



Synthesis, Cure and Thermal properties of Bismaleimide Resin and Allylnadic-imide

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ABSTRACT

Synthesis of Bismaleimide i.e. bis (4-maleimidophenyl) Sulphone (B) and Michael adduct of B with 4,42 - Di amino Diphenyl methane and blended with allylnadicimides i.e. bis (4-allylnadicimidophenyl) methane (S) , 1,6-allylnadicimidohexane(V) , and N-allylnadic-imide(L) was carried out at 280 °C for 1hr. The cure behavior of the blend resins was measured by DSC. The thermal stability of cured resins was characterized by thermogravimetric analysis. The thermal stability of the resins improved markedly with the higher content of chain extended bismaleimide (M) with solid allylnadic-imide resin in blends.

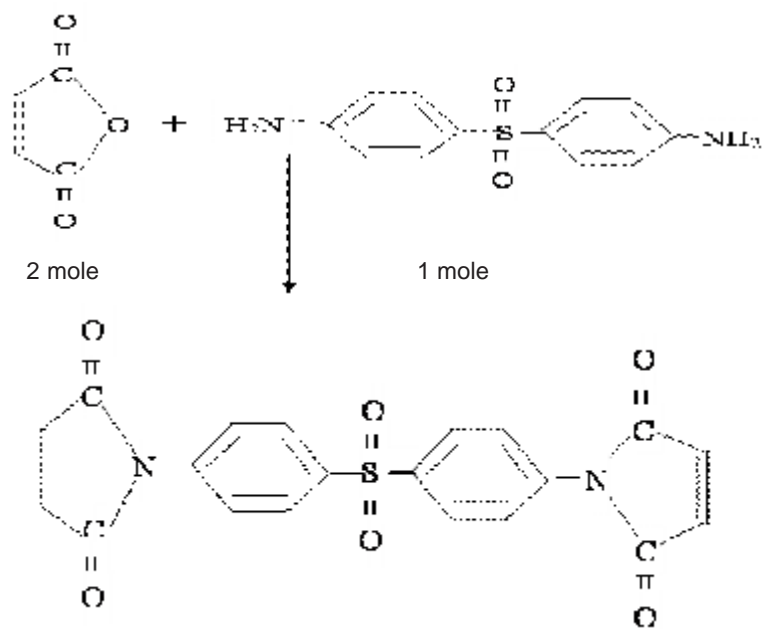
Key words: Bismaleimide, Allylnadic-imide resin, Blends, Thermal properties.

