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Studies on the adhesive properties of solid elastomer-modified novolac epoxy resin

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Abstract

Adhesive properties like lap shear strength and T-peel strength of novolac epoxy resin modified with carboxyl terminated butadiene acrylonitrile (CTBN) solid resin and cured with two different curing agents namely, dicyandiamide (DICY) and 3,3′-diaminodiphenyl sulphone (DDS) were evaluated using aluminium adherends. Substantial improvement in adhesive properties was obtained by the inclusion of moderate concentrations of CTBN in the formulations. Adhesive properties of the formulations were evaluated when used as paste, nylon-carrier supported and unsupported film adhesives. Optimum concentrations of 20 parts by weight (pbw) and 25 pbw of solid CTBN in epoxy were obtained for the DICY and DDS cured systems, respectively. Inclusions of larger amounts of CTBN led to flexibilisation of the systems thereby reducing the adhesive properties. CTBN also reduced the glass transition temperatures and high-temperature strength retention of both the systems. The development of two-phase morphology for the CTBN-modified systems was evident from scanning electron micrographs (SEM). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Epoxides; A. Toughened adhesives; B. Aluminium and alloys; C. Lap shear; Film adhesive

1. Introduction

Epoxies dominate the field of structural adhesives due to their better wetting ability, superb mechanical properties and good chemical and high-temperature resistance. However, fully cured epoxies have the limitation of high brittleness and in order to overcome this limitation, extensive research has been carried out to toughen epoxies by incorporating a reactive liquid rubber [1–5]. The rubber which is initially compatible with the epoxy–hardener mixture, separates out during the cure reaction, thereby developing the characteristic two-phase morphology of the toughened system. The toughness improvement takes place without much deterioration of thermal or mechanical properties of the base matrix [6,7] and consequently when used as an adhesive, the lap shear and peel strength properties get enhanced [8,9]

Most of the work reported in the field of toughened epoxies deal with diglycidyl ether of bisphenol A (DGEBA) based epoxy resin and liquid CTBN (carboxyl-terminated butadiene acrylonitrile copolymer). The present study deals with the modification of novolac epoxy resin which has been studied to a lesser extent [10]. The primary requirement for high-temperature performance necessitates the selection of polyfunctional epoxy resins and curing agents capable of creating high crosslink densities [11]. Thus, novolac epoxy resin, being multifunctional, can produce a more tightly crosslinked three-dimensional network compared to DGEBA and hence can give better adhesive strength retention at elevated temperatures. Solid CTBN, rather than the liquid rubber, was chosen as the modifier for epoxy resin since the aim of the present investigation was the development of film adhesives based on these formulations. The film adhesives offer convenience and reliability over the paste adhesives and are particularly efficient for the fabrication of light-weight, high-strength sandwich structures and hence occupy an important position among the different structural adhesives. Most of the thermosetting film adhesives are microscopically heterogenous with a continuous phase of a rigid resin such as the phenolic or epoxy and a discontinuous phase of a high molecular weight elastomer, like solid CTBN. Film adhesives should be non-tacky for handling purposes and in the present study, the addition of solid CTBN could control the tackiness of otherwise highly tacky formulations containing the novolac epoxy and curing agents.

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Dicyandiamide (DICY) is the most commonly employed latent epoxy curing agent which can provide potlives of approximately six months for epoxy systems by virtue of its insolubility in the resins at ambient temperature. When heated in the presence or absence of catalysts, rapid polymerisation commences to yield highly crosslinked molecules exhibiting high strength and moderate heat resistance. 3,3′-diamino diphenyl sulphone (DDS) is commonly employed in aerospace laminating applications requiring enhanced honey-comb peel strength. It has the advantage of providing the highest heat resistance when compared to other aromatic amines. In the present study both DICY and DDS have been used as latent epoxy curing agents for novolac epoxy-CTBN adhesive system, used as paste, nylon-carrier supported and unsupported films. In addition to the adhesive properties like lap shear strength (LSS) and T-peel strength (TPS) of the epoxy formulations, SEM (scanning electron microscopy) studies on the morphologies of the unmodified as well as the CTBN-modified epoxy systems are also presented in this paper.

2. Experimental

2.1. Materials

The chemical structures of the materials used in the present study are shown in Table 1. The novolac epoxy resin, EPN 1138 (EPN), having epoxy functionality 3.6 and epoxy value 5.4 eq/kg, was obtained from Hindustan Ciba Geigy, Mumbai, India. The solid grade of CTBN, Nipol 1072 (Zeon Chemicals. Inc, USA) with molecular weight M_n of 65 000 has 26–28% acrylonitrile content and 0.07–0.08 ephr (eq/100 parts of resin) carboxyl content. DICY, DDS and triphenyl phosphine (TPP) were the commercial grades and were used as received. The solvents used were analar grade dimethyl formamide (DMF) and methyl ethyl ketone (MEK). Mono No. 12 nylon cloth (Saryu Textiles, Ahmedabad, India) of thickness 0.1 mm and weight 30 g/m^2 was used as received, as the carrier for making the supported film adhesive.

