

Estimation of Polymer Crystallinity by Dynamic Mechanical Techniques

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Synopsis

Dynamic mechanical techniques can be used for a rapid estimation of polymer crystallinity with an accuracy of better than $\pm 20\%$. The advantage of our proposed procedure is that it is absolute and the crystallinity can be instantaneously estimated when the dynamic mechanical analysis (DMA) data is available. A serious limitation is its applicability to crystallizable polymers (e.g., a quenched nylon 6) where higher values are obtained due to crystallization during the DMA experiment. Another limitation is that our technique cannot be applied to as polymerized samples, e.g., powders or pellets; only fabricated products such as films, fibers, or plaques are suitable for this determination using DMA. Using a variety of polymer systems, the underlying principle, advantages, disadvantages, and recommendations on crystallinity evaluation by DMA are presented. At present we consider this method to be more of a different approach rather than value it as a crystallinity measurement technique, especially for quenched polymers.

INTRODUCTION

The measurement of polymer crystallinity has been reviewed by Miller¹ and more recently by Runt² in 1986. Due to the availability of this excellent review,² we are not providing the literature background on this subject. According to Runt,² the following are the five widely used analytical methods for evaluating polymer crystallinity.

- i. X-ray diffraction (XRD) affords a direct determination of 3-dimensional order, but there can be problems with absolute crystallinity measurements, owing to the arbitrary nature of constructing the baseline delineating crystalline and amorphous scattering.
- ii. Density measurements are limited in accuracy due to the reliability of completely amorphous and crystalline density values.
- iii. Differential scanning calorimetry (DSC), probably the most widely used² method for estimating crystallinity, suffers from many uncertainties e.g., pre- and postmelting baseline, further crystallization prior to melting, and the availability of undebatable heat of fusion data of equilibrium crystals (ΔH^0) of a polymer.
- iv. Infrared (IR) and Raman spectra require the identification of true crystallinity bands, which can also be associated with regularity or preferred conformations.
- v. Nuclear magnetic resonance (NMR) method measures the fraction of immobile protons that do not necessarily originate from the crystalline phase.

Other techniques have also been used throughout the years to assess crystallinity but have proved less popular because of a less exact relationship between the degree of crystallinity and the property being measured.² Correlation of modulus with crystallinity has been known for a long time,^{1,3} but the imprecision in modulus measurements and its influence on crystallinity, does not allow a reasonable evaluation of polymer crystallinity. In DMA, the $\tan \delta - T_g$ peak (e.g., at half-height) broadens with crystallinity; for example, in nylon 6 it broadens by 1°C for 1% increase in crystallinity⁴ for a sample crystallinity range of 20–60%. However, the effect of experimental conditions and the availability of a prior calibration curve make this approach undesirable.

In this paper we are presenting a crystallinity estimation procedure which is simple, rapid, absolute in nature, and requires no prior knowledge of any calibration or polymer constants.

EXPERIMENTAL

Polymer samples were compression molded into plaques of about 50 mil (0.125 mm) thickness and thin strips cut for dynamic mechanical analysis. A Polymer Laboratories DMTA unit was used in obtaining the mechanical spectra. Samples were analyzed in the bending mode of deformation at a heating rate of 3°C/min from -130°C to just below the polymer melting temperature, under an argon atmosphere. A constant frequency of 1 Hz and a constant strain level were used.

RESULTS AND DISCUSSION

In this section we discuss the underlying principle, advantages, disadvantages, and compare the crystallinity by DMA vs. XRD for various polymers of crystallinity between 25 and 75%.

Underlying Principle. It has been known for several decades that an amorphous polymer exhibits about a 3-order-of-magnitude drop in modulus upon going from a glassy to rubbery phase. In order to determine precisely the exact change in modulus, we have summarized for various amorphous systems the change in modulus ($\Delta \log E'$) associated with the glass \rightarrow rubber transition, the latter being defined by the damping peak as shown in Figure 1. As shown in Table I, $\Delta \log E' = 2.46 (\pm 0.14)$ defines the glass \rightarrow rubber transition of various polymers of differing structural entities. Thus, if $\Delta \log E' = 2.46$ corresponds to a 100% amorphous phase, $\Delta \log E'$ determined across the T_g for a semicrystalline polymer should yield crystallinity.