INTRODUCTION

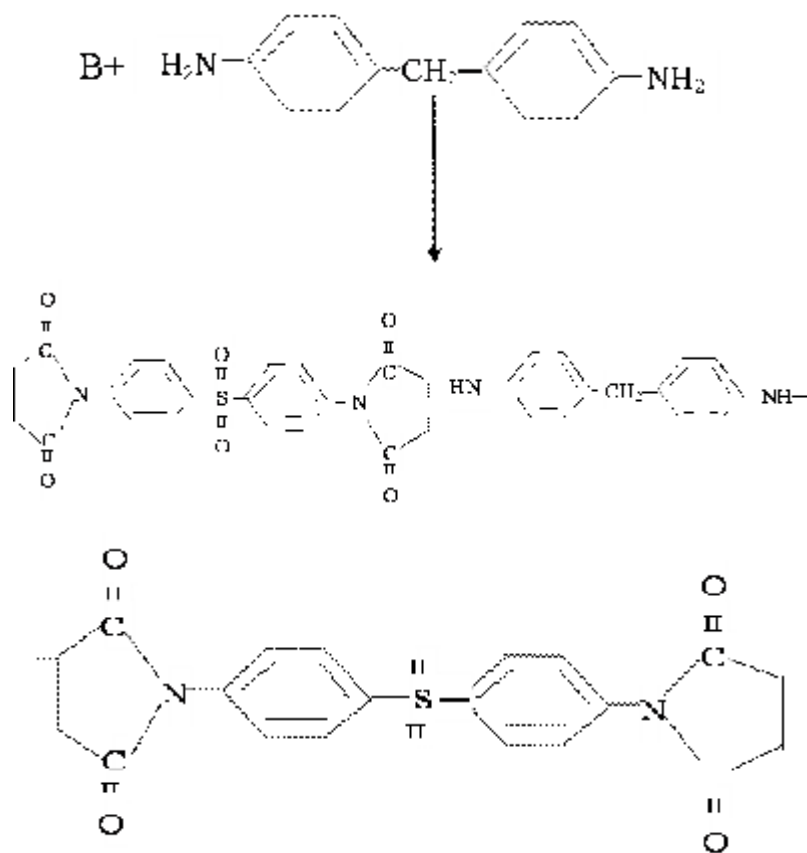
Addition polyimide are low molecular weight, imide prepolymer end-capped with reactive groups such as acetylenic or olefinic. The olefinic end group in addition polyimides may be cycloaliphatic (i.e. norbornene) or aliphatic (i.e. bismaleimides) in nature. Among addition polyimide, bismaleimides (BMIs), as a kind of high performance materials have received more and more interest because of their good thermal stability, excellent processability, aerospace structure composites²⁻⁶, fire resistance and excellent resistance to humidity at elevated temperatures⁽²⁻⁴⁾. These low molecular weight monomers and oligomers cure thermally to yield a highly cross linked infusible polymer network which is insoluble in all organic solvents. However, due to their highly cross linked structures, bismaleimide resins are

extremely brittle and thus are often modified for application⁷⁻¹¹. Cross-link density of maleimide resins has been successfully reduced by chain extension reaction with appropriate nucleophiles (Michael addition reaction) such as diamines^{12,13}, amino acid hydrazide¹⁴, etc. Stoichiometric mixing of bismaleimide with diamine leads to the formation of linear polyaspartimides which could be cast into a flexible film with poor thermal stability¹⁵.

The main drawback in the use of neat BMI resin is its highly brittle characteristic after curing, caused by its aromatic molecular structure and high cross link density. The problem becomes exacerbated in composite structures. Blending of addition polyimides with several thermoset resins and thermoplastics has been carried out in the past with an aim to improve the processability and phosphorus containing nadimide resin¹⁶ yielded



4,4'-bismaleimidophenyl Sulphone (B)



Scheme 1:

