Effect of a reactive interfacial agent on the properties of a nitrile-rubber-modified epoxy film adhesive

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EFFECT OF A REACTIVE INTERFACIAL AGENT ON THE PROPERTIES OF A NITRILE-RUBBER-MODIFIED EPOXY FILM ADHESIVE

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Reactive interfacial agents are often used to homogenise the morphology of immiscible polymer blends and to improve the level of adhesion between the phases to achieve enhanced properties. This paper demonstrates the ability of hydroxyl methyl bisphenol A (HMBPA) to function as a reactive interfacial agent (compatibilizer) in a nitrile-epoxy film adhesive made from nitrile rubber (NBR) and solid epoxy resin blend. The curing of the adhesive film was achieved at 170°C by adding dicyandiamide, a latent curing agent for epoxy resin, and rubber vulcanising agents. Hydroxyl methyl bisphenol A resins with different hydroxyl methyl content, synthesised by the base-catalysed reaction of bisphenol A and formaldehyde in various mole ratios, were used to compatibilize a blend of nitrile rubber (NBR) and epoxy resin 50/50 wt/wt. The effect of addition of HMBPA on the morphology, adhesive, thermal, and mechanical properties of the adhesive film was investigated. The nitrile-epoxy adhesive films were characterised by measurements of adhesive joint strength, stress-strain properties, DSC, TGA, TMA, DMA, and SEM. Results revealed that significant improvement in joint strength occurred at low levels of HMBPA, and the optimum strength was obtained at about 15 wt% of HMBPA in the blend. The hydroxyl methyl content in HMBPA was found to influence the properties of the adhesive film. The concept of strengthening the interphase between NBR and epoxy through the coupling reactions of HMBPA was used for interpreting the results. The effect of addition of silica, alumina, and aluminum fillers on the properties of the nitrile-epoxy adhesive film was also studied, and a comparison of properties with and without HMBPA is presented.

INTRODUCTION

Epoxy resins are a family of thermoset polymers of increasing importance in engineering as high performance adhesives [1, 2]. Thermoset epoxy resins are generally brittle. They are frequently modified with elastomers to impart greater toughness, and the rubber-modified epoxies have been the subject of continued interest in the field of structural adhesives [3, 4]. Rubber-modified epoxies have emerged as a favoured class of material for film adhesives that provides structural bonds with greater toughness and resistance to peel propagation. Rubber-modified epoxy films [5, 6] form structural adhesives for a variety of substrates such as metals, rubbers, etc., and they have the advantage of easy handling, controlled glue line thickness, uniformity, and weight. Nitrile-rubber-modified epoxy films have been widely used in the fabrication of lightweight honeycomb sandwich assemblies for bonding face skins to each side of the core material to withstand mechanical stresses.

The well-practised chemical technique used for making nitrile-epoxy film adhesives is the introduction of carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) into the epoxy resin by the epoxide-carboxyl prereaction and then curing the film by heat using the latent curing agent dicyandiamide (DICY). There have been several publications detailing functional-group-terminated (amine or carboxyl) liquid or solid polybutadiene acrylonitrile rubber and other toughening agents for epoxy thermosets [7−12]. A considerable amount of study has been done by CK Riew et al. [14, 15] in the direction of toughening of epoxies with functional rubbers, particularly those based on copolymers of butadiene and acrylonitrile, focussing on the chemical criteria for toughening epoxy resin with rubbers. The main factors that determine the toughening are the final blend morphology and the adhesion between the two phases. In CTBN-toughened structural adhesives, the epoxide-carboxyl reaction promotes the interfacial bonding between the rubber and epoxy phases. However, there is little published work on the modification of epoxy resin with the general commercial nitrile rubber (NBR), probably because NBR has no reactive functional group for establishing strong chemical interaction at the rubber-epoxy interface to prevent premature debonding between the phases. We have investi-

gated the effect of strengthening the NBR/epoxy resin interface using hydroxyl methyl bisphenol A (HMBPA) on the properties of a nitrile-epoxy film adhesive. Riew et al. [15] described the toughness synergism as resulting from the inclusion of bisphenol A (BPA) in a CTBN-DGEBA system due to the bimodal distribution of rubber particles. Bisphenol A is known to be miscible with epoxy resin and increases the fracture energy of CTBN-modified epoxy systems [16]. It is considered probable that HMBPA can improve the bonding of the NBR/epoxy resin interfacial region through the reactions of phenolic and hydroxyl methyl groups with epoxy resin and NBR.

