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Importance of sample dimensions in dynamic mechanical analysis

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Both the size of samples and the type of clamp geometry should be considered during testing of epoxy resins to ensure accurate modulus measurements are obtained.

Dynamic mechanical analysis (DMA) is a common technique used to characterize polymers. DMA often involves the measurement of a sample's response to an applied oscillatory force.[1] The response—as a function of the oscillatory force frequency or temperature—is also simultaneously probed. Sketches of three DMA geometries that are commonly used to test polymers are shown in Figure 1. These geometries are the three point bending (3pt), dual cantilever (DC), and single cantilever (SC) clamps. The tension geometry—also shown in Figure 1—is also commonly used, but mainly for polymeric films or thermosets that are above their glass transition temperature (T_g). Although several ASTM standards address polymer characterization by DMA,[2–5] these standards are vague on sample dimensions. Furthermore, these standards do not account for the fact that stiffness can change by orders of magnitude during a test. Since the ASTM standards do not favor specific geometries for specific tasks, there is not yet a consensus on which geometries to use for polymer testing.

For viscoelastic materials (e.g., polymers), there is an intermediate lag (δ) between the displacement and the application of the oscillatory force. In DMA measurements, the lag can be broken into in-phase and out-of-phase components. This means that the storage (elastic) and loss (viscous) moduli can be obtained from a measured stiffness.[6] In addition, the ratio of the loss modulus to the storage modulus (i.e., tan δ) is one of the basic properties that can be measured by DMA. From these measurements, other properties can be determined. These include the T_g and other relaxation temperatures, gelation, and vitrification.

As all DMA clamp geometries have their own advantages and disadvantages, in this work we have characterized five epoxy-amine networks on the 20mm 3pt, the 35mm DC, and the 17.5mm SC clamps to find the most effective setup.[7] We have compared the results from each clamp, with a focus on the glassy and rubbery modulus values, as well as the T_g results from a TA Instruments Q800 DMA. In the first of our comparisons we maintained a constant thickness across the samples of a given resin (about 3.2mm), and in the second comparison we maintained a constant span-to-thickness (S–T) ratio (about 11:1). We followed an ASTM standard[8] to get an independent modulus value. We were thus able to obtain flexural modulus values for all the polymers at room temperature (i.e., 23°C).

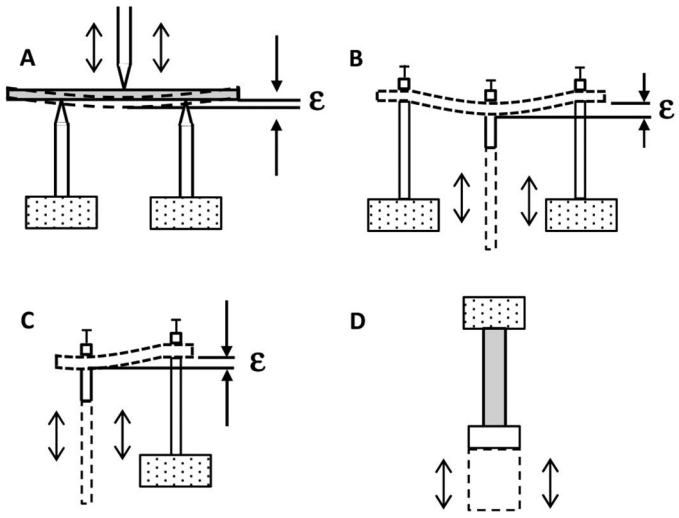

Figure 1. *Sketches of different geometries for dynamic mechanical analysis (DMA) of polymers. (A) Three point bending (3pt). (b) Dual cantilever (DC) clamp. (C) Single cantilever (SC) clamp. (D) Tension fixture. ε: Oscillatory strain being applied to the samples in the various clamps.*

To produce our epoxy-amine resins, we used a high-purity diglycidyl ether of bisphenol A. We cured this material with five different amines, i.e., 4,4′-methylenebiscyclohexanamine (PACM),

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Table 1. *Summary of DMA geometry test results and recommendations for suitable size dimensions. T_g: Glass transition temperature. S–T: Span-to-thickness ratio.*

Clamp	Sample size requirements for DMA properties		
	T_g	Glassy data	Rubbery data
3pt	Any, but maintain size across samples	S–T > 10	Follows theory of rubber elasticity if stiff enough, but lower results than SC
DC	Any, but maintain size across samples	S–T > 10	Not suited
SC	Any, but maintain size across samples	S–T > 10	Preferred, but samples must be thick enough to ensure stiffness

1,3-phenylene diamine (PDA), 1,3-diaminopropane (DAP), as well as the polyetheramine diamines Jeffamine D230 and Jeffamine D400. We maintained a stoichiometric ratio of one epoxy per amine hydrogen in all the resin formulations (which we identify by their amine component).

