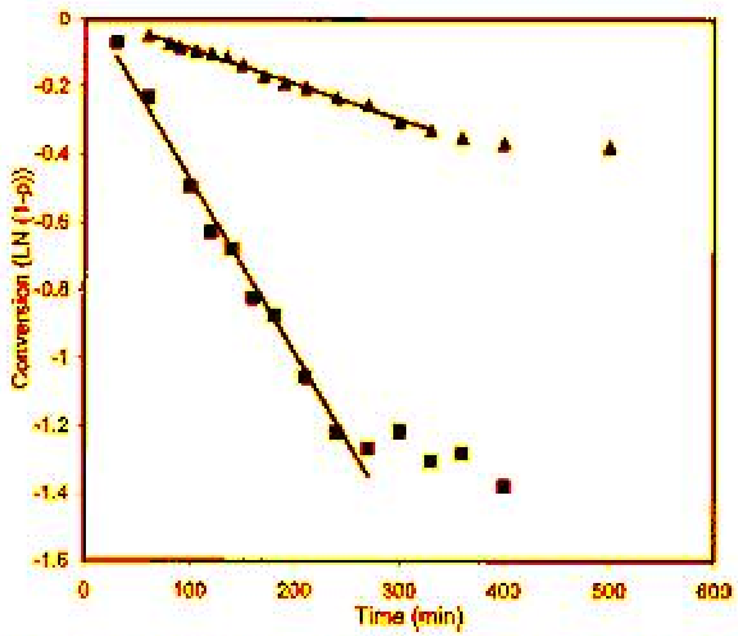

Figure 2. Decay dynamics of epoxy groups at 80 °C (▲, $\alpha = 200$; ■, $\alpha = 20$).

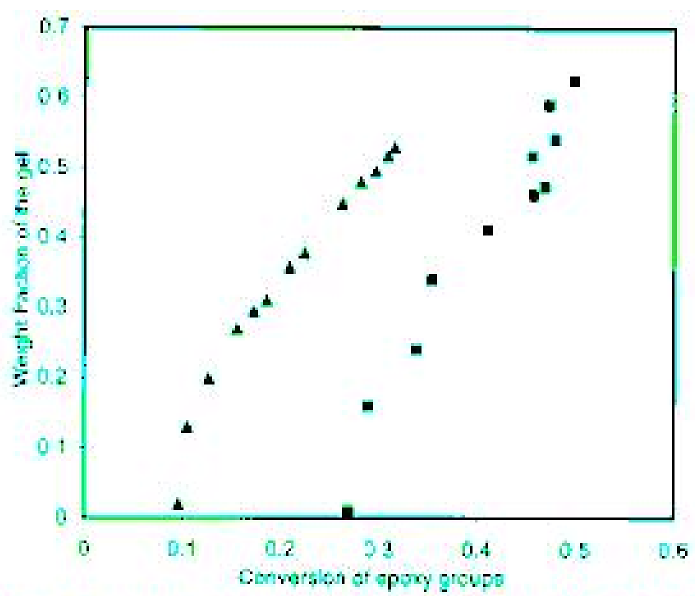

Figure 3. Evolution of the sol-gel partition of DGEBA/NMA/BDMA (▲, $\alpha = 200$; ■, $\alpha = 20$)

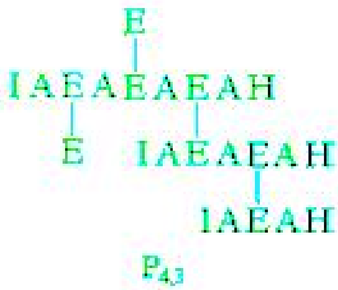

Figure 1. Representative molecule $P_{i,j}$ for the resin DGEBA/NMA/BDMA.

