Load-bearing entanglements in polymer glasses

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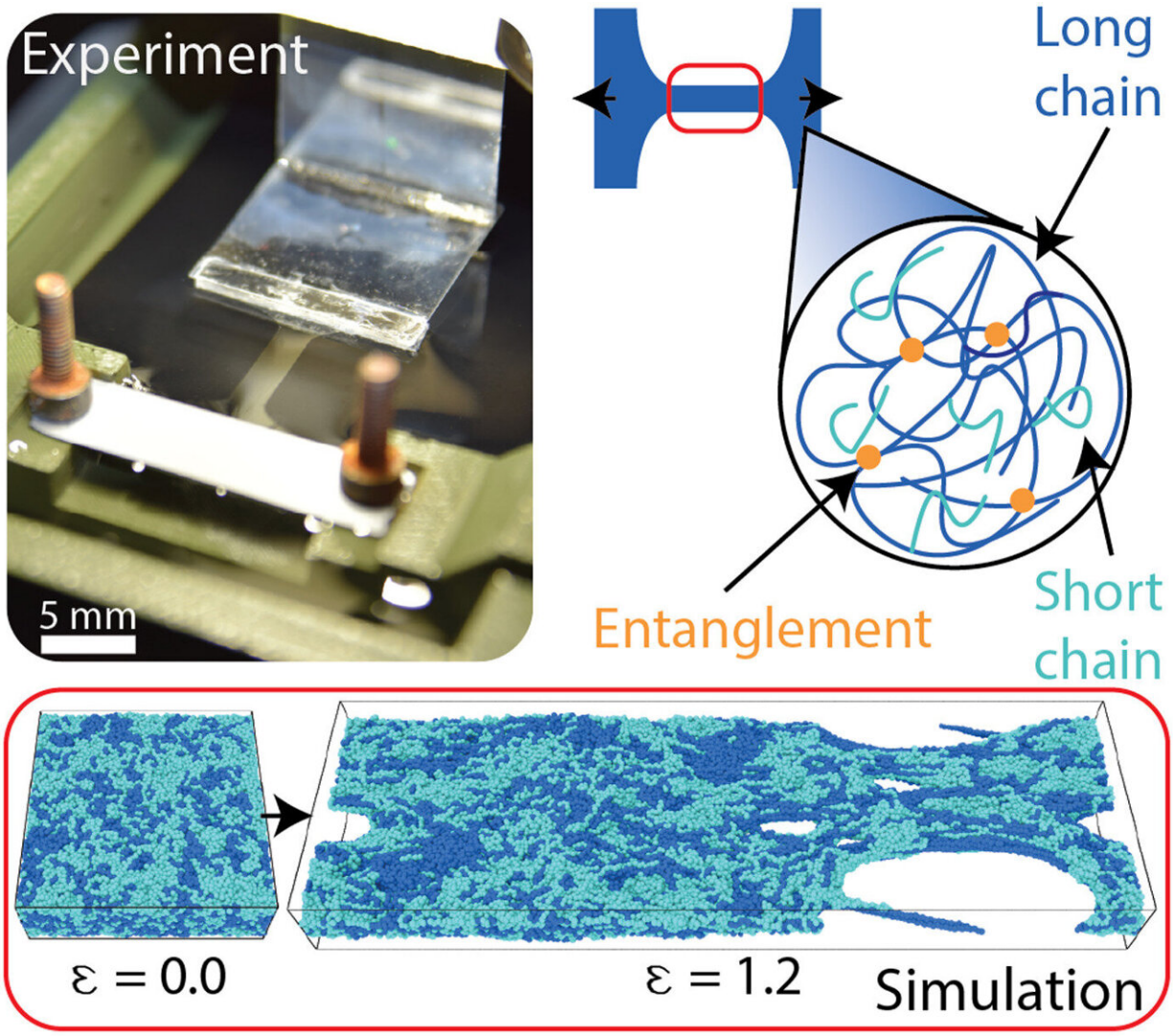


