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STUDY OF CURING BEHAVIOUR AND THERMAL PROPERTIES OF ELASTOMER-MODIFIED BISMALEIMIDE RESIN

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Abstract

Bismaleimide resin (Compimide 353) was modified with the liquid elastomer carboxyl-terminated acrylonitrile butadiene (CTBN). The prereaction synthesis and curing of the CTBN-bismaleimide resin is discussed. The structure of the modified resin was identified by IR and NMR spectroscopy. The basic curing mechanism is also discussed. DSC and TG were used to study the curing behaviour and kinetic parameters, viz. the order of reaction, energy of activation and pre-exponential factor. Adhesive properties such as lap shear strength and peel strength at room temperature and elevated temperature were evaluated and are discussed.

Keywords: bismaleimide resin, CTBN, curing behaviour, DSC, TG

Introduction

Although bismaleimide resins are new materials, their chemistry and application are developing rapidly. After polymerization, these resins yield hard, brittle cross-linked products with high glass transition temperatures. They are high-modulus, low-strength materials with very low elongation at break. For improved toughness and flexibility, these resins are modified by the incorporation of a linear structure between two terminal imide linkages [1–5].

The present paper deals with the synthesis of modified bismaleimide resin, its curing and thermal behaviour and adhesive properties. The object is to establish the relationship of the micro and macro properties for an elastomer-modified bismaleimide system.

Experimental

Bismaleimide resin [Compimide 353, Technochemie GmbH, West Germany] was obtained as a yellow-brown transparent solid. It is a basic hot melt-type eutectic mixture of three types of bismaleimide resin:

(a) 4,4′-bismaleimido diphenylmethane
(b) 2,4-bismaleimido toluene and
(c) 1,6-bismaleimido 2,2,4-trimethylhexane

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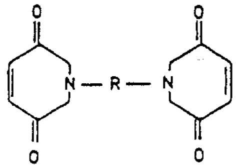
The basic general structure of bismaleimide resin is as follows:



where *R* may be aliphatic or aromatic.
Hycar reactive carboxyl-terminated liquid elastomer CTBN 1300×8 (CTBN) (Goodrich), containing 18% acrylonitrile and 30% carboxyl, was used for modification of bismaleimide resin.

$$HOOC - (CH_2 - CH = CN - CH_2)_x - (CH_2 - CH - CN)_y \; COOH$$

CTBN

Synthesis

Modified bismaleimide resin was synthesized by prereaction of bismaleimide resin and CTBN in the molten state, without solvent, at 160°C for 5 h in the presence of nitrogen. The prereaction was followed by analysis of the carboxyl function every half an hour. Different formulations containing 10 to 80 phr of CTBN were prepared.

The various formulations were cured in an air-circulatory oven at 170°C for 2 h. After curing, modified samples wee postcured at 210°C for 5 h.

Characterization

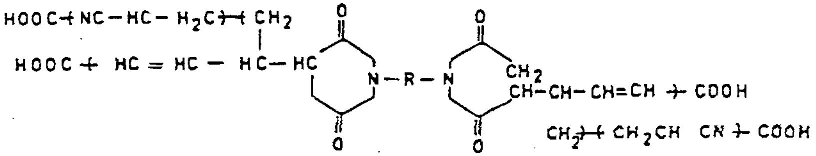
The modified bismaleimide resin was identified by IR (Perkin Elmer 377) and NMR (Varian E.M. 390, 90 MHz) spectroscopy.

The curing behaviour of these samples was studied by DSC [DSC-DuPont 1090 thermal analyzer].

The thermal stability and degradation kinetics of cured elastomer-modified samples were studied with a Stanton-Redcroft TG-750 thermogravimetric analyzer at a programmed heating rate of 10°C min^{-1}. Adhesive properties such as lap shear strength (2.5×2.5 cm) and peel strength (2×5 cm) were studied by making metal to metal (aluminium alloy) joints, with testing on a universal testing machine at room temperature. Lap shear strength was also tested at elevated temperature (200°C).

Results and discussion

During the reaction between bismaleimide resin and the elastomer (CTBN), no change occurred in the carboxyl number, demonstrating that the COOH group does not participate in the reaction, e.g. by addition to the maleimide ring. Synthesis took place by a free radical reaction mechanism, involving the allylic position of the butadiene unit of the elastomer, with addition across the α, β-unsatured linkage [6] in the bismaleimide resin. By following the free radical route, bismaleimide copolymerizes with the elastomer, and the remaining monomer continues to polymerize to form a highly cross-linked network which is a continuous matrix phase of the system [7, 8]. The cross-linked network contain linkages between the allylic carbon of the CTBN and the maleimide double bond. Kovacic and Richard [9] mentioned the same type of interpretations.