2.2. Adhesive preparation

CTBN was masticated in a double roll mill and then dissolved in MEK to get nearly 20% solution. The exact dry residue was determined by evaporating a weighed quantity of the solution to constant weight in a hot air oven maintained at 100°C. Pre-reaction of carboxyl groups of CTBN with epoxy groups of EPN was then carried out at 80°C in nitrogen atmosphere, using 0.25 pbw (parts by weight) of TPP as the catalyst. For this, CTBN (solution in MEK) and EPN were taken on 1:1 weight basis (approximately) 1:100 carboxyl/epoxy molar ratio). Completion of the pre-reaction was confirmed by monitoring the acid value. The exact dry residue of the pre-reacted solution was determined as before by evaporating a known quantity of the solution to constant weight. The adhesive compositions were formulated with varying ratios of CTBN and EPN, ranging from 10:90 to 50:50 by weight. The pre-reacted CTBN-EPN solution was mixed with the calculated quantity of EPN to get the different compositions (the pre-reacted solution was used as such for the 50:50 composition). The required quantities of DICY/DDS were separately dissolved in DMF or MEK and added to the rubber–epoxy mixture. All the ingredients were then thoroughly mixed together to get the desired composition in the paste adhesive form.

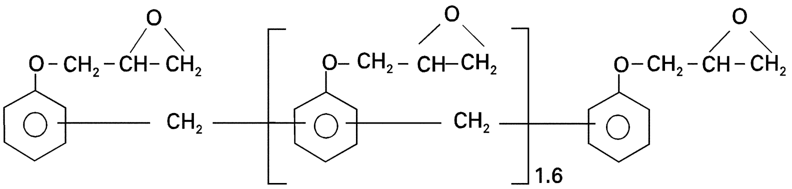
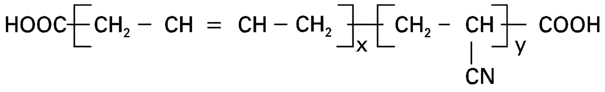
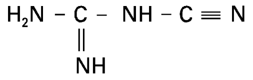
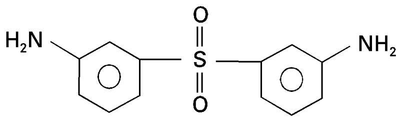
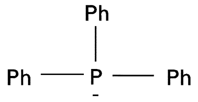
In the present study, system A refers to adhesive formulations containing EPN, CTBN and DICY as curative and system B refers to the formulations containing DDS as curative. Even though the stoichiometric requirement of DICY is about 11 g for curing 100 g of epoxy resin having an epoxy value of 5.4 eq/kg, the studies of Yu-der Lee et. al [12] revealed that 6 g is sufficient to produce maximum values for LSS and T-peel strength on aluminium substrates. Preliminary studies carried out on epoxy-DICY system also supported this view and hence in the present study, 6 g of DICY per 100 g of EPN resin was used for system A. For system B, 34 g of DDS per 100 g of EPN resin was used as per the stoichiometric requirement.

Nylon carrier supported film adhesives of approximate weight 250 g/m^2 and thickness 0.22 mm were made by brushing the adhesive on both sides of the carrier cloth. The unsupported film adhesives of approximate weight 200 g/m^2 and thickness 0.18 mm were cast on polythene sheets which would be removed easily while bonding. The weight and thickness of the films were maintained by giving repeated coatings at an interval of 1 h. These films were given a drying time of 48 h at room temperature for solvent removal before determining their adhesive properties. It was not possible to make films of all compositions used as the paste adhesive; only those compositions which could be cast as non-tacky films were tested for the adhesive properties.

2.3. Test methods

LSS and TPS were determined on chromic acid etched B-51-SWP aluminium alloy substrates as per ASTM methods D-1002 and D-1876 respectively [13 pp. 44–47 and 105–107]. The bonded specimens were cured at 175°C for 120 min in a hot air oven, applying an average pressure of 0.2 MPa for lap shear specimens and 0.1 MPa for T-peel specimens, using the lever press arrangement. The adhesive strength was measured in an Instron UTM Model 4202 at a crosshead speed of 10 mm/min. For determining the joint strength at 100°C, the specimens were soaked at that temperature for a period of 10 min.

Table 1
Chemical structures of materials used

1. EPN 1138	 (Polyglycidyl ether of phenol-formaldehyde novolac)
2. NIPOL 1072	 $HOOC\left[CH_2-CH=CH-CH_2\right]_x\left[CH_2-\underset{\substack{\vert\\CN}}{CH}\right]_y COOH$ (Carboxyl terminated butadiene acrylonitrile copolymer solid)
3.	 $H_2N-\underset{\substack{\Vert\\NH}}{C}-NH-C\equiv N$ Dicyandiamide (Epoxy curing agent)
4.	 3,3′ diamino diphenyl sulphone (Epoxy curing agent)
5.	 $Ph-\overset{\substack{Ph\\\vert}}{P}-Ph$ Triphenyl phosphine (catalyst for epoxy-carboxyl reaction)

DSC of the systems was taken using Mettler TA 3000 system at a heating rate of 10°C/min over the temperature region 25–300°C. Thermogravimetric analysis was carried out using Dupont model 900 TGA, at a heating rate of 10°C/min in nitrogen atmosphere. Scanning electron microscopy (SEM) was used to observe the morphological features of the CTBN-epoxy systems. The fractured surfaces of the specimens were coated with gold using a vacuum sputterer and examined using a Stereoscan 250 MK-3 Cambridge instrument.

