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THERMAL ANALYSIS OF BISMALEIMIDE MATRIX RESINS

David A. Spieker

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ABSTRACT

Commercial bismaleimide (BMI) resins for composite applications have mechanical properties with values between those of high temperature epoxies and fully aromatic polyimides. The former have the disadvantage of poor hot-wet strength and the latter have the disadvantages of being difficult to process and costly. Current commercial BMI formulations offer good properties retention under hot/wet conditions, comparative ease of processing, and moderate cost. We have used thermal analysis extensively to study commercial BMI materials. This paper will survey the results of TGA, TMA, and DMA analyses which were performed to characterize the thermal behavior of cured BMI resins.

INTRODUCTION

High temperature epoxy resins for composite applications have a properties limitation in that they lose much of their strength in hot-wet environments.[1] Applications exist within the aerospace industry for composite matrix materials which can be processed like epoxies, yet maintain their mechanical properties under such conditions.[2] One such class of materials is bismaleimides (BMIs). BMIs are addition cured thermosets that homopolymerize to a highly crosslinked three dimensional network. In commercial resin systems they are supplied either as two component systems with the second component as a

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comonomer or as prepolymers that have been partially reacted with chain extenders and/or toughenners. The chain extension and toughening comonomers are incorporated to improve the fracture properties of the cured material.[3] The purpose of this work was to use thermal analysis to characterize some commercially available bismaleimide resins.

EXPERIMENTAL

The commercial materials used in this study were Ciba-Geigy's Matrimid 5292, and Shell's Compimide 65FWR, 353, 796 (BMI resins), TM-121, and TM-123 (toughenners). The chemical composition of these resins is discussed below and was taken from the vendor material safety data sheets and literature. Neat specimens of the cured resins were obtained by degassing the melt blend of the final mixture at approximately 130°C and pouring it into silicone molds. To prevent outgassing and resulting void formation in the cured specimens, all samples were held at the manufacturer's initial recommended cure temperature for 6 to 16 hours, depending on the specific system's outgassing characteristics. The samples were then cycled through the balance of the manufacturer's recommended cure and cooled slowly to room temperature before removing them from the mold. Thermal analysis was done using either the DuPont 1090 or 2100 Thermal Analyzer and the associated 912 Differential Scanning Calorimeter, 951 Thermogravimetric Analyzer, 943 Thermomechanical Analyzer, and 983 Dynamic Mechanical Analyzer. Data were analyzed using standard DuPont thermal analysis software.

RESIN CHEMISTRY

Ciba-Geigy's Matrimid 5292 system is a two component system, one component being 4,4'-methylenedianiline (MDA) based BMI (referred to hereafter as MDA-BMI) and the other being o,o'-diallylbisphenol A. Shell's Compimide 65FWR and 796 both contain MDA-BMI which has been prepolymerized with m-aminobenzhydrazide. Compimide 65FWR also contains free TM-121 toughener. Compimide 353 is a proprietary extended MDA-BMI resin. Shell's Compimide TM-121 and TM-123 are both bis(allylphenyl)ethers. The exact structure of TM-121 is proprietary. TM-123 is 4,4'-bis(o-propenylphenoxy)benzophenone. The mix ratios of

the comonomers and toughening modifiers employed were those recommended in the manufacturer's product literature.

RESULTS AND DISCUSSION

Figure 1 shows the results of TGA analyses in air of cured samples of the materials. The extrapolated onset of weight loss is taken as the intersection of tangents on either side of the weight versus temperature curve. The figure shows that all of the materials have a weight loss onset at 400°C or above, with the highest value found to be at about 425°C. Weight loss rates were measured by subjecting cured samples to a 300°C air environment in the TGA for twelve hours. The data are shown in Figure 2. The weight loss rate values range from 0.11 to 0.25 %/hr. The TGA data indicate that these BMI systems oxidatively degrade at somewhat higher temperatures than high temperature epoxy matrix resins.

