# THERMOANALYTICAL STUDIES
# ON
# BISMALEIMIDES AND MODIFIED BISMALEIMIDES

by

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## CERTIFICATE

This is to certify that the thesis entitled "Thermoanalytical studies on bismaleimides and modified bismaleimides" being submitted by Mrs. Ranjana Sharma to the Indian Institute of Technology, Delhi for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Mrs. Ranjana Sharma has worked under my guidance and supervision and has fulfilled the requirement for the submission of this thesis which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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## ABSTRACT

The application of advanced fibre reinforced organic matrix resin composites to aerospace hardware has significantly increased over the past decade and is expected to increase further in future. Replacement of metals by such composites can affect substantial weight and energy savings and improve their performance characteristics. Epoxy resins are generally used for fabrication of such composites. However, due to poor performance of epoxy resin in hot wet environments several other matrix resins have been investigated in last 15 years. Bismaleimide resins have emerged as one of the most suitable candidate materials for better performance in hot wet environments. The present thesis is primarily concerned with the thermoanalytical characterization of bismaleimide resins.

Bismaleimides are synthesised by reacting maleic anhydride with appropriate diamine to give an intermediate bismaleamic acid which is then cyclodehydrated to bismaleimide either by heating (thermal) or chemical means (sodium acetate and acetic anhydride). In the present work systematic studies on thermal cyclodehydration of bismaleamic acid were carried out by heating it at 120°C, 130°C and 140°C for 1-4h. Chemical cyclodehydration was also done by treating them with sodium acetate/acetic anhydride mixtures. Extent of thermal cyclodehydration

reaction depended on (a) temperature (b) duration and (c) nature of bismaleamic acid. Even after heating at 140°C for 4h incomplete cyclodehydration was indicated by FT-IR, acid number determination and elemental analysis. The conversion was higher at higher temperatures for the same duration of thermal treatment.

Bismaleimides such as 4,4'-bismaleimidophenyl methane (BM) and 3,3'-bismaleimidophenyl sulfone (BS) were prepared in the laboratory. In order to study the effect of increasing bridge length between maleimido group on thermal characteristics of the resin, chain extension reaction of bismaleimide resin was done by treating with 4,4'-diamino-diphenyl methane (M) and 4,4'-diaminodiphenyl ether (E) in acetone solution. Chain extension of BS was also done in DMF solution using tris(m-amino phenyl) phosphine oxide (TAP) and diamine (M). The resins have been referred to as in situ chain extended BS:M and BS:TAP resins. The resins were characterized by using elemental analysis and IR spectroscopy.

Blending of bismaleimides having electron withdrawing group (BS) with bismaleimide having electron donating group (BM) was carried out using different weight ratios (3:1, 2:1, 1:1, 1:2 and 1:3). Blending of bismaleimides and chain extended bismaleimides BM/BS:BM-E/ BS-E was also carried out.

A decrease in $T_m$ values was obtained on blending BM:BS and BM-E:BS. No $T_m$ was observed in BS-E:BM blends.

A significant decrease in peak temperature of curing exotherm ($T_{exo}$) was observed by blending BM with BS resin. Similar decrease in $T_{exo}$ values was observed in BM-E:BS and BS-E:BM blends. A bimodal behaviour was observed in neat BS-E. With the increased BS-E content in BS-E:BM and BM-E:BS-E blends, the bimodal behaviour became more obvious. Thermal stability of cured resins improved on blending. Glass fibre reinforced laminates were fabricated from some of these resins and evaluated for their mechanical properties.

Blending of bismaleimides and diglycidyl ether of bisphenol A (epoxy resin)was also carried out. For this purpose bismaleimide was blended with 5, 10, 15, 20, 30, and 50% of epoxy resin with stoichiometric amount of amine added for curing of epoxy resin.

A reduction in $T_{exo}$ was observed by blending. However, thermal stability of bismaleimide resins decreased significantly by blending with epoxy resins.

Blends of bismaleimides with polycarbonate were also investigated. For this purpose 5,10, 15, 20, 30 and 50% of polycarbonate was blended with bismaleimide BS/chain bismaleimide BS-E or BS-M.

In these blends an endothermic transition was observed around 99-104°C. Exothermic transition was observed around 165°C. The exotherm had a bimodal character when 30% polycarbonate was blended with BS-M and BS-E. However, only single exotherm was observed when polycarbonate content was increased to 50%. $T_m$ of BS reduced on blending polycarbonate. The $T_{exo}$ and heat of curing ($\Delta H$) decreased significantly.

Neat sheets of the blends containing 50% polycarbonate were prepared by compression molding technique. IR spectra of the blends and sheets before and after post curing were recorded. In the IR spectra of these blends typical absorption bands for polycarbonate were observed at 1784, 1227, 1190 and 1163 $cm^{-1}$ besides the characteristic imide band at 1720 $cm^{-1}$. An increase in polycarbonate content resulted in an increase in intensity of polycarbonate blends. No additional peaks indicative of chemical reaction were observed. The extent of curing were determined before and after post curing of sheets at 220°C for 16h. IR spectra of soluble and insoluble fraction of uncured and cured sheets showed the presence of bismaleimide as well as polycarbonate component thereby indicating physical entrappment of polycarbonate in the polymer network. Thermal stability decreased significantly on blending.

Neat sheets prepared from blends were tested for mechanical properties. Best results were obtained for $C_{10}$:BS system. Chain extended bismaleimide/polycarbonate blends exhibited poor properties. SEM studies showed phase separation in bismaleimides/polycarbonate blends. No phase separation was observed in chain extended bismaleimide/ polycarbonate blends.

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