Blended homopolymer thin films. Macroscopic experimental dog bone–shaped specimen (pictured) loaded in TUTTUT for uniaxial extension. Molecular-level simulations depict chains sliding past one another to form openings in the film as

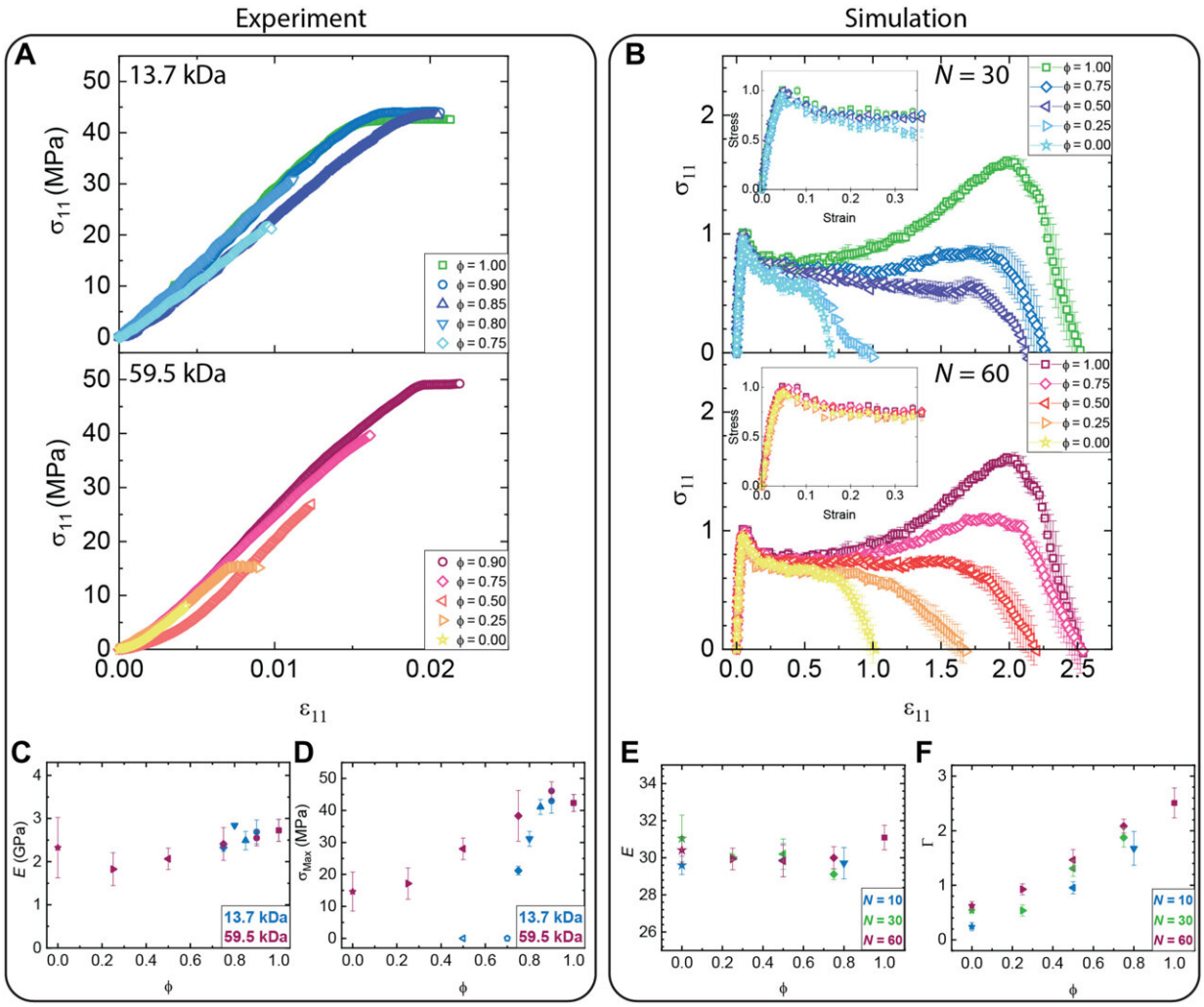
it is strained. Blended systems are composed of long (dark blue) and short (light blue) chains where most load-bearing entanglements (orange dots), if not all, are among the long polymer chains. Photo credit: C. Bukowski, University of Massachusetts Amherst. Credit: *Science Advances*, 10.1126/sciadv.abg9763

