Effect of Thermal Aging on Mechanical Properties of an Epoxy Resin System

INTRODUCTION

The thermal stability of a polymeric material is often described in terms of the weight loss which occurs after a given thermal treatment. For many applications the polymer may be a load-bearing component whose strength retention is critical. In such cases, knowledge of weight loss parameters may be of little use in predicting the service life of the component.

The aim of this work was to determine the effect of thermal exposure on selected mechanical properties of a crosslinked epoxy resin system.

The usual effect of thermal exposure on cured epoxy resins is initially to continue the cure reaction and thus to increase T_g. A plateau in the T_g–time curve is often reached, but higher plateaux may be reached if the temperature is raised. If the aging temperature is sufficient to cause bond scission, a reduction in T_g will occur together with the evolution of volatile decomposition products. At aging temperatures above T_g, there will be less hindrance to evolution of volatiles, so rapid weight loss, probably accompanied by a rapid deterioration of mechanical properties, will occur. From these facts it is expected that at T_g there will be a discontinuity in the stability–temperature curve.

EXPERIMENTAL

The resin system chosen was the commercially available Epikote DX-209 cured with Epikure $BF_3$400, which is designed for use as a matrix for carbon fiber composites. The resin is a condensate of a diglycidyl ether of bisphenol A and an amine; the curing agent is an amine adduct of boron trifluoride which catalytically cures the resin.

Four resin plates 3 mm thick were prepared using separate resin–curing agent blends. The resins were gelled for 2 hr at 120°C and cured for 6 hr at 170°C in metal molds. Great care was taken to degas the materials to produce void-free castings.

Aging was carried out in air-circulating ovens maintaining the nominal temperature ±2°C. For each time–temperature combination, one sample was tested from each resin plate.

Resin strips 120 mm long by 10 mm wide were waisted before aging to give a gauge section 4.5 mm wide by 30 mm long. Strengths and moduli were determined using the Instron testing machine and strain gauge extensometer.

Dynamic mechanical properties were determined by a torsion pendulum oscillating at approximately 0.7 Hz. The visibly oxidized surface layer was removed before these measurements were made.

RESULTS

Tensile strengths and moduli measured at 23°C, as well as weight loss of the tensile dumbbells are shown in Figures 1 and 2 as a function of the aging time and temperature. Table I shows the glass transition temperatures of the resin aged at the two intermediate temperatures.

On aging the resin system at 160°C, the tensile strength and modulus did not change significantly after 36 days, even though about 2% weight loss had occurred.

Aging for one day at 175° raised T_g to 198°C from an initial value of between 158° and 188°C (range of T_g after initial cure cycle). The T_g remained above the aging temperature for at least 29 days. Modulus and strength did not alter significantly during this time, even though 2.9% weight loss had occurred.

When aged at 190°C, the T_g of the resin rose in the first day to 192°C and then fell rapidly. Modulus and strength increased, but both properties fell rapidly after about