TMA was used to measure the T_g and service temperature range of these materials. Figure 3 shows a typical TMA thermogram for a cured BMI sample, in this case Compimide 353. The curve shows that the material has a T_g of about 300°C and a softening temperature of about 383°C. The softening temperature is reported to indicate the approximate temperature region in which the matrix would be expected to fail. Figure 4 shows the results of the TMA analyses, listing the materials in order of increasing T_g. The range of values is from 289 to 339°C for the T_g, and 289 to 404°C for the softening temperature. In some cases the T_g and softening temperatures are the same. These data taken with the TGA data indicate that BMI matrices do indeed have a useful temperature range in excess of 250°C.

The flexural behavior and T_g of the BMI systems was measured using the DMA. Figure 5 shows an overlay chart of these results, with the materials listed in order of decreasing flexural modulus at 30°C. The values so obtained ranged from about 2.1 to 3.2 GPa at room temperature. An interesting highlight to this data is that the upper and lower bounds on the range are both occupied by Matrimid 5292. The 5292D, which had the highest modulus, was cured using the cure cycle recommended by Ciba-Geigy, and the 5292-5, which had the lowest modulus, was cured using the extended low temperature cure

mentioned previously. It is apparent from those two curves that, as would be expected, the extended low temperature cure resulted in lower modulus because such a cure increases chain extension and distance between crosslinks. As can be seen on the chart, the effect of different cure cycles was not manifested in the Tg. Figure 6 illustrates the effect of moisture on the dynamic mechanical properties of Matrimid 5292. The top curve shows a plot of flexural storage modulus versus temperature for a freshly cured sample, and the lower trace is of a sample of the same material after 144 hours in boiling water (3.5% H_2O). The high moisture content has broadened and lowered the Tg of the sample, however at 200°C the wet material still retains over 80% of its dry flexural modulus.

CONCLUSIONS

Basic TMA, TGA, and DMA experiments have been completed on a group of commercial BMI resin systems. All of the materials were found to exhibit favorable mechanical properties across a broad temperature range.

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1. Parker, J.A., et al , in High Temperature Polymer Matrix Composites, Serafini, T.T., ed. (1987)
2. Stenzenberger, H. D., in Structural Adhesives: Developments in Resins and Primers, Kinloch, A.J., ed. (1986)
3. ibid