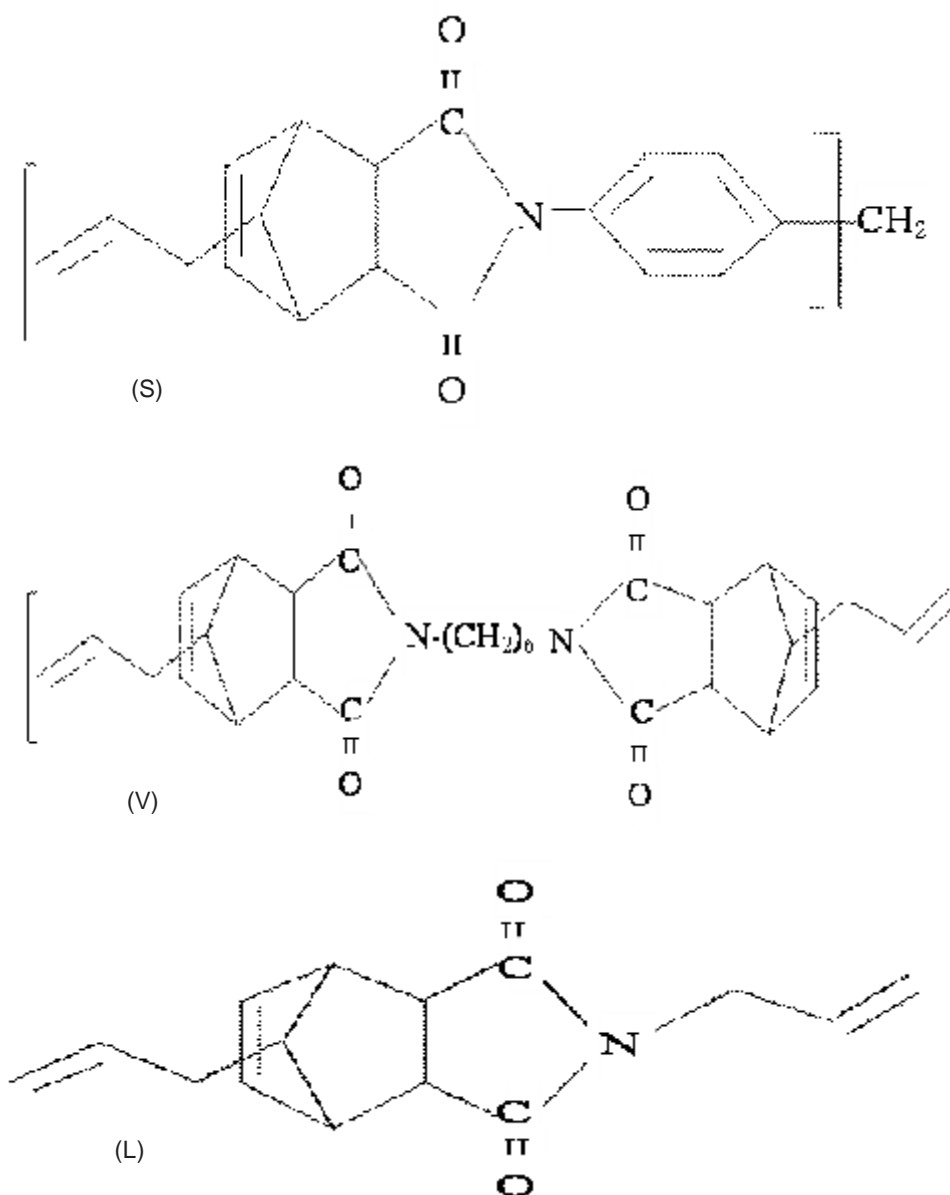
products with improved char yield and better processability.

Effect of blending bismaleimide monomer and chain extended bismaleimides with allylnadic-imides on curing characteristic and thermal stability of cured network is now being reported here. Two resin samples B and M having the structure shown in scheme-1, were synthesized for this purpose.

EXPERIMENTAL

Materials

Na_2CO_3 (BDH), KOH pellets (E.Merck), glacial acetic acid (BDH) methyl ethyl ketone (MEK, BDH), chloroform (E.Merck) and maleic anhydride were used as such. Acetic anhydride (BDH) was distilled before use. The diamines 4,4'-diaminodiphenyl methane



Scheme 2: Structure of allylnadic-imides (letter in parenthesis indicate the designation of these resins)

(Fluka), 4,4'-diaminodiphenylsulphone (fluka) were dried under vacuum. Acetone (BDH) was dried over K_2CO_3 (BDH) and distilled before use. Anhydrous sodium acetate (BDH) was obtained by fusion. Allylnadic-imides bis (4-Allylnadic-imido phenyl) methane (S), 1,6-Allylnadic-imidohexane (V) and N-allylnadic-imide (L) of the structure shown in scheme-2, were procured from Ciba-Geigy.