However, complications arise in semicrystalline polymers since the glass transition zone is not well defined, e.g., the T_g broadens with crystallinity^{4,5} and orientation.⁵ In addition, the description of a semicrystalline polymer in terms of a two-phase model, i.e., a discrete amorphous and a discrete crystalline phase, is not adequate because of the third, so-called interfacial phase, i.e., chain folds, loops, tie molecules, cilia, etc. The interfacial phase is to be regarded as part of the overall amorphous fraction since such a phase has no 3-dimensional order. The relaxation of interfacial amorphous phase compared to that of the discrete amorphous, normally if not exclusively, occurs at a higher temperature, either as a sharp^{3,6,7} or as a broad and continuous process

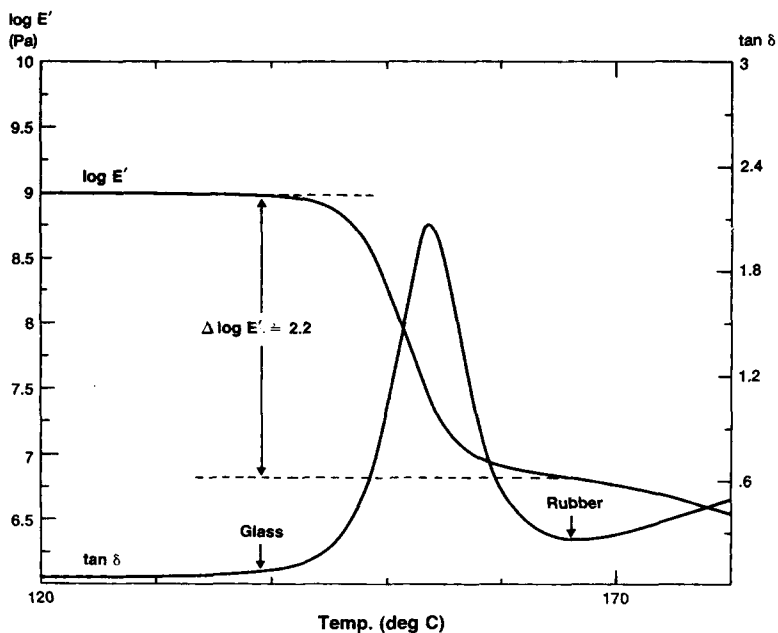


Fig. 1. Dynamic storage modulus (E') and damping ($\tan \delta$) vs. temperature curves for a polycarbonate.

TABLE I
Modulus Drop ($\Delta \text{Log } E'$) for the Glass \rightarrow Rubber Transition for Amorphous Polymers

Polymer		
Name	Structure	$\Delta \text{Log } E'$
Polysulfone (PS)		2.42
Polyether Sulfone (PES)		2.47
Polyether Imide (PEI)		2.38
Polycarbonate (PC)		2.22
Polyester Carbonate (COPEC)		2.30
Polyphenylene Oxide (PPO)		2.67
Polystyrene (PS)		2.50
Hexamethylene Phthalamide (HMPA)		2.55
Polyvinyl chloride (PVC)		2.41
Plasticized PVC (50/50)		2.65

For Amorphous Polymers, $\Delta \text{Log } E' = 2.46(\pm 0.14)$

TABLE II
DMA vs. X-ray Crystallinity for Various Semicrystalline Polymers

Thermal History	Sample description	% Crystallinity	
		DMA	X-ray
Annealing	Poly(caproamide); high temperature annealed for 17 hours	58	56 62
	Poly(ethylene/chlorotrifluoroethylene, 1/1); annealed @ 200°C for 100 hours	47	44
	Poly(chlorotrifluoroethylene)	60 63	56
	Poly(tetrafluoroethylene)	58	57
	Poly(ethylene/chlorotrifluoroethylene, 1/1)	41 42	38
Standard Cooling*	Poly(ethylene/chlorotrifluoroethylene, (1/1) containing 6% termonomer)	27	27
	Poly(ethylene); $\bar{M}_w = 160 \times 10^3$, branching 2.5/1000 CH ₂ by NMR	72	74
		74	75
	Poly(ethylene); $\bar{M}_w = 250 \times 10^3$, branching 6.2/1000 CH ₂ by NMR	65	63
62			
Quenching**	Poly(caproamide)	65	54
	Poly(ethylene/chlorotrifluoroethylene, 1/1)	42	30
	Poly(caproamide)	59	32

*Compression molded pieces allowed to cool @ RT following the molding.