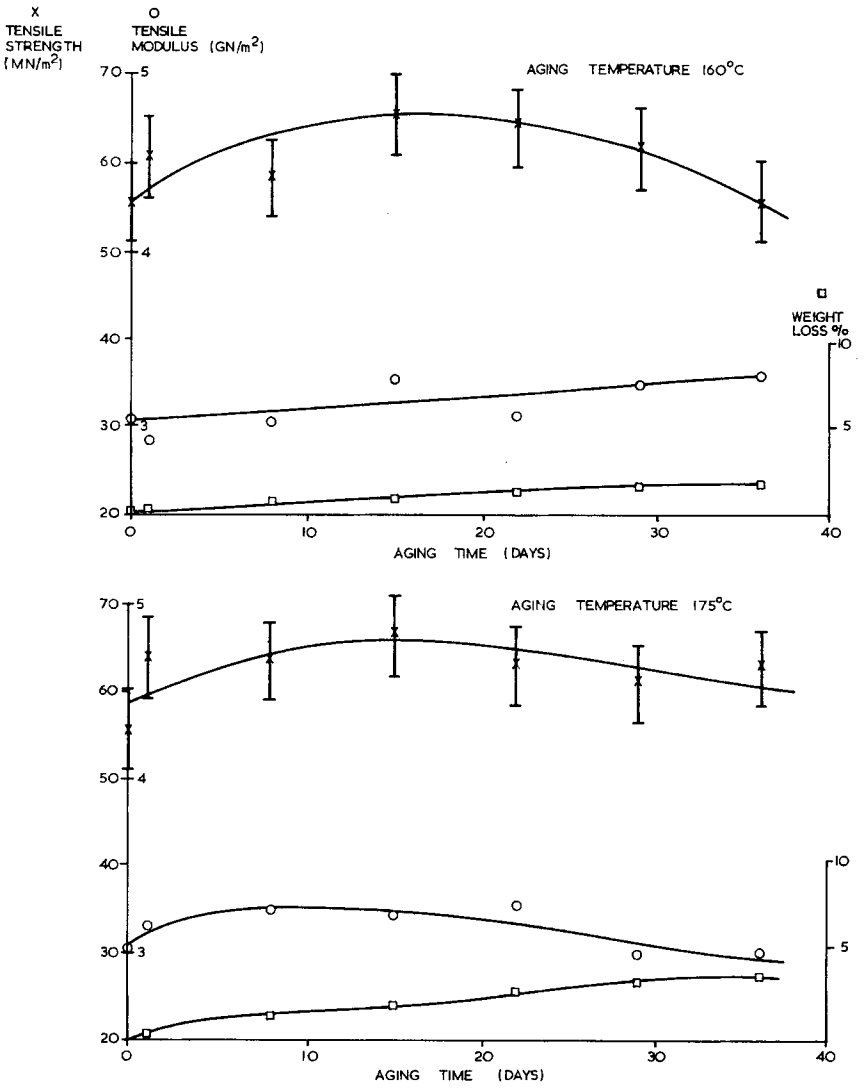

Fig. 1. Effect of aging on room temperature properties of Epikote DX 209–Epikure $BF_3$400 resin.

22 days, leveling out after about 29 days. The large drop in properties occurred well after T_g had fallen below the aging temperature.

At the highest temperature studied, 205°C, which was at all times above the sample T_g, the fall in modulus again occurred after about 22 days, but loss of strength occurred much earlier.

DISCUSSION

The initial effect of aging this resin system is to raise the tensile modulus. At the higher temperatures, the modulus reaches a maximum before it falls below its unaged value. Increases in modulus can be caused by furthering the cure reaction and by the