Synthesis of Bismaleimide B

In a three necked flask equipped with a condenser and nitrogen inlet tube, 0.5 mole of 4,4'-diaminodiphenylsulphone was placed and 350 mL of dry acetone was added. The temperature was raised to 60 °C and solution was stirred by magnetic stirrer. Maleic anhydride (0.10 mole) was then added in several portions and solution was stirred for 2 h at 60 °C, cyclization of the amic acid intermediate was done by adding fused sodium acetate and acetic anhydride and heating the solution at 60 °C for another 2h. Bismaleimide was isolated by precipitation using water as a non solvent. The precipitate were repeatedly washed with water and sodium bicarbonate and finally with water. Purification of bismaleimide was done by using silica gel (60-120 mesh) column using chloroform as the solvent. The solution was concentrated on a rotary evaporator and crystals of bismaleimide separated out on cooling.

Yield = 85.88% m.p.= 247-248°C

Preparation of chain extended bismaleimide M

Chain extension reaction of B with 4,4'-diaminodiphenyl methane (DADPM) was carried out in acetone/methyl ethyle ketone solution using a molar ratio of 1:0.33. The appropriate quantity of bismaleimide and amine was added to the solvent with continuous stirring and the solution was refluxed for 4 hr till a homogenous solution was obtained. The solvent was removed under reduced pressure using a rotary evaporator and shining powder of bismaleimide-amine adducts were obtained.

Preparation of resin blends

Three blend composition were prepared by dissolving bismaleimide/chain extended bismaleimides (B,M) in acetone and allylnadic-imides (S,V,L) in the ratio of 1:3, 1:1, 3:1. These compositions have been designated by writing the letter designation of bismaleimide/chain extended

bismaleimide and allylnadic-imides (S,V,L) and a subscript indicating the ratio of the two components. For example BS, BS₃- and B₃S indicate 1:1, 1:3, 3:1 w/w ratio of resin B (bismaleimide) and S (allylnadic-imides) respectively. For homogenous mixing solution technique was used (acetone as solvent). Curing was done at 280°C for 1hr in a muffle furnace.

Characterization

Structural characterization of various resin samples was done by recording FT-IR spectra in KBr pellets using Perkin- Elmer 580B infrared spectrophotometer ¹H-NMR spectra recorded in DMSO-d₆ using a Jeol JNM-FX100 FT-NMR spectrophotometer. A DUpont 9900 thermal analyser with 910 DSC Module was used for studying the curing behaviour of resin formulations. A DUpont 1090 thermal analyser with a 951 TG module was used for assessing relative thermal behaviour of resin formulations. Thermogravimetric traces of 10±2 mg size samples were recorded in nitrogen atmosphere (flow rate 50mL/min) at a heating rate of 10°C/min .

RESULTS AND DISCUSSION

In the IR spectra of various maleimide resin sample (Fig. 1) the characteristic carbonyl group was observed at 1780±5 cm⁻¹ and 1720±5cm⁻¹. The other prominent absorptions arising due to phenyl group 1576±10 cm⁻¹ and 1490±10cm⁻¹, C-N (1370±5 cm⁻¹) and SO₂ group (1150±5 cm⁻¹ and 1330±5cm⁻¹). In the chain extended bismaleimide, presence of N-H group was indicated by absorption band at 3380-3400cm⁻¹(fig.1). Existence of methyl group in the chain extended M resin confirmed from the C-H stretching vibrations which appears at 2950 and 2879cm⁻¹ (Fig 2).

In ¹H-NMR spectrum aromatic proton appeared as a multiplet at 7.22-8.08 ppm and olefinic protons at 6.49 ppm. A singlet due to methylene group at 3.34 ppm was observed. These studies confirmed the structure of various samples. The melting and curing behaviour of these resins was investigated by DSC. A sharp endotherm associated with melting was observed in bismaleimide B at 247°C. Exothermic transition associated with curing was observed in the temperature range of 248-350°C. The exothermic

peak temperature, Texo, was observed at 272°C (Fig 3). Presence of the strong electron withdrawing group (Sulfone) in B resin may be responsible for the observed increase in the curing temperature. Heat of curing (ΔH) was found to be 77.5J/g for B resin. The Texo decreased on chain extension of B with amines and the value of 220°C was observed in sample M.