**Compression molded pieces quenched in ice/water following the molding.

extending up to the premelting region.⁸ Therefore, if we consider the modulus drop between the beginning of the T_g and the beginning of the melt (T_m) as indicated by the $\tan \delta$ or E' curves, this can be attributed to the overall amorphous fraction of the semicrystalline polymer. Thus,

$$\text{DMA crystallinity} = \left[1 - \frac{\Delta \log E'(T_g - T_m)}{2.46} \right] \times 100$$

Results and Recommendations

Table II shows that the match between DMA and X-ray crystallinities is reasonably good for annealed or slowly cooled polymers. However, it is also apparent that DMA crystallinity tends to be much higher when the polymers had been quenched; this is attributed to the crystallization occurring between T_g and T_m during the DMA experiment. Figures 2-6 illustrate the applicability of DMA in evaluating the crystallinity of various polymers. Following are some recommendations regarding the use of DMA technique for crystallinity

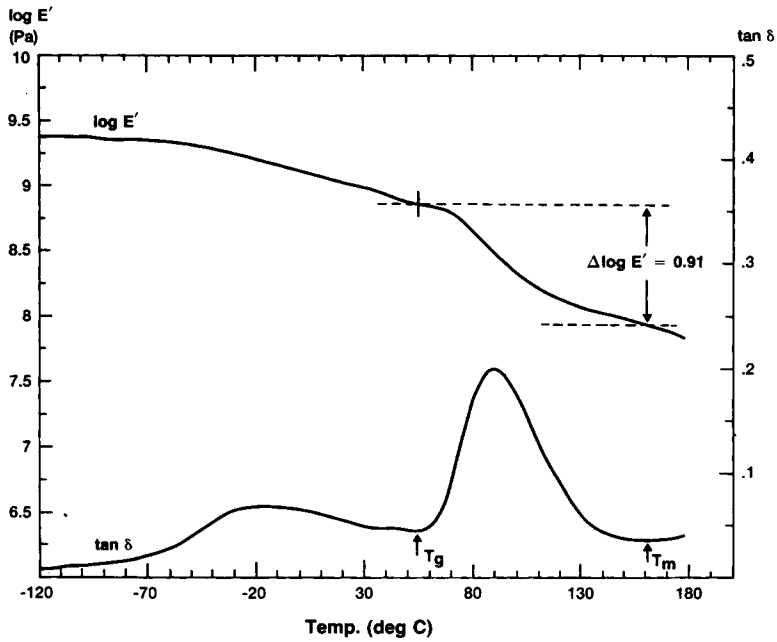


Fig. 2. Crystallinity of poly(chlorotrifluoroethylene) by DMA.