In this article, we report the effect of the addition of HMBPA on the adhesive, mechanical, thermal, and morphological behaviour of cured adhesive films derived from a solid epoxy resin/NBR (50/50 wt/wt) blend containing epoxy-curing agents and rubber-vulcanising agents. A series of HMBPA were synthesised by the base-catalysed reaction of bisphenol A and formaldehyde in various mole ratios and employed for the investigation. The blend formed good adhesive films and the addition of HMBPA dramatically improved the properties of the cured film. The property improvement is found to be dependent on the concentration of hydroxyl methyl groups in HMBPA. The effect of silica, alumina, and aluminium fillers on the properties of the nitrile-epoxy film adhesive was also studied and compared, with and without HMBPA modification.

EXPERIMENTAL

Materials

Solid epoxy resin Araldite 6071® (epoxy value 1.9 eq/kg), obtained from Hindustan Ciba Giegy, Mumbai, India, was used as received. The solid nitrile rubber used in this work was Perbunan NS 3307(a copolymer of butadiene and acrylonitrile containing 33% acrylonitrile unit, where the number average molecular weight, the weight average molecular weight, and polydispersity by GPC analysis are 33665, 101190, and 3.006, respectively) obtained from Bayer, Germany. Bisphenol A (2,2-dihydroxyl phenyl propane) and formaldehyde solution were obtained from S.D. Fine Chemicals Limited, Mumbai, India. Hydroxyl methyl bisphenol A with different hydroxyl methyl content were synthesised in the laboratory by the reaction of bisphenol A and formaldehyde.

Precipitated silica, obtained from Xerophils Baroda, India (average particle size, 24.3 μm; average size below which 50% of particles are found, 17.2 μm), alumina, obtained from Associated Cement

Companies, Thane, India (average particle size, 1.7 μm; average size below which 50% of particles are found, 0.84 μm), and aluminium powder, obtained from Metal Powder Company, Madurai, India (average particle size, 32.7 μm; average size below which 50% of particles are found, 24.8 μm) were used as fillers.

HMBPA, Synthesis and Characterisation

HMBPA resins with different hydroxyl methyl content were synthesised by reacting bisphenol A and formaldehyde in the mole ratio 1:1 (HMBPA-a), 1:2 (HMBPA-b), 1:3 (HMBPA-c), and 1:4 (HMBPA-d) using 0.02 mole NaOH as catalyst. Bisphenol A (99%), formaldehyde solution (37%), and NaOH were added to a three-neck flask equipped with a stirrer and thermometer, and the solution was stirred at $80-85°C$ for 8 h. The HMBPA formed was neutralised and isolated by removing water at 60°C under reduced pressure using a rotary evaporator until the weight remained constant. The HMBPA was characterised by ^1H NMR and thermal analysis.

Blending, Film Formulation, and Cure Procedure

NBR and solid epoxy resin, 50/50 wt/wt, were blended with 5 phr (parts per 100 parts by wt rubber) ZnO, 1.5 phr sulphur, 1.5 phr 2-mercapto benzothiazole, 5 phe (parts per 100 parts by wt epoxy resin) DICY, 0.5 phe triphenyl phosphine (TPP) with or without 30 wt% silica, alumina, or aluminium filler and varied concentration of HMBPA in a two-roll mill. The blend was compression-moulded at room temperature into a film of thickness approximately 250 μm between two Teflon-coated release cloths and used for the evaluation of adhesive properties. The cure temperature of the film was determined by Differential Scanning Calorimetry (DSC) measurement and the curing was carried out at $170 \pm 2°C$ for 90 min at 5 MPa pressure in a hydraulic press.

Measurements

The ^1H NMR spectra of the HMBPA samples were recorded in CD_3-CO-CD_3 using a JEOL-FX-90Q instrument.