FIGURE 1

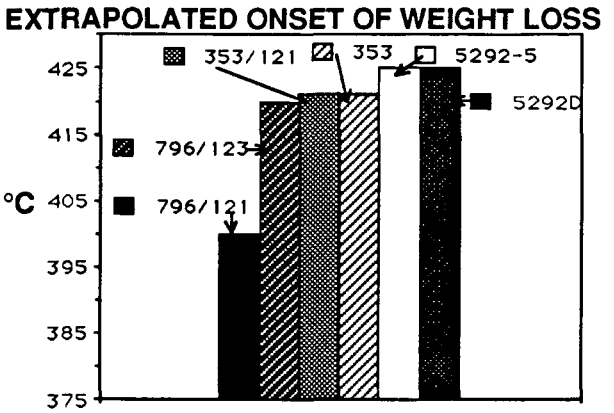

FIGURE 2

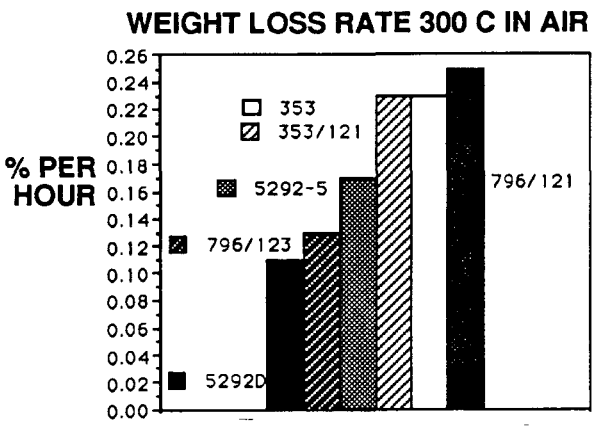

FIGURE 3

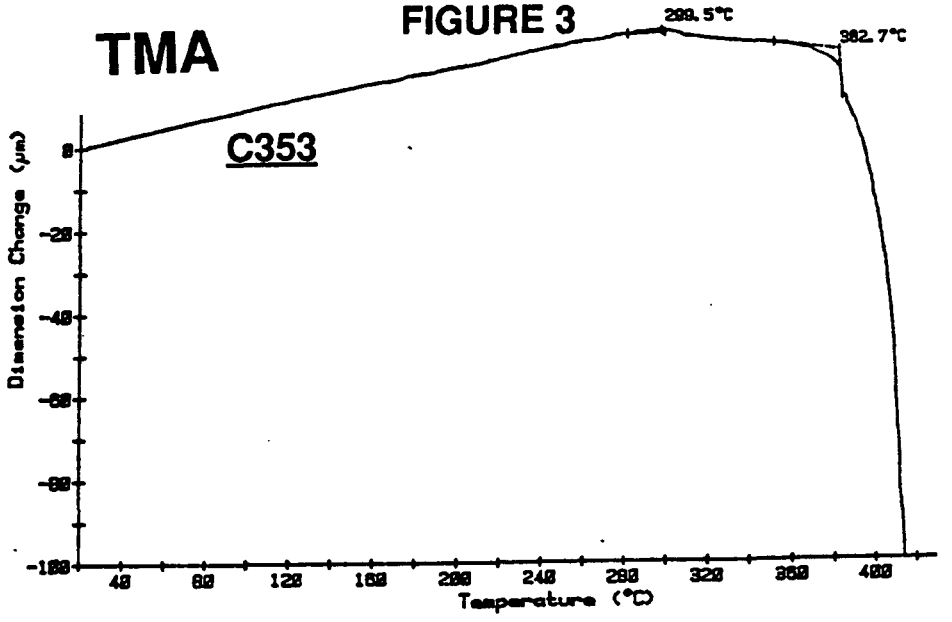

FIGURE 4

Material	Tg, °C	Softening, °C
796/121	289	289
353	300	383
796/123	301	301
796/121	303	303
5292-5	304	336
5292D	337	404
353/121	339	398

FIGURE 5

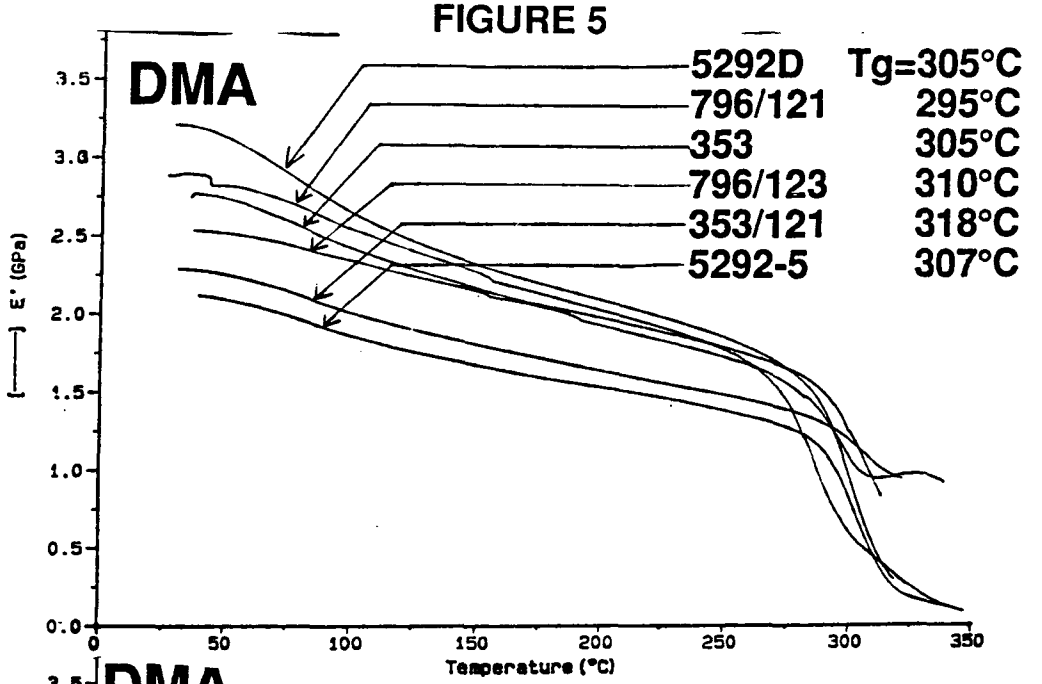

FIGURE 6