The room temperature storage modulus results we obtained are shown in Figure 2. These results are normalized to the flexural moduli for constant thickness and constant S–T ratio. For the 3.2mm-thick samples—see Figure 2(A)—the results from the DC geometry match well (i.e., within 90%) with the flexural moduli in all cases. The 3pt results, however, show poor agreement (they range from 53 to 81% of the flexural moduli). The SC results—between 82 and 89% of the flexural moduli—are intermediate between the DC and 3pt data.

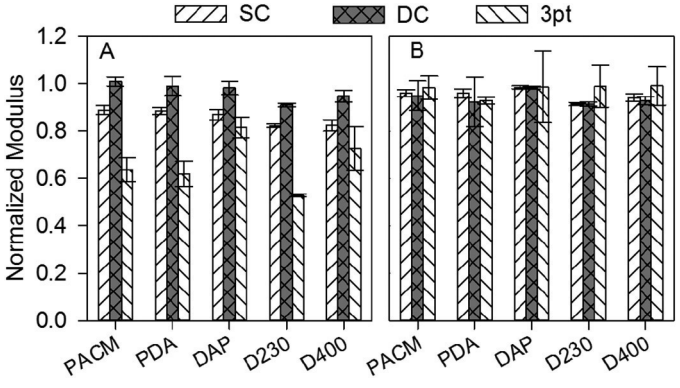

Figure 2. *Room temperature storage modulus results, normalized to the flexural moduli for (A) constant thickness (3.2mm) and (B) constant S–T ratio (11). The S–T ratio was 5 for the SC measurements, 6 for the 3pt measurements, and 11 for the DC measurements in (A). PACM: 4,4′-methylenebiscyclohexanamine. PDA: 1,3-phenylene diamine. DAP: 1,3-diaminopropane. D230 and D400: Polyetheramine diamines Jeffamine D230 and Jeffamine D400.*

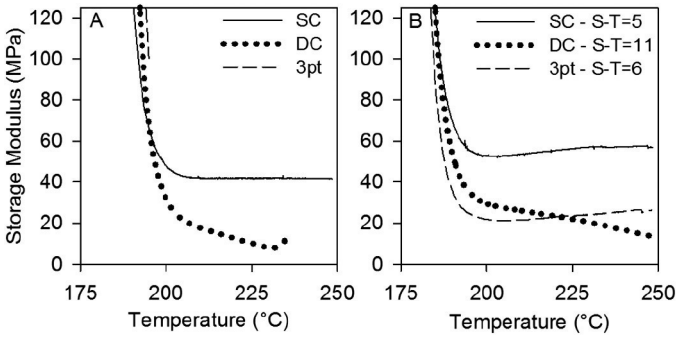

Figure 3. *Rubbery modulus of PDA as a function of temperature, measured using three clamp (SC, DC, and 3pt) geometries. (A) Measurements made on constant S–T samples. (B) Measurements made on constant thickness (3.2mm) samples.*

In contrast, when we maintained a constant S–T ratio—see Figure 2(B)—the modulus values are all very similar to the flexural modulus (within 9%). Indeed, neither clamp type, nor the S–T ratio, had a significant influence on the measured T_g.

For temperatures above the T_g, stiffness and thermal expansion effects need to be considered during DMA. Conflicting rubbery behavior of PDA is illustrated in Figure 3. The samples that we tested on DC clamps display a constantly decreasing modulus. For thin (i.e., constant S–T ratio) samples—see Figure 3(A)—that we tested on SC clamps, however, the modulus appears to be flat. Moreover, thicker samples—see Figure 3(B)—that were tested on the SC and 3pt clamps seem to follow the theory of rubber elasticity,[9] which predicts an increase in modulus with increasing temperature. We also observe that the behavior for thin SC samples—see Figure 3(A)—corresponds to a sample stiffness that has dropped outside the sensitivity limits of the

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instrument, whereas for the same samples tested on the DC clamp (i.e., which has three fixed points), the thermal expansion can cause buckling or sagging. Both lead to the formation of artifacts in the modulus measurements. Our results from tests on the tension clamp match those of the thicker SC samples. These observations also adhere to the theory of rubber elasticity and can be used to independently verify these two clamp geometries.

We have conducted a series of DMA tests—using different clamp geometries—on five epoxy-amine samples. Our results show that (when the S–T ratio was 11) the glassy room temperature modulus matched the flexural modulus for all five of the epoxy-amine networks. We note that in the rubbery region, thermal expansion and sample stiffness also need to be considered. Above the T_g, we find that the stiffness of the samples (with S–T ratios greater than 10) were outside the sensitivity limits of the machine. In addition, high-expansion materials cannot be tested accurately on a DC clamp because of its three fixed points. Our results indicate that the SC geometry is best suited for characterizing rubbery moduli. A thicker sample than would be tested for glassy measurements may be required, however, to maintain adequate stiffness. Our findings and sample size recommendations for DMA are summarized in Table 1. Although we have only conducted tests on epoxy-amine networks so far, it is likely that our findings can also be applied to other thermoset polymers.

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