The role of entanglements can determine the mechanical properties of glass polymer blends. In a new report now published on *Science Advances*, Cynthia Bukowski and a research team in polymer science and biomolecular engineering at the University of Massachusetts and the University of Pennsylvania, U.S., developed a combined method of experiments and simulations to quantify the role of entanglements on polymer glasses. The team conducted uniaxial extension experiments on 100 nm thin films with a bidispersive mixture of polystyrene, for comparison with molecular dynamics simulations of a coarse-grained model of polymer glasses. The bidispersive blends allowed systematic tuning of the entanglement density present in both systems and the scientists measured the film strength experimentally and described the simulated film toughness using a model to account for load-bearing entanglements.

Breaking glassy polymers

Glassy polymers are important for a range of technologies from additive manufacturing to clean water filtration membranes. The stiffness and processability of the materials make them attractive for many applications for researchers to determine their lifetime and performance limits. The entanglements between polymer molecules in the glassy state play a significant role to determine strength. Glassy polymer materials are excessively brittle below a critical number of entanglements per molecule and can break at diminishing levels of stress. Polymer materials can dissipate energy above a critical entanglement density to

enhance their strength and toughness. These processes are unique and give rise to wide-ranging technologies. Enlargements are important for strength but require volatile and costly solvents or excessive temperatures during processing. In this work, Bukowski et al. combined new experimental strategies with molecular dynamics simulations to reveal how all entanglements did not equally contribute to a polymer glass. The team developed and validated a scaling theory to describe the number of strengthening entanglements per polymer chain to provide a framework to maximize strength with minimal entanglements in a polymer glass.