In allylnadic-imide resins the curing exotherm was observed in the temperature range of 230-350°C. Based on the results of the DSC scan, it was decided to carry out the isothermal curing of various resin samples at 280°C for 1 hr.

Thermogravimetric analysis of cured resin samples was done to evaluate relative thermal stability. Typical TG trace is shown in fig. 3(a) & (b). The initial decomposition temperature (T_i) and temperature of maximum rate of weight loss (T_{max}) were noted down from these traces and the results are summarized in the Table-1. Char yield at 800°C was also determined. The highest char yield of 49% was observed in M sample and lowest value was in allylnadic-imide L (16%). The highest char yield in cured M can be attributed to more cross linking (oxidative coupling of methylene group) in this resin system, which is initiated by benzylic methylene groups leading thereby to formation of condensed ring system.

Blending of bismaleimide B with allylnadic-imides affected the thermal stability and the char yield changed with the composition of the blend. An increase in bismaleimide content resulted in an increase in the char residue in these blends (Table-2). The char yields in the co-cured resin samples were also calculated by rule of mixtures. The observed char yields were higher than the calculated values. A synergistic improvement in the char yield was observed in blends of bismaleimide B and allylnadic-imide resin S (fig 4). However replacement of S by V or L did not show such synergism (fig 5).

Blending of chain extended bismaleimide and allylnadic-imide also affected the thermal behavior of the cured resins (Table-3). The highest char yield 45% was observed in M_3S blends. In these resin samples also a synergistic behavior

was observed when allylnadic-imide S was used (fig 3). Whereas with resin L no synergism was observed with bismaleimide BS (fig 4). An improvement in char yields was observed when chain extended bismaleimide sample M was used along with V or L in the blends (fig 4).