3. Results and discussion

3.1. Cure reactions

Novolac epoxy resin, when cured with either DICY or DDS, gets converted into a very highly crosslinked, brittle, three-dimensional structure. The mechanism of curing epoxy resins with DICY is complex [14, pp. 49–50] and involves the initial reaction between all four active hydrogens with epoxy groups and simultaneous epoxy homopolymerisation. This is followed by a final cure reaction between hydroxyl groups produced in the partially cured epoxy resin and the cyano group in DICY. The mechanism of cure of epoxy resin with DDS is typical of the reaction between epoxy and any primary amine [14 pp, 38 and 39]. The reaction steps include the addition of primary amine active hydrogen to an epoxy group, followed by the addition of the resulting secondary amine hydrogen to another epoxy group.

In order to fix the cure conditions, DSC of systems A and B as such and with 20 pbw of elastomer were recorded and the results are given in Table 2. The DSC onset temperature (T_i) is slightly lower for DDS cured system B probably because of its higher reactivity compared to DICY. The DSC peak temperature (T_p) is nearly the same for both systems. Both T_i and T_p are not appreciably affected by the presence of CTBN. Therefore, a cure condition of 120 min at 175°C was chosen for both the systems and after subjecting the samples to this cure condition, DSC did not show any residual cure exotherm in both cases. The only transitions recorded in these specimens were due to glass transition and these results are also included in Table 2.

Table 2
DSC results of systems A and B

Sample	Temp. of cure initiation (T_i) °C	Temp. of cure Maximum (T_p) °C	Glass transition temp. of cured sample (T_g)°C
Unmodified system A	154	189	134
System A with 20 pbw of CTBN	150	188	124
Unmodified system B	130	183	182
System B with 25 pbw of CTBN	129	184	163

3.2. Adhesive properties

The tight network of DICY or DDS-cured novolac epoxy resin gives rise to brittle cured products in both the systems, resulting in poor adhesive properties. Thus, low LSS values of 10.3 and 8.3 MPa were obtained for the unmodified systems A and B, respectively. With a view to reduce brittleness of these systems, CTBN was added in varying amounts and the adhesive properties were evaluated when used as paste, unsupported and nylon-carrier supported film adhesives. The carrier present in the supported film adhesive enables easy handling of the film, assists in controlling the glue-line thickness, provides a means for venting reaction volatiles, if any, and improves the peel strength properties. For more weight-critical applications, the unsupported film adhesive in which the carrier is not present, is used.

3.2.1. System A

Fig. 1 gives the variation of LSS with CTBN content for system A when evaluated as paste, unsupported and nylon-carrier supported film adhesives. For the paste adhesive, LSS values increased with CTBN, showed a maximum, and then decreased with more of CTBN content. The maximum LSS of 17.9 MPa (which is 1.7 times the value of the un-modified system) was obtained at 20 pbw of CTBN. Unsupported and supported film adhesives with CTBN content < 20 pbw could not be made or tested, since the tackiness of these formulations was very high, making it difficult to handle them. As CTBN content increased from 20 to 50 pbw, LSS decreased steadily for both types of films, and hence it is presumed that the optimum would be in the vicinity of 20 pbw of CTBN as in the case for the paste adhesive. Also, the curve for unsupported film closely follows that of the paste adhesive with a difference in LSS values $< 6\%$. This is expected since the formulation remains the same, the only difference being the form in which the adhesive is applied. However, the same formulation, in the form of supported film adhesive, provided better adhesive properties. LSS values were approximately 10–20% more than that of the unsupported film. This may be due to the reinforcement and better control of glue-line provided by the nylon carrier.

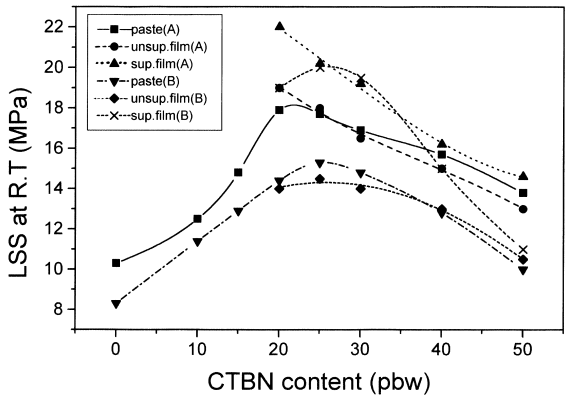


Fig. 1. Variation of LSS wih CTBN content for systems A and B. System A evaluated as (a) paste adhesive –■–, (b) unsupported film adhesive –●–, (c) supported film adhesive –▲–, System B evaluated as (d) paste adhesive –▼–, (e) unsupported film adhesive –◆–, (f) supported film adhesive – × –.