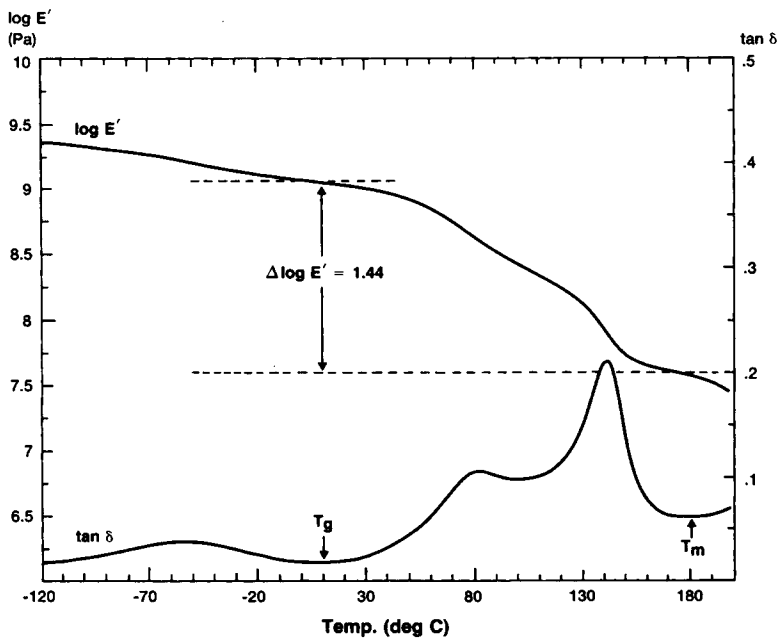


Fig. 3. Crystallinity of poly[ethylene/chlorotrifluoroethylene (1/1)] by DMA.

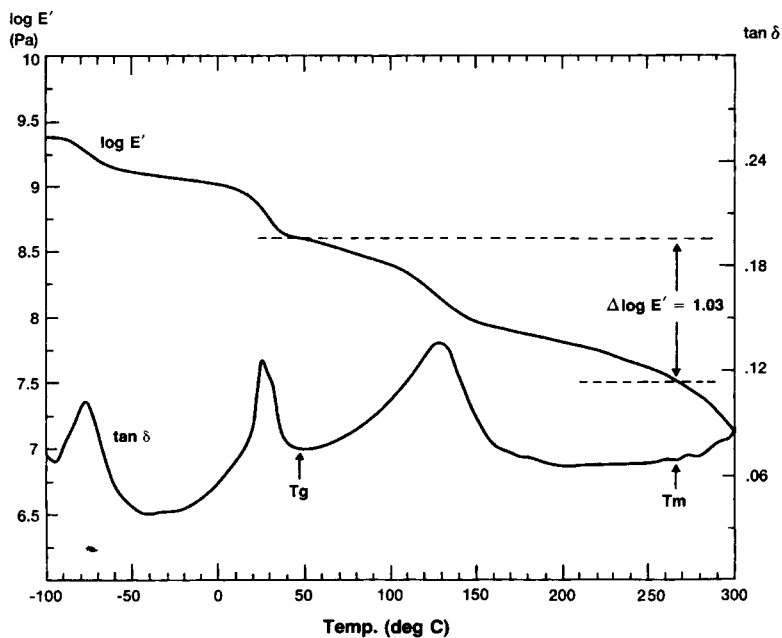


Fig. 4. Crystallinity of poly(tetrafluoroethylene) by DMA.

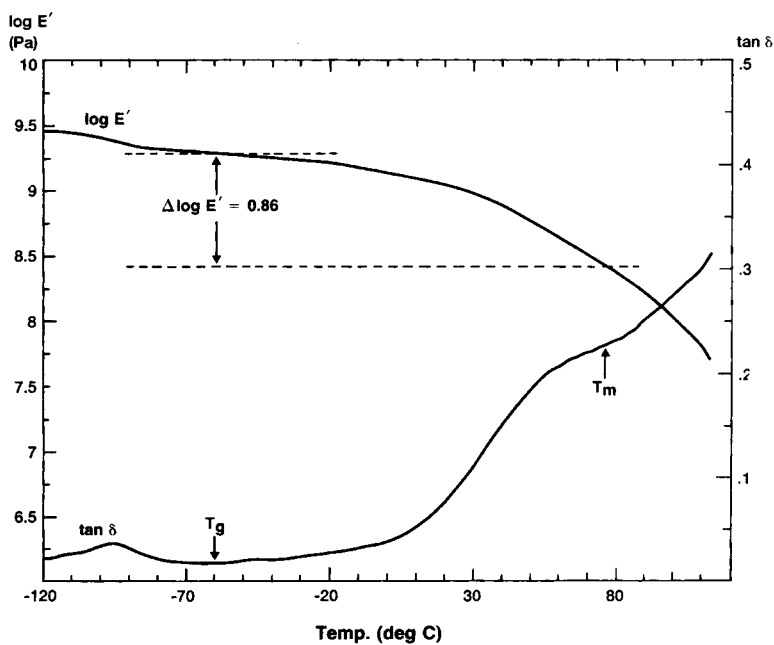


Fig. 5. Crystallinity of poly(ethylene) by DMA.