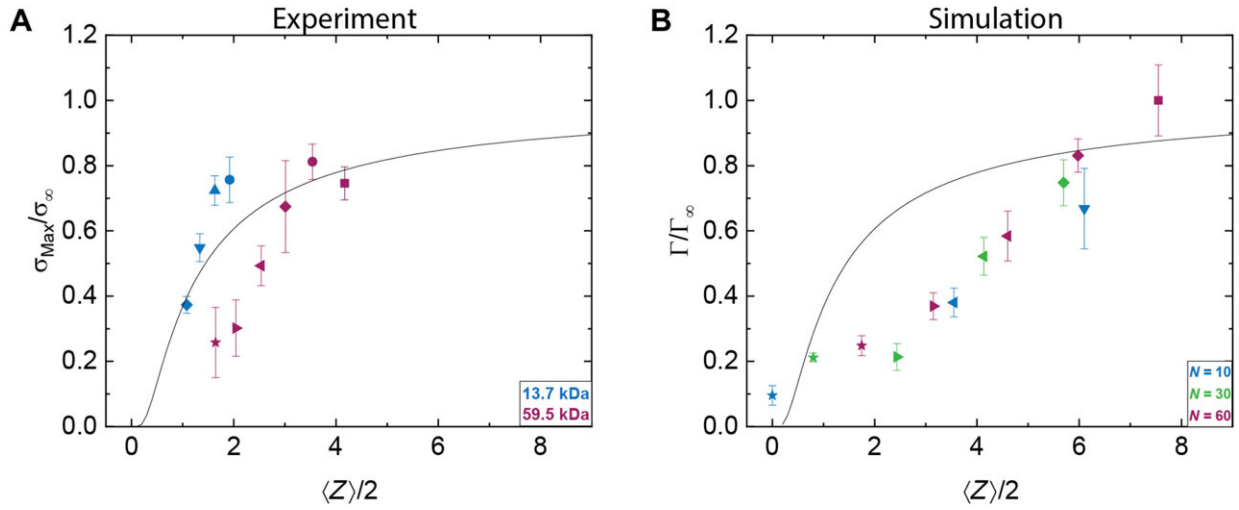


Stress-strain behavior of polymer blends. (A) Representative uniaxial deformation stress-strain response for each blend tested experimentally on TUTTUT. ϕ represents the volume fraction of long chains in the system. The top graph is blends with 13.7 kDa as the short chain diluent and the bottom with 59.5 kDa. (B) Uniaxial deformation stress-strain responses of N = 250 (⟨Z⟩ = 15.9) blended with N = 30 (top) and 60 (bottom) at a temperature of T/Tg = 0.71. ⟨Z⟩ is 1.8 and 3.6 for each short chain, respectively. Low-strain response is included in the inset of each section. (C) The elastic modulus (E) for each experimentally measured blend. (D) The average maximum stress for each blend measured experimentally. Error bars are 1 SD of five to nine averaged films. Open symbols represent blends that were attempted but too brittle to manipulate in TUTTUT and stretch uniaxially. (E) The elastic modulus for each simulated blend. (F) The toughness value for each simulated blend. Credit: *Science Advances*, 10.1126/sciadv.abg9763

The interplay of forces

The mechanical properties of the polymer glasses depended on the interplay of van der Waals forces and entanglements. Plastic deformation is often associated with shear deformation zones that precede crack growth. Entanglements play a significant role in shear deformation zones and their stability or resistance to form a crack is a function of entanglement density as well as temperature and strain rate. These deformations can be tracked experimentally with optical and transmission electron microscopy. Bukowski et al. overcame existing limits of the study by using a recently developed experimental method to measure the stress-strain response of ultrathin polymer films. Molecular dynamics (MD) simulations have provided valuable insights to the process of entanglements in polymer melts and glasses, where the simulations agreed very well with the experiments. In addition to the simulations, the scaling theories also contributed to define the role of entanglements in the mechanical properties of polymer glasses. The

combined approach of experimental and MD approaches allowed the team to examine the macroscopic perspective of experimental films and the molecular view of local dynamics simulations, to understand polymer strength.