Besides LSS, TPS is another important and common adhesive property test. Peel testing indicates the ability of the adhesive to resist stripping forces. The TPS variation of system A with CTBN content, when evaluated as a paste and supported film adhesives is shown in Fig. 2. The curves exhibit a similar trend of changes as in the case of LSS. The unmodified system, being highly brittle, gave very poor peel strength. The optimum formulation with 20 pbw of CTBN gave a TPS of 0.89 kN/m, which was about 7 times the strength of the unmodified system. The supported film gave marginally better strength than the paste adhesive due to the presence of the carrier.

The substantial increase in the adhesive strength observed for the CTBN-modified system can be attributed to the increased toughness of the cured epoxy matrix brought about by the inclusion of the elastomer [3–5]. The enhancement in impact and fracture toughness properties by adding elastomer upto a certain amount has been reported for liquid CTBN-modified DGEBA-based epoxy systems [15]. Donatelli et al. [8] reported the effect of CTBN on the adhesive properties of EPON 828 cured with DICY. In all such cases, the increase in adhesive strength was possible because of the capability of the added elastomer to separate out as a discrete phase while curing, which can arrest crack propagation to a greater extent when the material undergoes fracture by

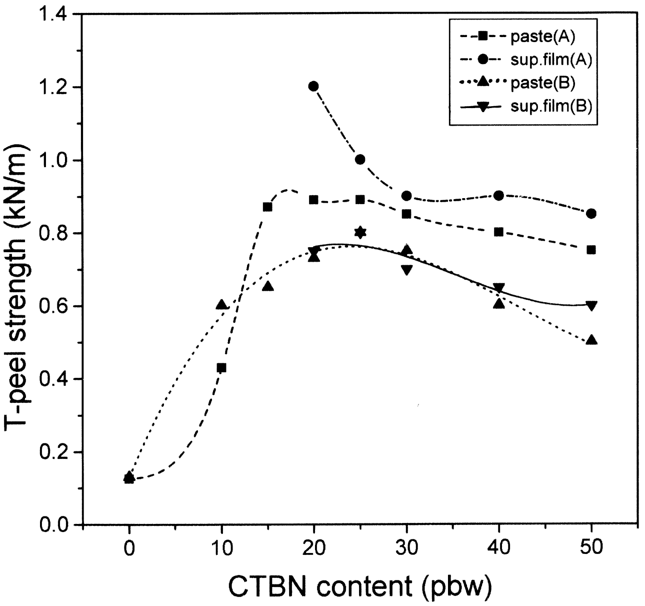


Fig. 2. Variation of TPS with CTBN content for systems A and B. System A evaluated as (a) paste adhesive -■-, (b) supported film adhesive -●-, System B evaluated as (c) paste adhesive -▲-, (d) supported film adhesive -▼-.

distributing the applied stress over the whole bonded area. Earlier studies have shown that the chemical linking of the elastomer with the epoxy matrix is a primary requirement for the toughening of the bulk matrix; otherwise, the unreacted elastomer can act as a weak boundary layer in the adhesive joint [16–18]. Hence in the present study, to ensure the formation of the epoxy-CTBN link before the cure reaction, the epoxy was pre-reacted with the carboxyl groups of CTBN. CTBN, which was compatible with the epoxy initially, phase separated during the cure reaction as evidenced by SEM (discussed later) and this dispersed elastomeric phase caused the increase in adhesive strength. The nature of failure of the adhesive joint (visually observed), changed from adhesive for unmodified system to cohesive for CTBN-modified system.

For compositions containing higher concentrations of CTBN, the adhesive strength was found to decrease steadily and the strength reduction was drastic for compositions with > 30 pbw of CTBN. At higher loadings of CTBN, the flexibilisation of the crosslinked epoxy matrix by the added elastomer resulting in loss of mechanical properties overweighs the advantages mentioned earlier. In addition, the inclusion of higher amounts of high molecular weight CTBN can adversely affect the wetting properties of the adhesive, which is one of the pre-requisites for a good adhesive. It was observed that with CTBN levels > 30 pbw, wetting properties were reduced, changing the nature of failure of the adhesive joint from cohesive to a mixed mode.

Retention of strength at elevated temperatures is one of the requirements of structural adhesives. Therefore, the system with varying CTBN content was evaluated for LSS at 100°C, and the results are presented in Fig. 3. The % retention of LSS at 100°C, compared to the LSS at ambient temperature, is shown in Fig. 4. The un-modified epoxy produced the highest LSS of 15 MPa at 100°C with 146% retention. This increase in strength could be due to the higher flexibility of the adhesive that takes place at the test temperature leading to higher strength. For the CTBN-modified epoxy formulations, the LSS decreased steadily with CTBN content at high temperature. This is attributed to the presence of rubbery CTBN in the formation which causes a reduction in glass transition temperature (as observed from DSC; values given in Table 2). The optimum formulation containing 20 pbw of CTBN that gave maximum LSS at ambient temperature showed a retention of 41 and 50% at 100°C, when evaluated as the paste and supported film respectively.