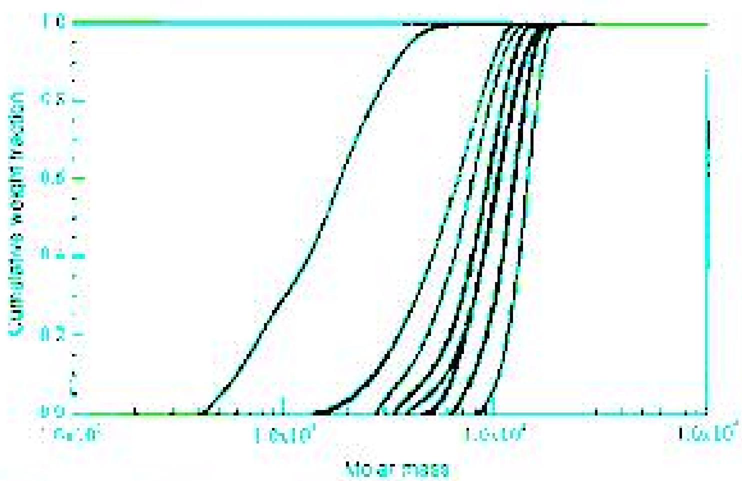

Figure 4. Evolution of molecular weight distribution of DGEBA/NMA/BDMA Reaction (II.DGEBA ratio 0.01 at 80 °C. Right to left: 135 min, 120 min, 100 min, 150 min sol, 80 min, 60 min, 190 min sol, 290 min sol)

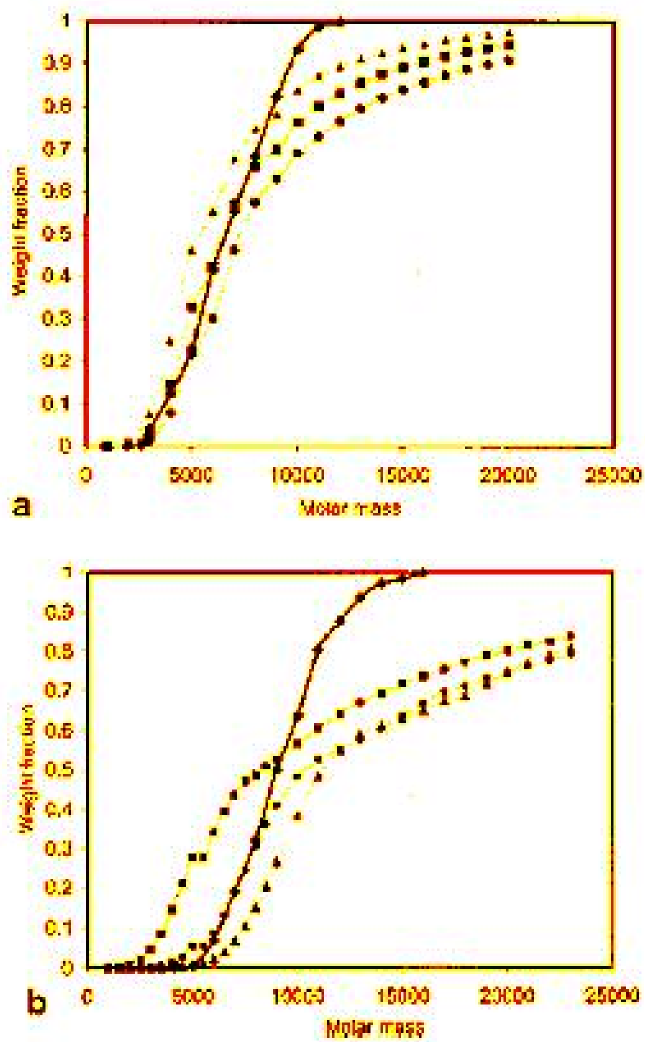

Figure 5. Molecular weight distribution of DGEBA/NMA/BDMA: (a) initiator/DGEBA ratio 0.01, 60 min at 80 °C [(◆) experimental; theoretical (●) α = 200, (■) α = 150, (■) α = 175]; (b) initiator/DGEBA ratio 0.01, 100 min at 80 °C [(◆) experimental; theoretical (●) α = 160, (▲) α = 200, (■) α = 120].

