Under pressure at the nanoscale, polymers play by different rules

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Scientists putting the squeeze on thin films of polystyrene have discovered that at very short length scales the polymer doesn't play by the rules.

From buttons to storage bins, the molding of polymers is big business. At the nanoscale, processes such as nanoimprint lithography squeeze polymers to form patterns during the manufacture of semiconductor devices, organic electronics and optics. Thin films of polymer are important in adhesives, coatings and lubricants.

"Although applications for nanoscale polymer flow are being widely investigated, the underlying, fundamental polymer physics is not," said William P. King, a Kritzer Faculty Scholar and professor of mechanical engineering at the University of Illinois.

"Understanding the way a polymer flows during nanoscale molding or imprinting processes is essential for designing new, nanoscale manufacturing processes," said King, who also is a researcher at the university's Beckman Institute.

In a paper to be published Thursday (Oct. 2), by *Science Express*, the online version of the journal *Science*, King and collaborators at the U. of I. and Trinity College, Dublin, report polymer squeeze flow measurements made at unprecedented, short length scales.

"We found an unexpected increase in the squeeze flow of thin films when the film thickness was smaller than 100 nanometers," King said. "This seemed backwards. Normally, you would expect the polymer to become harder and harder to press into thinner films."

The effect was even more pronounced in polymers of higher molecular weight, King said. "We expected the viscosity to increase with increasing molecular weight, but we found the opposite to be true when the films were thin enough."

Film thickness and molecular entanglement was the key, King said. In thick films, polymer chains are tangled together like cooked spaghetti. However, when the polymer film starts with a smaller initial thickness, a point is reached where the polymer chains change the way they interact with their neighbors. In very thin films, the polymer chains can no longer intertwine, and become like isolated blobs. This change in entanglement decreases the viscosity and increases the lateral squeeze flow.

To make the measurements, the researchers used a modified nanoscale indentation technique, which pressed a flat "punch" into very thin films of polystyrene. The punch, which was much wider than the thickness of the film, forced the polymer to flow around it. This lateral squeeze flow governs the dynamics of polymer movement during processes such as nanoimprint nanomanufacturing.

The research is a significant step forward in the understanding of polymer deformation that is directly related to nanoscale manufacturing, King said. "Our results suggest that polymer flow during nanoscale manufacturing may be enhanced by selecting polymers of higher molecular weight."

With King, co-authors of the paper are former U. of I. postdoctoral researcher Harry Rowland, and physics professor John Pethica and physics lecturer Graham Cross, both at Trinity College.

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