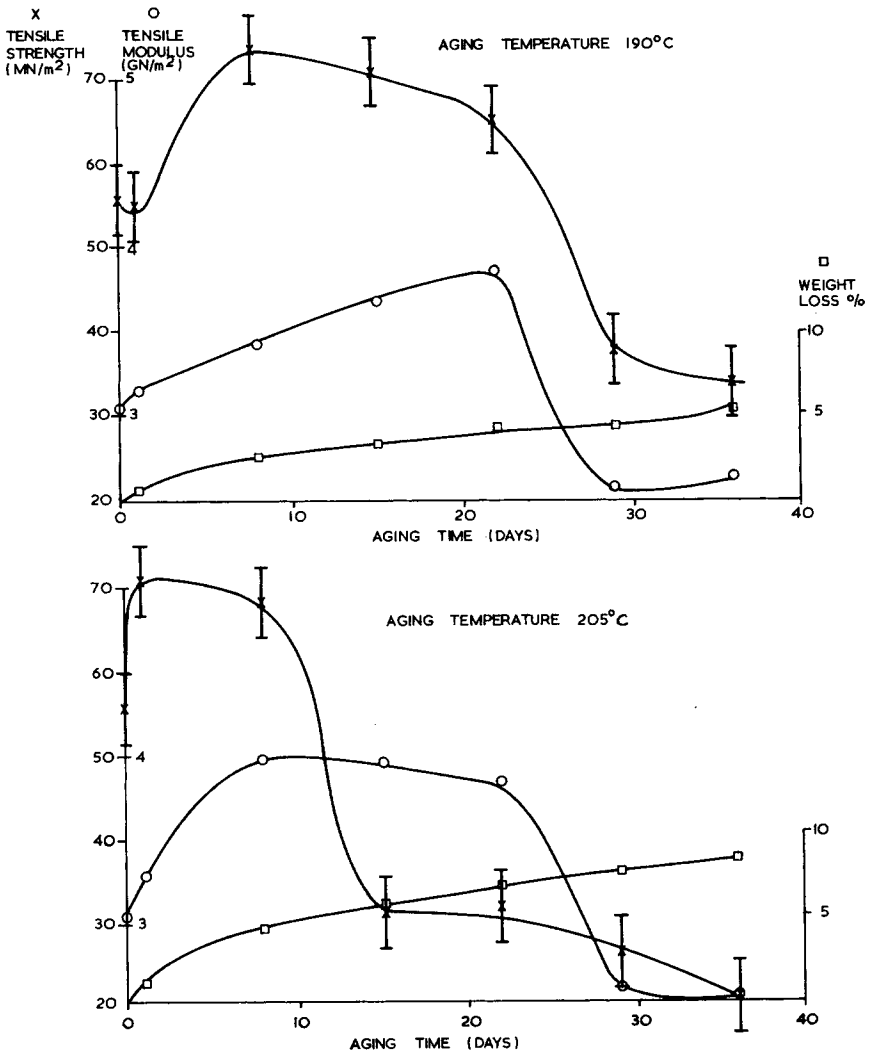

Fig. 2. Effect of aging on room temperature properties of Epikote DX 209–Epikure $BF_3$400 resin.

production of a stiffer oxidized surface layer on the test piece. If chemical degradation occurs, elimination of volatile products will reduce the apparent modulus as an open char network is formed. It is also possible that the increased crosslinking which occurs at elevated temperatures causes a resistance to thermal contraction on cooling. Thus, a lower modulus and density would be measured at room temperature than would be expected for the degree of crosslinking of the material. The modulus of an aged material will depend on a competition between these processes, the higher activation energy reactions assuming greater importance as the aging temperature is raised. Tensile strengths of this material follow a similar pattern to that of the modulus changes, but the large decreases which were observed at the highest aging temperature were not concurrent. The large drop in strength takes place when about 5% weight loss has occurred (for aging temperatures of 190° and 205°C). A possible explanation is that at this weight

TABLE I
Glass Transition Temperatures (by Torsion Pendulum)

Aging time, days	T_g, °C	
	Aged at 175°C	Aged at 190°C
1	198	192
8	189	174
15	185	151
22	188	136
29	180	133
36	—	130

loss, the voids produced by degradation near resin surfaces are larger than "inherent flaws" and will initiate failure at lower stresses. Support for surface voids influencing tensile strengths is given by our observations that removal of oxidized surfaces from aged samples restores the measured tensile strength almost to the unaged value.

Table I shows the influence of aging time and temperature on the glass transition temperature of resin from which the oxidized surface layers have been removed. Aging at 175°C causes the T_g to fall slowly, but it does not reach the aging temperature during the period of observation. However, at 190°C, T_g falls rapidly to below the aging temperature, and at the same time large changes in mechanical properties occur. The glass transition temperature is determined inter alia by the molecular weight between cross-links and is thus related to the mobility of chain segments in the polymer. Thus, large reductions in room temperature strength and modulus of this resin occur when sufficient degradation has occurred to reduce the glass transition temperature below the aging temperature. Below T_g, aging has relatively little effect on the properties measured.

It would be instructive to determine the aging properties for long times below T_g and for short times at higher temperatures than those used here. In this way activation energies for property changes occurring above and below T_g could be determined and compared. Removal of oxidized surface layers or aging in an inert atmosphere would allow bulk resin properties to be isolated from surface effects. The limited evidence given here does suggest however that, as expected, a discontinuity in mechanical property–time relationships occurs when resins are aged in the region of the glass transition temperature.

G. T. Merrall
A. C. Meeks

Shell Research Limited
Egham Research Laboratories
Egham, Surrey, England

Received May 31, 1972