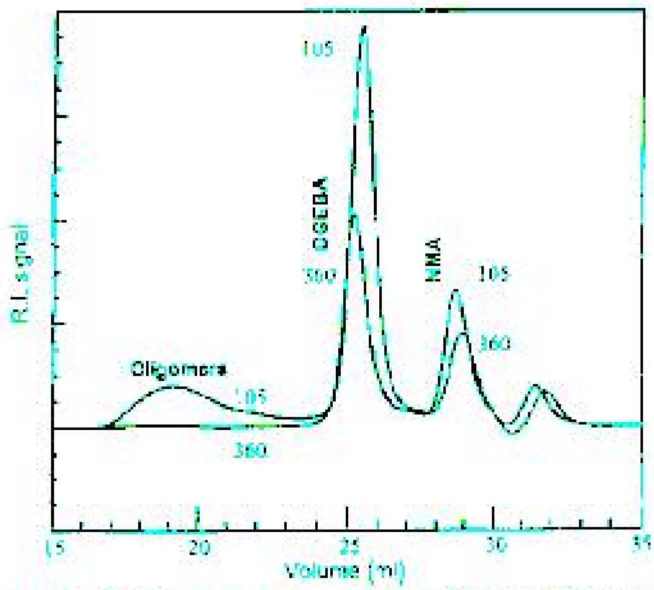

Figure 6. GPC chromatograms of DGEBA/NMA/BDMA reaction mixtures (initiator/DGEBA ratio 0.01, 80 °C).

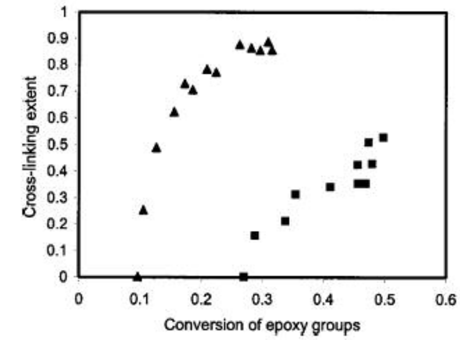

Figure 7. Cross-linking dynamics at 80 °C (▲, α = 200; ■, α = 20).

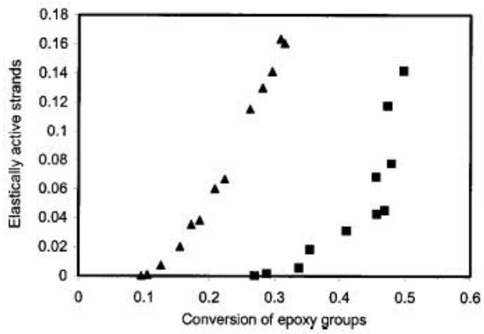

Figure 8. Theoretical growth of elastically active strands (▲, α = 200; ■, α = 20).

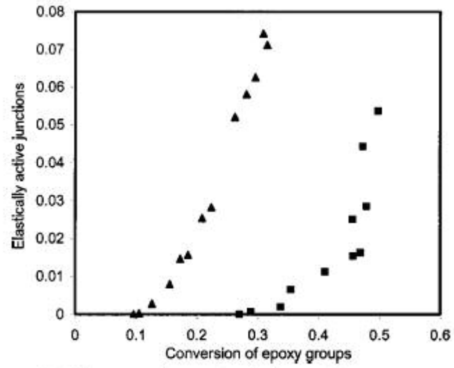

Figure 9. Theoretical growth of elastically active junctions (▲, α = 200; ■, α = 20).

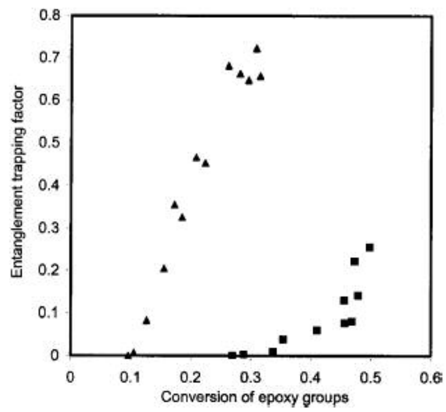

Figure 10. Prediction of entanglement trapping factor (▲, α = 200; ■, α = 20).

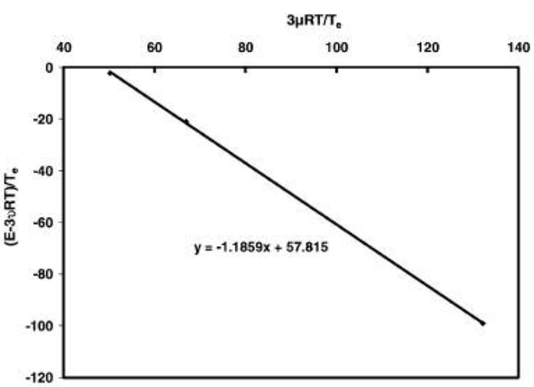

Figure 11. Experimental−theoretical comparison of rubber equilibrium modulus (assuming an affine network).