3.2.2. System B

The adhesive properties of system B with varying CTBN content are also presented in Figs. 1–4, which show the same trend as in the case of system A. For system B, the optimum composition based on LSS and TPS is with 25 pbw of CTBN (Figs. 1 and 2) which gave, respectively, 1.84 times and 6.15 times the LSS and TPS of the un-modified system. LSS properties of the unsupported films were nearly the same as that of the paste adhesive (difference < 5.7%), and those of the supported films were 25–40% more than that of the unsupported films. The LSS evaluated at 100°C (Fig. 3) continuously

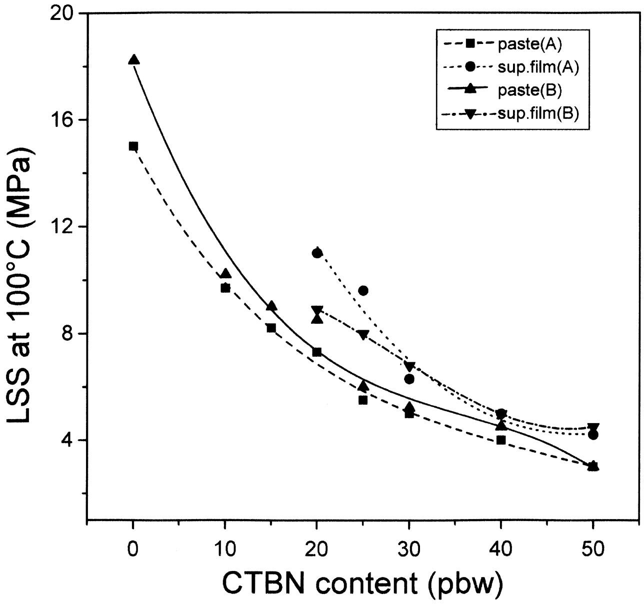


Fig. 3. Variation of LSS at 100°C with CTBN content for systems A and B. System A evaluated as (a) paste adhesive -■-, (b) supported film adhesive -●-, System B evaluated as (c) paste adhesive -▲-, (d) supported film adhesive -▼-.

decreased with CTBN content showing that the inclusion of CTBN in the formulation decreased the strength retention properties (Fig. 4) as well as T_g (Table 2) of system B. The maximum LSS value of 18.2 MPa at 100°C was given by the unmodified system, with 219% retention when compared to LSS at ambient temperature. The optimum formulation containing 25 pbw of CTBN gave LSS retention of 39 and 40% at 100°C when evaluated as paste and supported film, respectively.

Since the adhesive properties of systems A and B show similar variation with the inclusion of CTBN, it is inferred that both systems behave similarly under the experimental conditions. The adhesive properties obtained using the unmodified and optimum formulations of systems A and B are compiled in Table 3. When the unmodified systems are compared, the LSS at room temperature and TPS of system B is slightly less than that of system A, which is due to the more brittle nature of the highly crosslinked structure of system B, resulting from the aromatic primary amine curing agent. However, the LSS at 100°C as well as the retention of LSS at 100°C of system B is higher which is in accordance with the observed higher T_g of system B. The properties at higher temperatures are decided by the chemical structure of the network as well as the crosslink density. DDS which has the aromatic backbone structure is known to provide very high heat resistance to epoxy systems, whereas DICY with its aliphatic structure cannot be so effective. The CTBN-modified system A was found to provide better adhesive properties than system B, both as one-component paste and film adhesives probably because elastomer modification is more effective in less cross-linked, more ductile system A, compared to the highly cross-linked, rigid system B. The importance of ductility of the matrix has been reported in the modification with reactive rubbers such as CTBN [19,20]. Also, a higher CTBN content (25 versus 20) was required in the case of system B to attain the optimum level. Whereas the unmodified systems A and B gave 146 and 219% LSS retention at 100°C, respectively, their CTBN-modified optimum formulations could give LSS retention of the order of 40–50 only. This was expected because the presence of high molecular weight CTBN would drastically affect the T_g and hence the high-temperature properties.

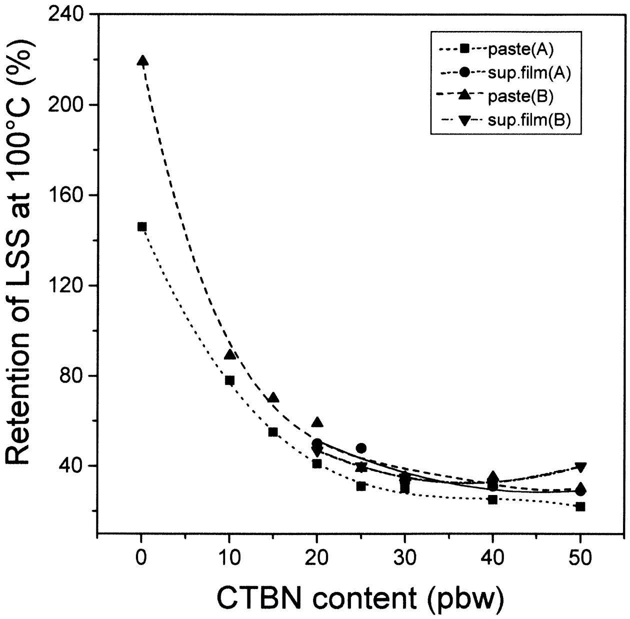


Fig. 4. Variation of % Retention of LSS at 100°C with CTBN content for systems A and B. System A evaluated as (a) paste adhesive -■-, (b) supported film adhesive -●-, System B evaluated as (c) paste adhesive -▲-, (d) supported film adhesive -▼-.