(CROSS-LINKED PRODUCT)

The molecular structure of the elastomer-modified bismaleimide resin was identified and confirmed by IR and NMR spectroscopy. In comparison with that of the neat resin, the IR spectra of the modified resin showed all the characteristic peaks/bands of the bismaleimide resin, together with additional peaks at 1710 cm^{-1} and 2180–2200 cm^{-1}, associated with the carboxyl group and the acrylonitrile group of CTBN. Peak shifting was also observed in the region 2900–3000 cm^{-1}. The NMR spectra of both the neat and the modified system exhibited multiplets at 7.5–8.1 δ, corresponding to the aromatic protons. The sharp singlet at 7.1–7.2 δ was due to the protons attached to the maleimide double bonds. The olefinic proton multiplets and the carboxylic proton singlet were observed at 6.55 and 10.80 δ respectively.

DSC scans of the bismaleimide resin systems (Fig. 1) revealed a sharp endothermic peak at 171.8°C, associated with melting, followed by exothermic transitions due to curing, which started at 194°C (T_1) and were completed at 322°C (T_2).

The DSC scans of all the modified samples (10–80 phr) displayed only exothermic transitions, which indicates that on heating the curing reaction starts immediately after the melting of the resin.

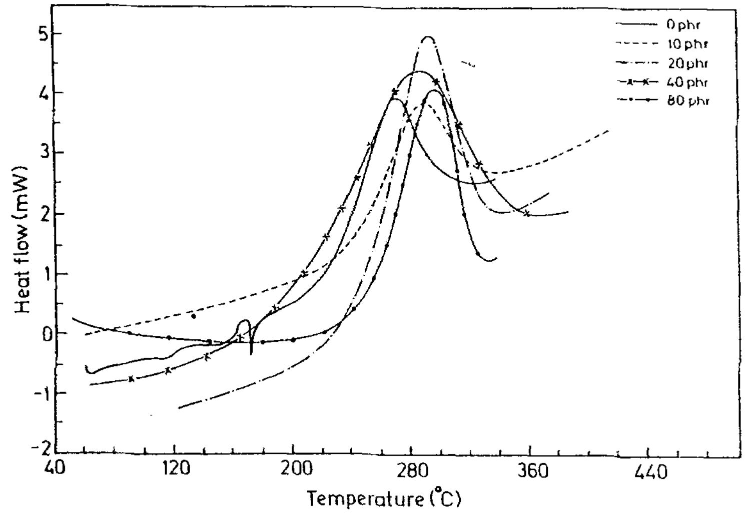


Fig. 1 DSC scans of modified bismaleimide resin at different concentration of CTBN

Table 1 Summary of DSC scan data for modified bismaleimide resin

CTBN/	$T_{cur.\ onset}$/	$T_{Extrap\ onset}$/	$T_{Exopeak}$/	ΔH/
phr		°C		J g^{-1}
0	194	227.0	269.1	105
10	196	228.2	271.0	254
20	197	232.7	272.2	254
40	200	235.0	273.9	221
80	200	235.5	275.5	198

phr - per hundred resin.

As the CTBN concentration was increased from 0 to 80 phr, the curing onset temperature and the extrapolated onset temperature increased from 194 to 200 and from 227 to 235.5°C (Table 1). This shows that a higher concentration of CTBN requires a higher energy for the curing of the whole system. The complex molecular structure of the copolymer of bismaleimide and CTBN hinders the participation of reactive sites of the curing reaction, which in turn increases the curing temperature of the system.

The increase in exothermic peak temperature was also due to the steric hindrance produced by the elastomer particles between the two reacting sites, which necessitated a higher temperature to increase the reactivity of the cross-linking sites at a higher concentration of CTBN.

The heats of the exothermic reaction, calculated as the areas under the peaks, are listed in Table 1. Figure 1 clearly reveals that as the CTBN concentration increased, the temperature for completion of the curing reaction decreased.