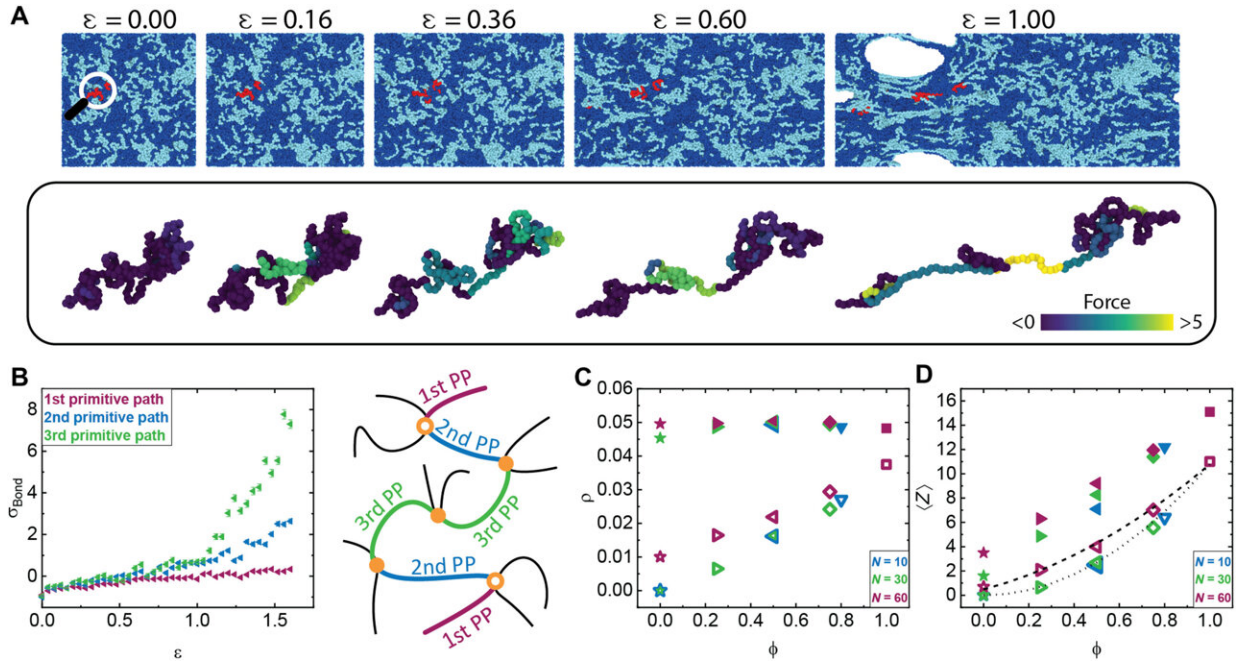


Data plotted against the Mikos and Peppas model. Normalized experimental maximum stress, σMax/σ∞ (A), and normalized simulated toughness, Γ/Γ∞ (B), as a function of entanglements, ⟨Z⟩. Here, ⟨Z⟩ is the Mn obtained from gel permeation chromatography of each blend divided by the Me of polystyrene (18.1 kDa). For simulations, ⟨Z⟩ is average chain length N for each blend divided by Ne (16). Maximum stress and toughness are normalized by the maximum stress of polystyrene chains Mn = 1.928 MDa and the toughness of chains N = 250, respectively. Credit: *Science Advances*, 10.1126/sciadv.abg9763

Mechanical properties of polymer blends and counting entanglements

Bukowski et al. regulated the number of entanglements in the system by mixing monodisperse polymers of the same chemical structure. This

method allowed them to sample a wide range of entanglements per chain. Both experiments and simulations provided qualitative insights to understand how the entanglement network contributed to the mechanical properties of glassy polymer materials. During the experiments, when the concentration of the longest chains decreased, the maximum stress and failure strain also began to decrease. The team noted different failure mechanisms by varying the degree of dilution and dictated the elastic modulus of the glassy state of the polymer by local intersegment interactions dominated by van der Waals forces. As Bukowski et al. integrated long chain polymers, the toughness measured in the simulations revealed a monotonic increase.