Table 1: Thermal behavior of cured resin samples

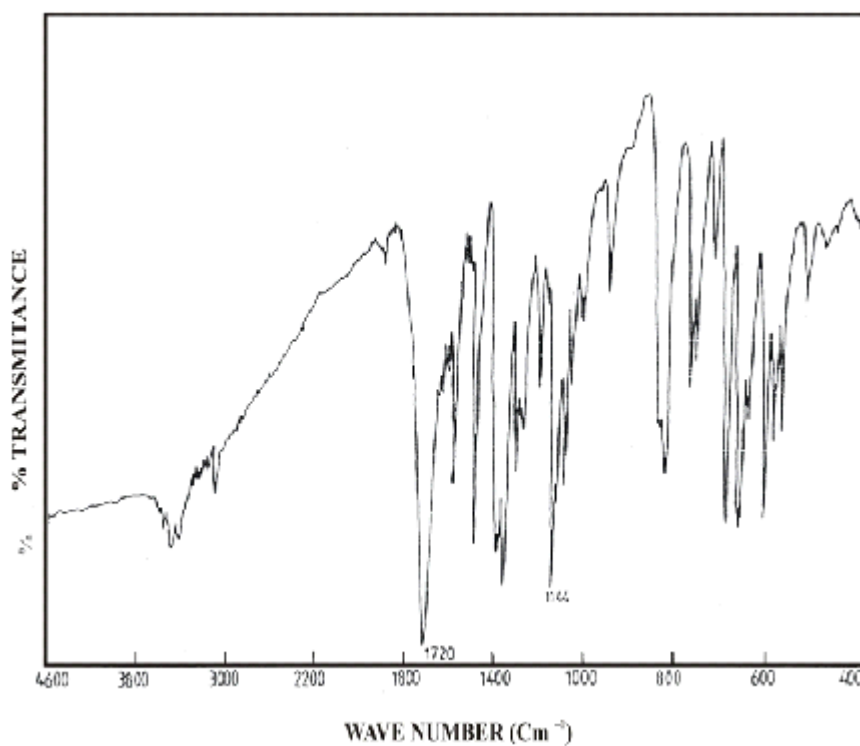
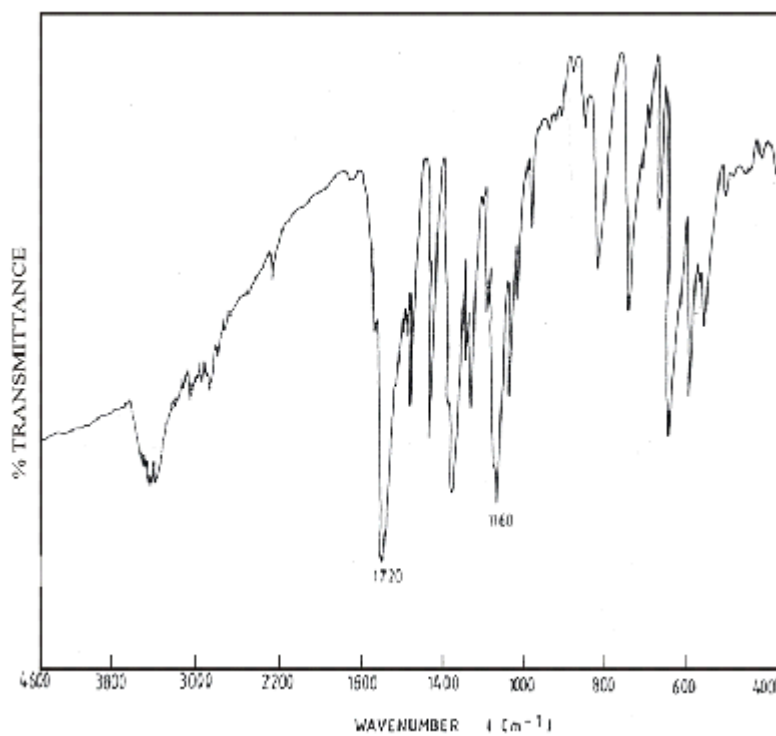
Resin Formulation	T_i °C	Tmax	Yc %
B	468	488	42
M	394	434	49
S	481	497	29
V	470	505	19
L	475	495	16

Table 2: Thermal behavior of cured bismaleimide B and allylnadic imide blends

Resin Formulation	T_i °C	Tmax	Yc %
BS_3	438	473	38
BS	437	469	43
B_3S	467	490	44
BV_3	457	503	26
BV	463	493	31
B_3V	468	491	37
BL_3	444	475	25
BL	438	473	33
B_3L	452	471	36

Table 3: Thermal behavior of cured chain extended bismaleimide and allylnadic-imide blends

Resin Formulation	T_i °C	Tmax	Yc %
MS_3	429	468	41
MS	414	457	43
M_3S	402	454	45
MV_3	432	475	25
MV	405	449	35
M_3V	426	476	30
ML_3	427	461	31
ML	408	446	41
M_3L	399	440	42