3.3. *Effect of filler*

The effect of variation of aluminium powder as the filler was studied for the optimum formulation of

Table 3
Adhesive properties of unmodified as well as CTBN-modified optimum compositions of systems A and B

Adhesive properties	Unmodified system A	System A with 20 pbw of CTBN	Unmodified system B	System B with 25 pbw of CTBN
1. LSS at RT (MPa)				
(a) paste form	10.3	17.9	8.3	15.3
(b) unsupported film	—	19.0	—	14.5
(c) supported film	—	22.0	—	20.0
2. LSS at 100°C (MPa)				
(a) paste form	15.0	7.3	18.2	6.0
(b) supported film	—	11.0	—	8.0
3. Retention of LSS at 100°C (%)				
(a) paste form	146	41	219	39
(b) supported film	—	50	—	40
4. TPS at RT (kN/m)				
(a) paste form	0.13	0.89	0.13	0.80
(b) supported film	—	1.20	—	0.80

Table 4
Effect of aluminium filler on the adhesive properties of system A, modified with 20 pbw of CTBN and evaluated as supported film adhesive

Filler concentration (pbw)	LSS (MPa)			T-peel strength at RT (kN/m)
	at RT	at 100°C	Retention at 100°C (%)	
0	22.0	11.0	50.0	1.2
5	20.1	11.7	58.2	1.1
10	17.3	12.0	69.4	1.0
20	15.0	10.0	66.7	0.7
30	13.4	6.5	48.5	0.6

system A containing 20 pbw of CTBN, as the supported film adhesive, and the results are given in Table 4. Aluminium powder was chosen since it is one of the most commonly used reinforcing filler in epoxy adhesives. The results show that the inclusion of filler was adversely affecting the LSS and TPS properties at ambient temperature. However, the LSS at 100°C as well as the percentage retention of LSS at 100°C were improved by the inclusion of aluminium. Above 20 pbw, aluminium caused a decrease in adhesive properties of the system. This could be due to the decreased wetting properties of the adhesive caused by the inclusion of solid filler particles.

3.4. Thermal properties

The systems were evaluated for thermal stability in nitrogen atmosphere by thermogravimetric analysis. The thermogravimetric (TG) as well as the differential thermogravimetric (DTG) traces obtained for the unmodified and the optimum CTBN-modified formulations of systems A and B are shown in Figs. 5 and 6, respectively. The data on initial (T_i), peak T_p and final (T_f) decomposition temperatures as well as the char residue at 600°C, derived from these traces are given in Table 5. The clear-cut two step mass-loss in TG trace of unmodified system and the shoulders observed in DTG traces of both unmodified and CTBN-modified formulations of system A indicate a two-step thermal degradation process. The degradation of system B is in a single step. When compared to system A, system B had higher char residue at 600°C. This can be attributed to the higher aromatic content of system B resulting from the DDS curing agent, imparting it better thermal stability. The relatively lower stability of DICY cured product is also reflected in its two-stage mass loss, the first stage probably corresponding to the chain zipping process at the DICY-cured epoxy linkages (the details of this aspect is under investigation). The inclusion of CTBN in these systems was found to bring down T_i, T_p as well as the char residue due to the relatively lower thermal stability of the CTBN.

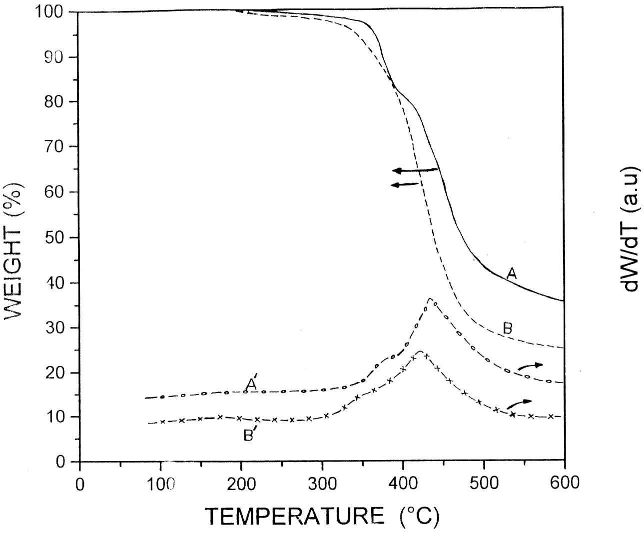


Fig. 5. TGA traces of system A: (A) un-modified (B) modified with 20 pbw of CTBN; (A′) and (B′) are the corresponding DTG traces.