DSC was done on a Dupont Thermal Analyser with a 902 DSC cell at a heating rate of 10°C/min.

Thermo-gravimetric analysis (TGA) was carried out in a Dupont 951 thermal analyser under N_2 atmosphere at a heating rate of 10°C/min.

The thermal expansion coefficient was measured by thermo-mechanical analysis (TMA). A cured sample of approximately $3 \times 3 \times 3$ mm was used for the TMA to measure the displacement as a function of temperature. The thermal expansion coefficient was calculated [17] by $1/L$ $(\partial L/\partial T)$, where L is the length of the sample and $(\partial L/\partial T)$ is the derivative of the displacement with respect to temperature. The results are reported as thermal expansion coefficient versus temperature plots.

Lap shear (Al-Al), T-peel (Al-Al), and rubber (NBR)-to-metal (Al) peel strength were measured using B51SWP aluminium alloy according to ASTM-D-1002, ASTM-D-1876, and ASTM-D-429B, respectively. The aluminium surface preparation by sodium dichromate-sulphuric acid etch was as described earlier [18]. The adhesive film was placed between the substrates to be bonded and the assembly was placed in a hydraulic press at a pressure of 5 MPa and a temperature of 170°C for 90 min. An Instron model 4202 operating at a crosshead speed of 10 mm/min at 25°C was employed for the measurement of adhesive properties.

Stress-elongation measurements were performed on an Instron model 4202 at a crosshead speed of 10 mm/min using dumbbell specimens cut from cured films of approximately 1 mm thickness, obtained by compression-moulding of the blend at $170 \pm 2°C$ and 5 MPa pressure for 90 min.

Morphological studies were performed by means of scanning electron miroscopy (SEM). The SEM micrograph of the tensile-fractured surface was obtained using a Stereoscan 250 MK-3 Cambridge instrument at an accelerating voltage of 15 KV. The specimen was cut and mounted on an aluminium stub using conductive silver paint and was sputter coated with a thin layer of gold before taking the micrographs.

Swelling studies were carried out in methylene chloride, and the extent of crosslinking of the rubber in the blend was calculated as previously reported [18].

RESULTS AND DISCUSSION

The synthesis of HMBPA resins from bisphenol A and formaldehyde is schematically outlined in Figure 1. A typical ^{1}H NMR spectrum for HMBPA is shown in Figure 2. The signals observed at δ 1.5 ppm, δ 3−3.5 ppm, δ 4−5 ppm and δ 6−7 ppm are due to -C(CH$_3$)$_2$-, -CH$_2$-(bridge), -CH$_2$-O-, and phenyl protons, respectively. The proton intensity ratio of -CH$_2$-O- to that of -C(CH$_3$)$_2$- increases with increase of the formaldehyde/BPA mole ratio (Table 1), which gives evidence
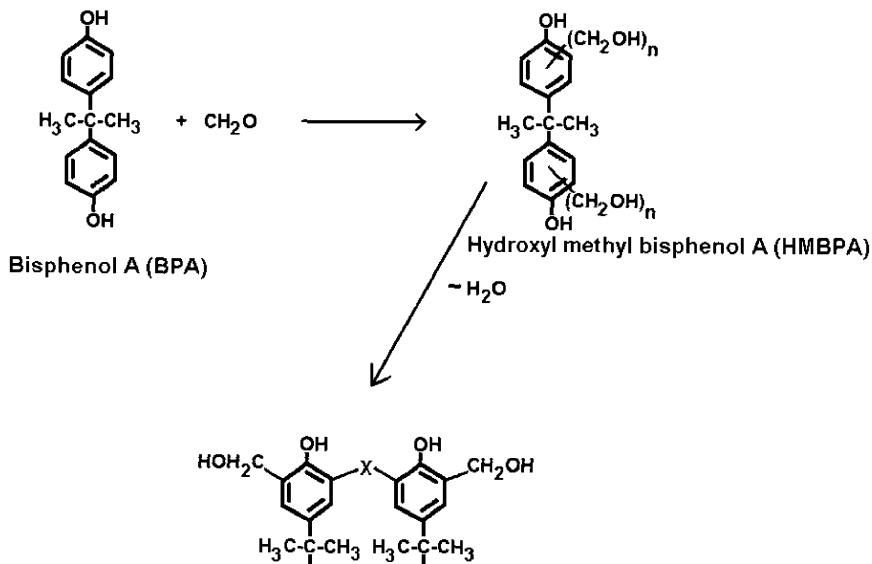
FIGURE 1 Formation of hydroxyl methyl derivative of bisphenol A.