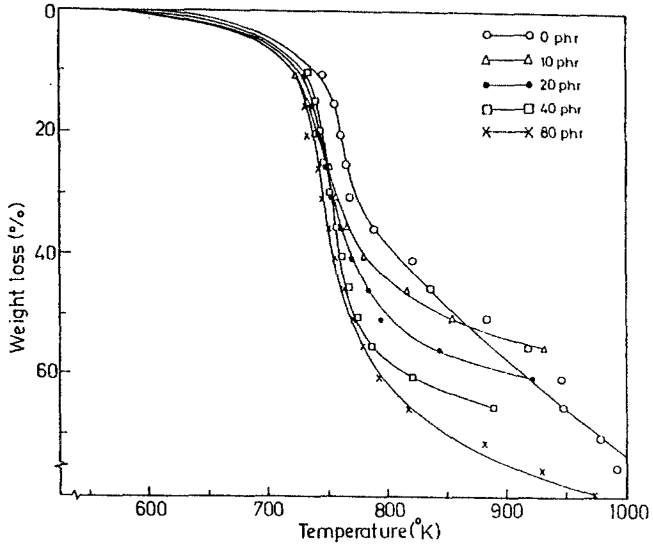


Fig. 2 Dynamic thermograms of modified, bismaleimide resin at different concentration of CTBN

The dynamic TG curves of the neat and modified bismaleimide resins (Fig. 2) show that a single-step reaction mechanism was operative during degradation of the modified and unmodified resins. Initially, the rate of degradation was low, but it increased at higher temperature. This means that in the initial stages of polymer degradation the extent of cross-linking was more than the extent of bond rupture. However, in the later stages the trend was reversed and hence the degradation rate was high [10].

Table 2 Kinetic data from TG for modified bismaleimide resin

CTBN/ phr	n	E/ kcal mol^{-1}	Z/ min^{-1}	Char Yield at 500°C/%
0	2.0	10.662	7.12×10^{-4}	68.5
10	1.5	49.357	3.92×10^{8}	62.0
20	1.5	53.013	2.80×10^{9}	62.5
40	2.0	63.981	7.06×10^{12}	46.5
80	0.6	27.420	1.45×10^{2}	40.0

n – Order or reaction
E – Energy of activation
Z – Pre-exponential factor.

After modification with CTBN, bismaleimide degrades at a higher rate, as is clear from the initial degradation temperatures (Fig. 2). This means that the relative thermal stability decreased on addition of CTBN. The relative thermal stability of the material was also assessed with the help of the char yield calculated at 500°C (773 K) in nitrogen atmosphere for 0–80 phr of elastomer (Table 2). A decrease in char yield represents a decrease in ablative performance of the material. This is supported by the literature data [11]. The kinetic parameters, viz. the activation energy (E), pre-exponential factor (z) and order of reaction (n) for the thermal degradation of modified bismaleimide resin, were evaluated by using the Coats-Redfern equation [12] (Table 2). The best-fit value of n for all formulations was calculated in the range 0–2.

From Table 2, it is clear that the energy of activation (E) increased with increasing CTBN concentration as compared to the neat resin. Elastomer-modified bismaleimide formulations having a low temperature range of degradation exhibit a higher slope of the degradation plot and a higher activation energy. The coiled structure of the elastomer evolved higher energy during decoiling, together with degradation. The neat resin involves only rupture of the bond of the homopolymer of the cured bismaleimide system. For each formulation, the values of E and Z closely agreed with each other.

At room temperature, the lap shear strength of the bismaleimide resin increased from 150 to 500 kg cm^{-2} on the addition of CTBN from 0 to 80 phr. This was explained in terms of the formation of a higher number of elastomer domains (copolymer of bismaleimide and CTBN) with increasing CTBN concentration. Most of the load could be taken by these elastomer domains to increase the joint strength

Table 3 Effect of CTBN concentration on adhesive properties of modified bismaleimide resin

CTBN/	Lap shear strength/kg cm^{-2} at		Peel strength/kg cm^{-1}
phr	30°C	200°C	30°C
0	150	135	0.56
10	230	120	0.70
20	310	105	0.85
40	470	75	1.15
80	500	71	1.73

against shear forces. A maximum 47% decrease in lap shear strength was observed at elevated temperature (Table 3). Surface degradation of the adherends and some thermal or oxidative degradation during processing at high temperature could cause this decrease in lap shear strength. The progressive addition of CTBN led to 1.25, 1.50, 2.05 and 3.08-fold increases in the peel strength at room temperature. This is indicative of an increase in toughness.

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