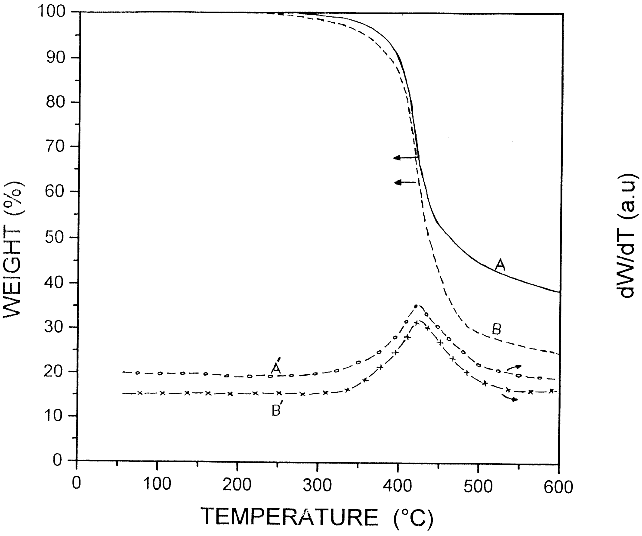


Fig. 6. TGA traces of system B: (A) un-modified (B) modified with 25 pbw of CTBN; (A′) and (B′) are the corresponding DTG traces.

Table 5
Thermogravimetric analyses data of unmodified and CTBN-modified systems A and B

System	Decomposition temperature (°C)			Char residue (%) at 600°C
	Initial (T_i)	Peak (T_p)	Final (T_f)	
Unmodified system A	355	445	505	36.5
CTBN-modified system A	310	412	505	25.0
Unmodified system B	365	425	505	39.3
CTBN-modified system B	340	422	505	27.0

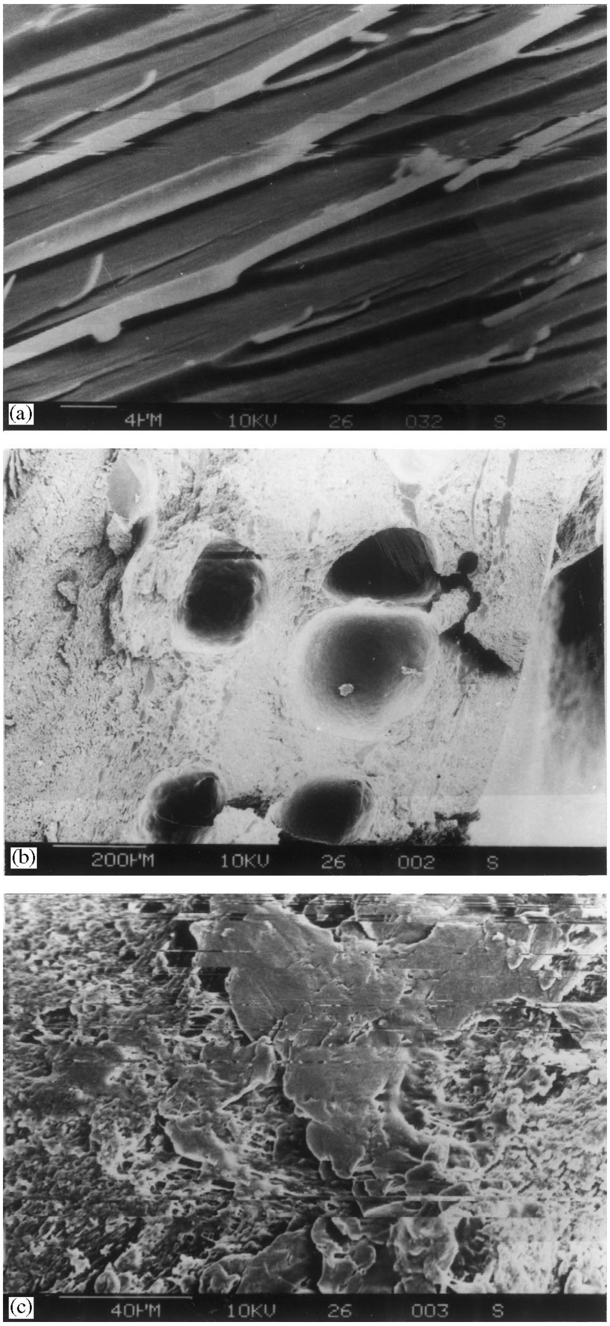


Fig. 7. Scanning electron micrographs of system A: (a) un-modified (b) modified with 20 pbw of CTBN and (c) modified with 50 pbw of CTBN.