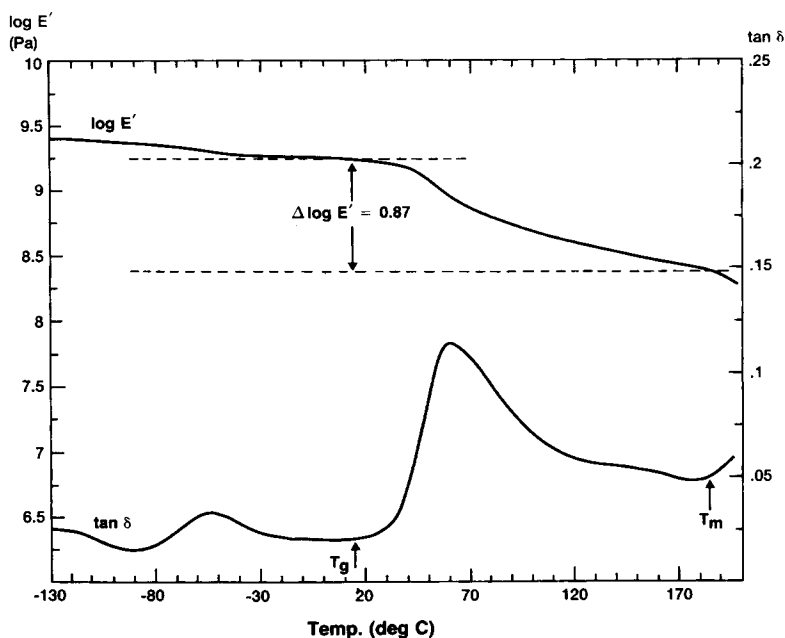


Fig. 6. Crystallinity of nylon 6 by DMA.

estimation:

1. Although the glass \rightarrow rubber transition zone will broaden with increasing heating rate and frequency, the net change in modulus should remain essentially unchanged. However, instrumental factors such as test geometry and especially modulus calibration may lead to variations in the $\Delta \log E'$ value for amorphous polymers from laboratory to laboratory. Thus, although we find $\Delta \log E' = 2.46(\pm 0.14)$ for amorphous polymers, each laboratory should determine its own reference value.

2. This procedure will lead to higher crystallinity values if the polymers were quenched and crystallized significantly during the DMA experiment. Although we have not attempted so, application of higher heating rates, e.g., 20–50°C/min rather than 3°C/min used here, may reduce this problem.

3. Before the DMA technique is applied, a knowledge of T_g and T_m is necessary, and this should be readily available at least for common polymers. Due to the sensitivity of modulus to molecular mobility, DMA would detect premelting much earlier than the DSC. As shown in Figures 2–6, premelting by DMA can be detected at 40–60°C lower than the melting peak temperature by DSC. Controversies can exist regarding the T_g , e.g., for polyethylene. In our own analysis of polyethylene, we have assumed that the β -relaxation peak beginning at about -60°C marks the T_g of polyethylene.^{3,7} On the whole, we feel that the T_g and T_m of most polymers are well known to facilitate the use of DMA in estimating polymer crystallinity.

4. Molding of samples (e.g., powders and pellets) for DMA will introduce a specific thermal history and, therefore, crystallinity. Thus, our approach is ideally suited for fabricated products such as films, fibers, and molded articles which would have a certain crystallinity representative of the processing history.

5. Finally, we wish to mention that DMA may be more valuable than the widely used DSC method² for crystallinity evaluation. For example, in DSC, as much as 100% variation in crystallinity can simply result from the ΔH_f^0 value chosen and, of course, there are additional sources of error as outlined earlier. For polytetrafluorethylene, the ΔH_f^0 values have ranged from 13.7 to 24.4 cal/g, according to the literature⁹ appearing between 1958 and 1982; thus an uncertainty of 80% occurs just due to the ΔH_f^0 value chosen.

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