for the formation of more hydroxyl methyl groups with the increase of the formaldehyde/BPA mole ratio. For BPA, the observed ^{1}H NMR signals are δ 1.5 ppm (6 protons) due to -C(CH$_3$)$_2$- and δ 6−7 ppm (8 protons) due to phenyl protons. For HMBPA, the δ value of ^{1}H NMR showed agreement with the structure, but the number of protons estimated by the integrated peak of protons is not in good agreement with the theoretical values, which might be due to side condensation reactions.

A typical DSC thermogram of HMBPA is shown in Figure 3. The peak endotherm (T_{endo}) at 115°C for HMBPA is due to the melting and vapourisation of volatiles (the volatile matter determined at 120°C is 0.07 wt%). The DSC thermogram of BPA (Figure 3) showed a sharp endothermic peak at 159°C due to melting. The exothermic peak in the DSC thermogram of HMBPA corresponds to the reactions of hydroxyl methyl groups. The features of the DSC thermograms of HMBPA (a-d) are basically identical, and the results are summarised in Table 1. The temperatures T_1, T_2, and T_3, are those at which the first energy
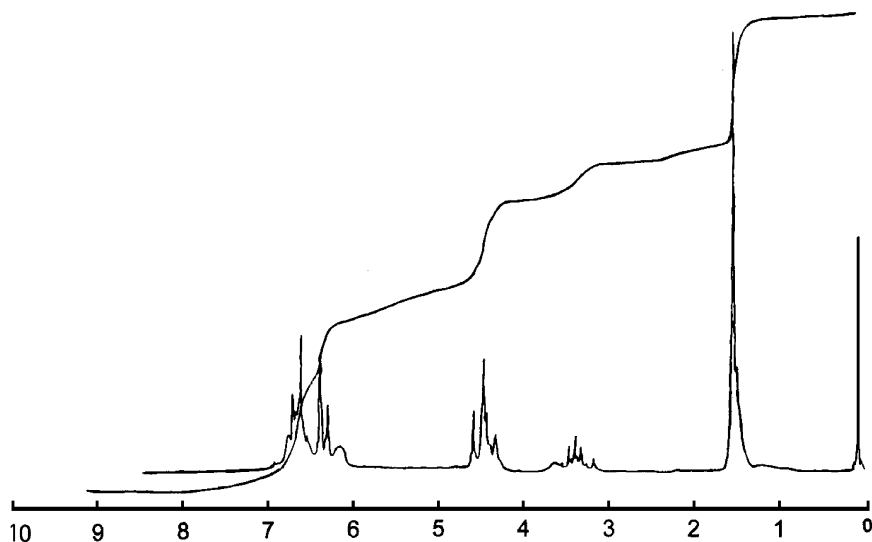
FIGURE 2 ^{1}H NMR spectrum of hydroxyl methyl derivative of bisphenol A (HMBPA-b).

release was detected, the exothermal peak temperature and the temperature indicating the end of the exotherm, respectively. As the formaldehyde/BPA mole ratio increases the exothermal heat of reaction (ΔH) increases, which indicates an increase of hydroxyl methyl content in the resin. On the basis of the DSC data, it was decided to cure the various compositions at 170°C.