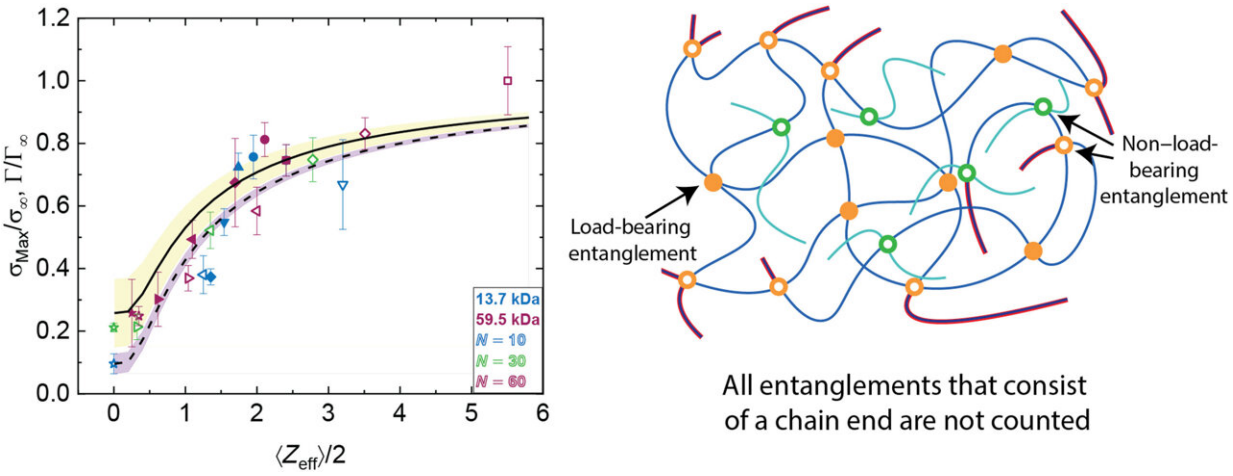


Force distribution on entanglements. (A) Simulation snapshots at various levels of strain. A single chain, highlighted in red in the top row, is shown in the row below at each of the indicated strains. The single chains are colored to show varying levels of average bond stress on each primitive path (PP) along the chain. (B) The average bond stress as a function of strain on each PP in a blend of N = 250 and 30 at ϕ = 0.50. The schematic next to the graph outlines where each

mentioned PP is located. PPs are color coded to match the plotted points. Entanglements occur at each orange dot. Hollow orange dots represent non–load-bearing entanglements at the end of chains. (C and D) Solid symbols represent calculations that consider all entanglements in the blend systems, and hollow symbols only consider load-bearing entanglements. (C) The density of entanglements, ρ, in each simulated system as a function of dilution, calculated as the total number of entanglements divided by the system volume. Note that there is a solid blue star at point (0,0). (D) The average number of entanglements per chain, ⟨Z⟩, as a function of dilution. The dashed line corresponds to N = 60, and the dotted line corresponds to N = 30 as the diluent chain. Credit: *Science Advances*, 10.1126/sciadv.abg9763

Experiments and simulations

The experimental maximum stress and simulated toughness values appeared to scale differently for different experimental models. The findings matched well with a physics model introduced by Mikos and Peppas. According to the simulations, not all entanglements in a system were load bearing. Later, the team noted the simulated strains to be much larger than those observed experimentally. To precisely account for changes in load-bearing entanglements, the team considered the average number of entanglements per chain. Bukowski et al. next developed a model and successfully applied the method to both experiments and simulations to study the relationship between entanglements and the maximum stress or toughness. When considering the load-bearing fraction of entanglements in the system, the experiments and simulations scaled similarly at the molecular level. By comparing the experiment and simulations of thin glassy polymer films thereafter, the data indicated a quantitative link between the maximum stress and toughness.



Strength and toughness of materials as a function of load-bearing entanglements. Normalization is carried out by the undiluted maximum stress of polystyrene at Mn = 1.928 MDa and the undiluted toughness of N = 250 for the experimental and simulation results, respectively. Experimental data are represented by solid symbols, and simulation data are represented by hollow symbols. The lines represent the modified Mikos and Peppas model calculated for both the experiment (solid line) and simulation (dashed line) including only load-bearing entanglements. Each shaded region represents 1 SD of error in each line. The schematic on the right shows a system of entanglements with long chains (dark blue) and short chains (light blue). Solid orange dots represent load-bearing entanglements. Orange hollow dots represent entanglements that cannot bear load because they contain a first PP. Green hollow dots represent non–load-bearing entanglements that are made with a short species of chain. Ends of long chains are highlighted in red. Credit: *Science Advances*, 10.1126/sciadv.abg9763

Outlook

In this way, Cynthia Bukowski and colleagues used a combination of experiments and simulations to show the importance of using load-bearing entanglements to improve the toughness of materials. To accomplish this, they systematically tuned the entanglement density

using bidisperse and chemically identical blends. When they added a short chain diluent to the blends, the tensile tests of the polymer showed a decreased maximum stress. Similarly, the molecular dynamics of solutions also showed a decrease in the toughness with added diluent. The combined experiments and simulations provided an enhanced understanding of polymers and a novel framework to tune the mechanical properties based on their molecular makeup. The work has many practical implications beyond providing fundamental insights into the origin and toughness in polymer glasses, including additive manufacturing strategies.

More information: Cynthia Bukowski et al, Load-bearing entanglements in polymer glasses, *Science Advances* (2021). DOI: 10.1126/sciadv.abg9763

Joshua D. McGraw et al, Swelling molecular entanglement networks in polymer glasses, *Physical Review E* (2010). DOI: 10.1103/PhysRevE.82.021802

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