**Fig.1: FT-IR spectrum of resin B****Fig. 2: FT-IR spectrum of resin M**

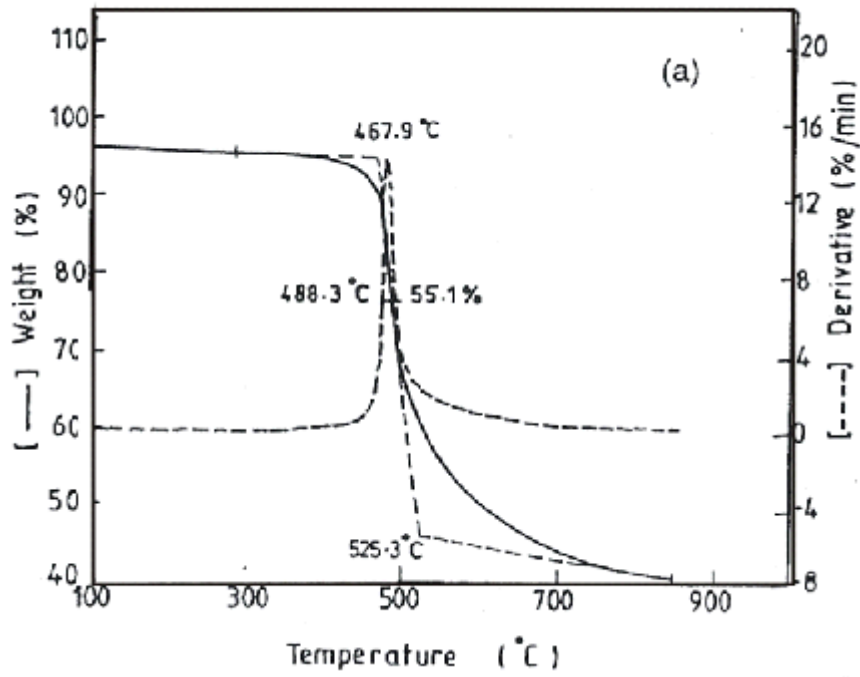


Fig. 3(a): TG trace of cured resin B

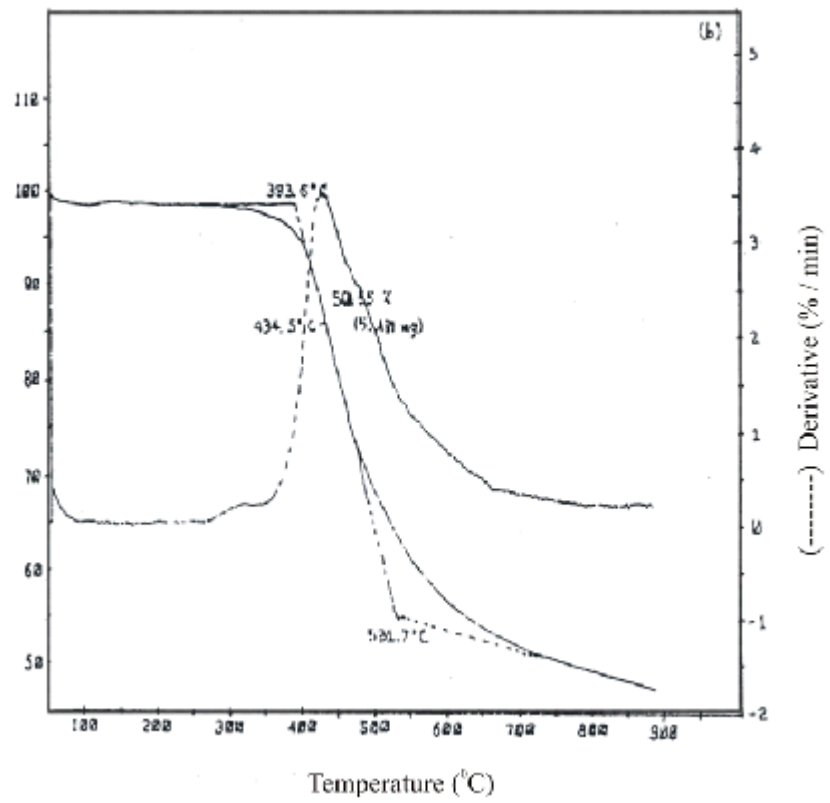


Fig. 3(b): TG trace of cured resin M

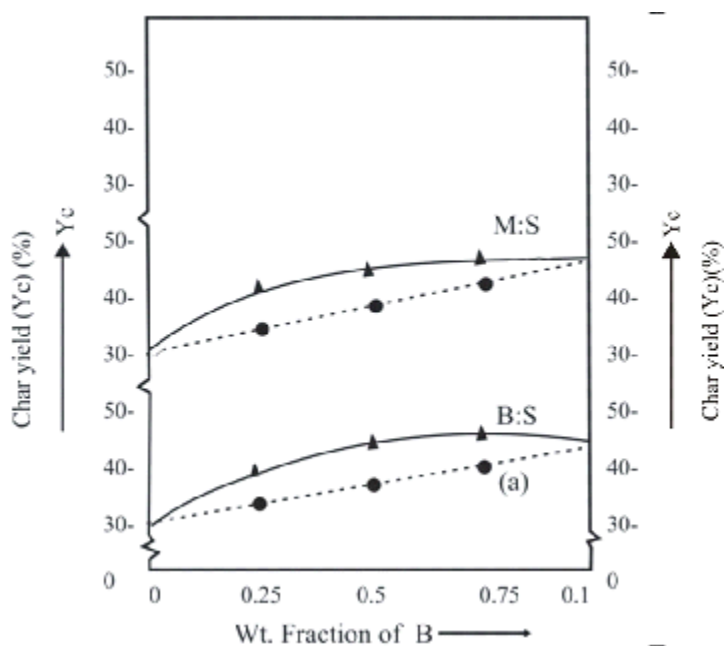


Fig.4: Plot of char yield (N₂ atmosphere, 800 °C) Vs weight fraction S in the blends of bismaleimide resin B and M

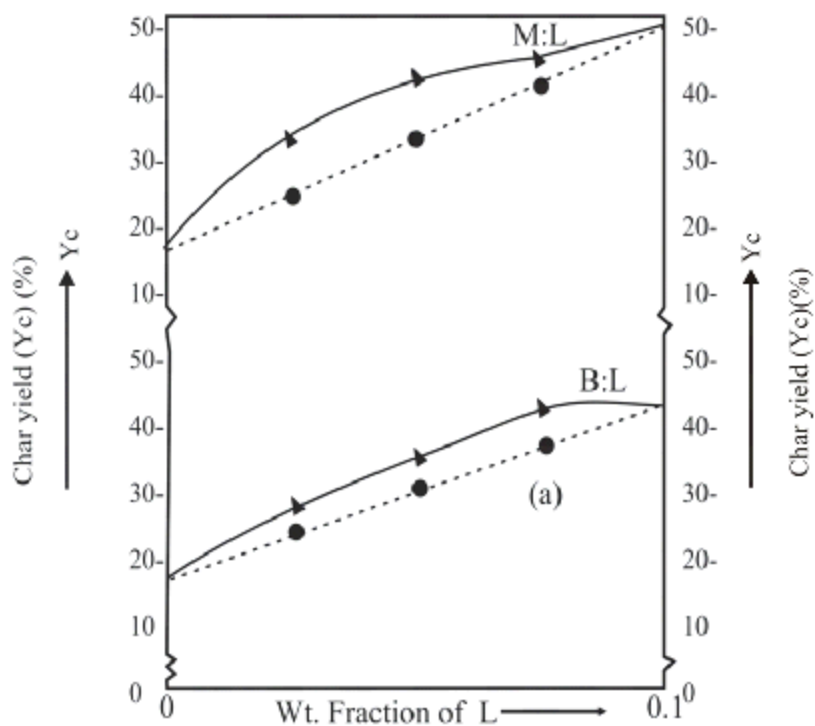


Fig.5: Plot of char yield (N₂ atmosphere, 800 °C) Vs weight fraction L in the blends of bismaleimide resin B and M

Co-curing of resin blends may result in a polymer network comprising both constituents. Thermal behavior therefore would be influenced by the structure of network formed. An improvement in the thermal stability on co-curing of allylnadimide S with different bismaleimide samples was observed. This synergism may be explained on the

basis of co-curing of resins, proposed earlier for a two component high performance resin system based on bismaleimide and 2,22 -diallyl bis phenol-A (14-16). Co-polymerisation of the constituent takes place via ene type linear chain extension reaction followed by Diels-Alder adduct formation.

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