3.5. Morphological characteristics

The increase in adhesive properties of the CTBN-modified epoxy systems is explained on the basis of toughness enhancement caused by the development of two-phase morphology during the cure process. The morphological features observed using SEM are shown in Fig. 7 (for system A) and Fig. 8 for system B). The pattern of morphology observed for the unmodified formulations (Figs. 7a and 8a) are characteristic of brittle systems having smooth, glassy fractured surfaces with cracks in different planes. SEM of CTBN-modified optimum compositions of systems A and B (Figs. 7b and 8b, respectively) show the presence of precipitated, discrete rubber particles which are dispersed throughout the epoxy matrix. The larger domain size (100–200 μm) of the precipitated rubber can be attributed to the high molecular weight of the solid rubber modifier used in this study. Even while using low molecular weight modifiers like CTBN and ATBN, domain sizes as large as 100 μm have been reported elsewhere [21]. The fractured surfaces of most of the rubber-toughened epoxy systems have a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles [22–24]. Different mechanisms like crazing, shear banding and elastic deformation of the rubber particles have been proposed and these mechanisms are thought to act alone or in combination, to produce the toughening effect in rubber-modified epoxies [20,24,25]. SEM of the two systems containing 50 pbw of CTBN are shown in Figs. 7c and 8c, respectively. It can be seen that with rubber levels higher than the optimum, the second rubbery phase gets more and more aggregated leading to that phase being less distinguishable from the epoxy matrix. This situation leads to flexibilisation of the matrix resulting in the reduction of adhesive properties.

4. Conclusions

The following are the main conclusions that could be drawn from our study on the evaluation of adhesive properties of novolac epoxy resin modified with solid

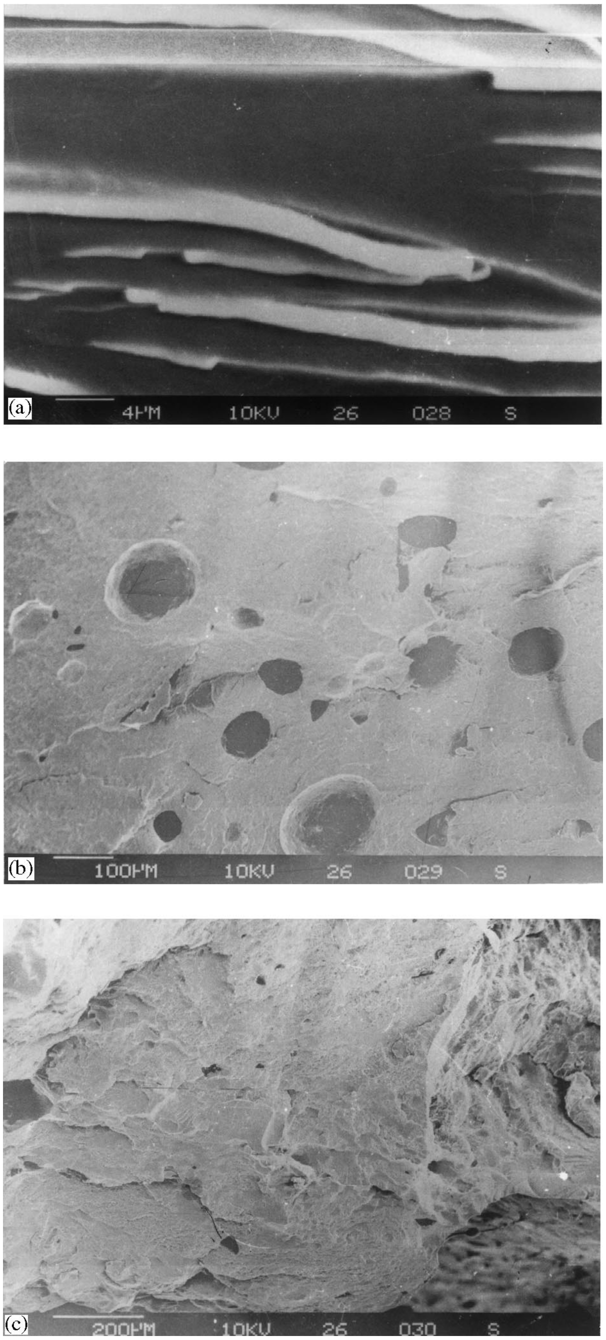


Fig. 8. Scanning electron micrographs of system B: (a) un-modified (b) modified with 25 pbw of CTBN and (c) modified with 50 pbw of CTBN.

CTBN and cured with two curing agents namely DICY (system A) and DDS (system B):

(1) Substantial improvement in adhesive properties is obtained by the inclusion of moderate levels of CTBN in the systems. The optimum formulations for systems A and B that produced the maximum adhesive strength are 20 and 25 pbw of CTBN, respectively. (2) With the inclusion of higher levels of CTBN (> 30 pbw), the systems got flexibilised leading to reduction in adhesive properties. (3) CTBN is more effective in improving the adhesive properties of the less rigid, DICY cured system A than the DDS cured system B. (4) CTBN adversely affects the glass transition temperature, thus decreasing the LSS at 100°C when compared to the unmodified systems. (5) The adhesive formulations provide nearly the same properties when evaluated as one-component paste and unsupported film adhesive. However, the nylon carrier-supported film adhesives give increased properties due to the reinforcement provided by the support. (6) SEM studies of the unmodified as well as the CTBN-modified epoxy systems indicate the development of two-phase morphology during the cure reaction of the modified systems.

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