The effect of formaldehyde/BPA mole ratio on the thermal stability of cured HMBPA was studied by thermogravimetric analysis (TGA). Figure 4 shows a typical TG-DTG thermogram of a HMBPA sample cured at 170°C for 90 min, which indicates that up to 300°C the weight loss is less than and close to 10 wt%. The temperature zone over which the decomposition at the highest rate takes place is 300−600°C. The effect of formaldehyde/BPA mole ratio on initiaal decomposition temperature (T_i), the temperature of maximum rate of weight loss (T_{max}), the final decomposition temperature (T_f), and the residue at 900°C are summarised in Table 1. Initial decomposition of HMBPA-a is less than HMBPA (b-d), which are higher in hydroxyl methyl content.

DSC was used to characterise the cure behaviour of the adhesive film. Figure 5(a) shows the dynamic DSC trace of pure epoxy resin containing 5 parts DICY per 100 parts epoxy resin. Figure 5(b) is the DSC curve of the uncured adhesive film F-IV, which contains epoxy resin, DICY, NBR, vulcanising agent, HMBPA (b), and TPP. The cure

TABLE 1 ^{1}H-NMR, DSC, TGA Data of HMBPA Resins

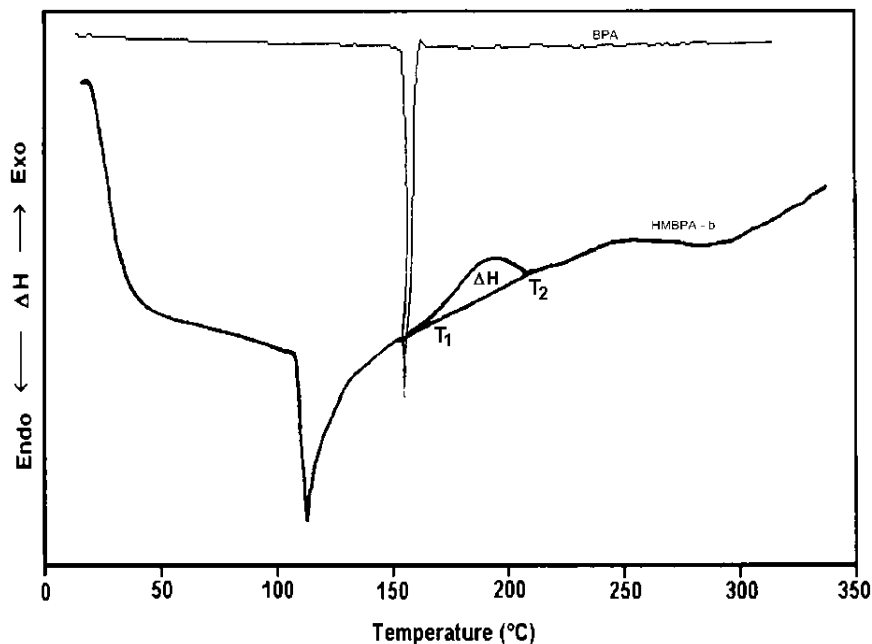| Sample designation	hydroxyl methyl/ g-dimethyl proton ratio determined from ^{1}H-NMR	DSC data					TGA data of cured samples			
		$T_{(endo)}$ (°C)	$T_{1(exo)}$ (°C)	$T_{2(exo)}$ (°C)	$T_{3(exo)}$ (°C)	ΔH (J/g)	T_i (°C)	T_{max} (°C)	T_f (°C)	Residue at 900°C (%)
HMBPA-a (CH_2O/BPA, 1:1 mole)	0.34	118	144	177	208	41.2	296	440	616	37.5
HMBPA-b (CH_2O/BPA, 2:1 mole)	0.66	114	153	187	208	54	316	431	615	45.8
HMBPA-c (CH_2O/BPA, 3:1 mole)	0.98	115	150	185	202	68	317	448	655	39
HMBPA-d (CH_2O/BPA, 4:1 mole)	1.25	115	160	180	200	74	315	436	562	31

FIGURE 3 DSC curve of hydroxyl methyl derivative of bisphenol A (HMBPA-b) and bisphenol A (BPA).

exothermic peak is shifted to higher temperature range for the blend, possibly due to the hindering of chain mobility. The DSC data indicated that the adhesive film must be cured above 150°C. Various compositions of the adhesive films were cured at 170°C and 5 MPa pressure for 90 m. Figure 5(c) is the DSC trace of the cured adhesive film, which showed that cure reactions were completed under the above cure conditions to give a crosslinked network structure.

