NOTES

Craze Relaxation: A Rapid and Simple Method for Glass Transition Temperature Determination in Amorphous Polymers

INTRODUCTION

Several methods exist for the determination of the glass transition temperature (T_g) of amorphous polymers. Various difficulties are encountered in the performance of T_g measurements according to these methods. A method was sought for a rapid determination of this parameter which would be as simple as conventional melting point determination.

Many amorphous rigid plastic films form crazes when folded. These crazes appear as a bright line along the fold. When located between two crossed polarizing Nicol prisms, an angle between the polarization plane and craze direction can be found at which light is transmitted through the crazed area only, leaving the rest of the sample area black.

It is currently accepted[1,2] that these crazes are areas of cold-drawn material where the refractive index is much lower than that of the undrawn polymer. The decrease in refractive index is due to air interspersed between the cold-drawn material.[3] Since no appreciable segmental movement occurs below the T_g, relaxation of cold-drawn polymer is not expected below this temperature during short periods characteristic of the performance of T_g measurement. This suggested that T_g might be determinable by following the temperature at which crazes disappear. Since the relaxation is a time-consuming process, heating rate dependence of the temperature at which the craze disappears was expected.

EXPERIMENTAL

A Leitz Wetzlar microscope heating stage Model 350 was used. This apparatus enables the simultaneous observation of the sample and temperature reading. Films, varying in thickness between 1 and 10 mil, were prepared by either pressing or solution casting. Crazes were prepared either by carefully folding the film and reflattening it, or by stretching it over a blunt edge. A 4×4-mm piece containing the craze was cut and placed on the hot stage microscope. Using a 258-fold magnification, the craze appears as bundles of dark needles of various lengths and widths. Observation of one of these needle-like crazes, while the temperature is increased, permits establishing the TCD—the temperature of craze disappearance.

It is important to distinguish between crazes and cracks, since only the crazes disappear before fluidification of the polymer mass. In order to do this, the Nicol prisms are crossed, and the sample stage is rotated to a position at which only the crazes appear as bright lines leaving the rest of the sample, including cracks, completely dark. Thus, the temperature at which the bright lines disappear, the TCD, is readily observable.

RESULTS AND DISCUSSION

Films of four amorphous materials, i.e., polystyrene, poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVAc), were examined at two different heating rates. The TCD's obtained were compared to the T_g's reported in the literature[4] as shown in Table I. It is obvious that there is a reasonable fit between TCD and T_g.

When semicrystalline materials, e.g., polypropylene, poly(ethylene terephthalate), and nylon 6 were examined, TCD appeared to be close to the melting point of the crys-

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TABLE I

Effect of Rate of Heating on the Correlation between
TCD and T_g for Four Amorphous Polymers

Material	Heating rate, °C/min	TCD, °C	T_g,[a] °C
Polystyrene	6	108	105
	2	105	
PVC	8	82	81
	2	79	
PMMA	6	106	105
	2	103	
PVAc	3	29	29
	1	29	

TABLE II

Correlation between TCD, T_m, and T_g for Three
Semicrystalline Polymers

Material	Heating rate, °C/min	T.C.D., °C	T_m,[a] °C	T_g,[a] °C
Polypropylene	4	167	176	−10
	12	164		
Mylar	6	258	270	69
	2	258		
Nylon 6	3	221	226	75
	9	221		

talline region (Table II). What appeared in this case as crazes, probably included oriented crystalline regions.

CONCLUSIONS

It seems that the procedure of craze relaxation discussed may serve as a rapid and simple means of T_g determination, though only for amorphous films, either oriented or unoriented. A first, high heating rate sweep for approximate location of the TCD may be carried out, followed by a more accurate low heating rate process for T_g.

References

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