As depicted in Figure 6, the possible cure reactions are crosslinking of the epoxy network by DICY [19–21], vulcanisation of nitrile rubber [22], condensation of HMBPA through the hydroxyl methyl group [23], and the formation of copolymer of nitrile rubber and epoxy resin by the reactions of HMBPA. HMBPA incorporation into the nitrile-epoxy adhesive film was expected to bring changes in adhesive, mechanical, thermal, and morphological behaviour because of the coupling reactions of HMBPA. HMBPA reacts with the rubber double bond through an o-quinone methide intermediate [24] and to the epoxy through the reaction of the phenolic hydroxyl [25, 26].
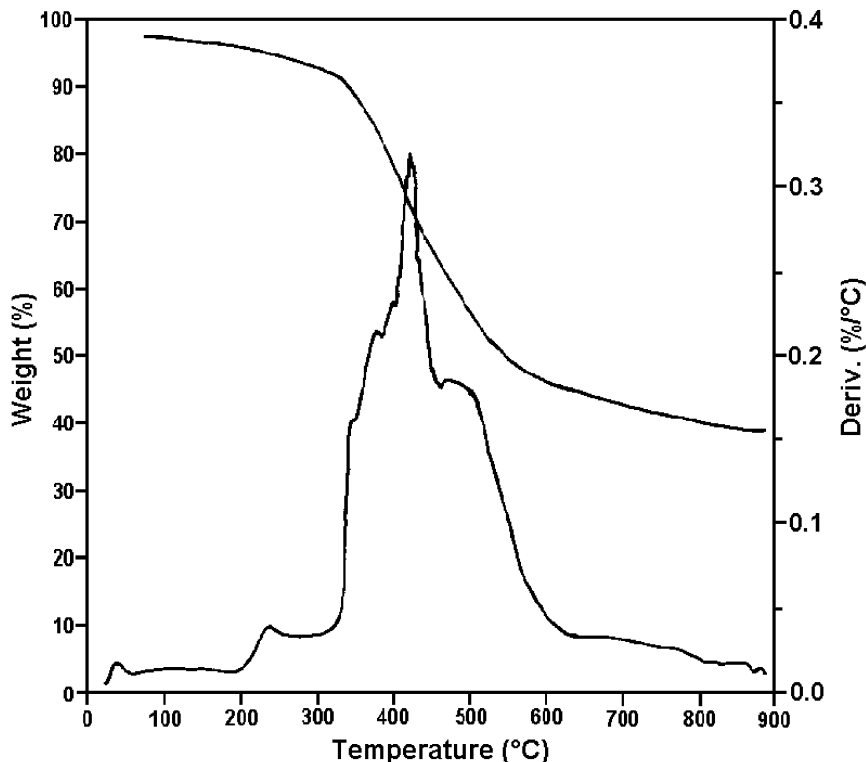
FIGURE 4 TG-DTG curves of hydroxyl methyl bisphenol A (HMBPA-b) after cure (170°C for 90 min).

Adhesive Properties

Figure 7 gives the plots of lap shear and T-peel strength of the aluminium/nitrile-epoxy film/aluminum joint as a function of HMBPA-b in the adhesive film. From Figure 7 it is evident that significant improvement in joint strength occurs at fairly low levels of HMBPA-b (10−15 wt%) and beyond this level does not lead to any significant enhancement in joint strength. The increase in joint strength achieved by the addition of HMBPA is believed to be due to the increase in cohesive strength of the adhesive film by the chemical bond formation between epoxy resin and NBR through HMBPA. In order to verify this, we have examined the effect of HMBPA with varying hydroxyl methyl content (varying BPA/CH$_2$O mole ratio) while holding the total amount of HMBPA content at 15 wt% in the adhesive film. The results are described in Figure 8.

FIGURE 5 Curing dynamic DSC thermogram for (a) Epoxy/DICY, (b) Nitrile-epoxy Film-IV (uncured), and (c) Nitrile-epoxy film F-IV after cure at 170°C, 90 min.

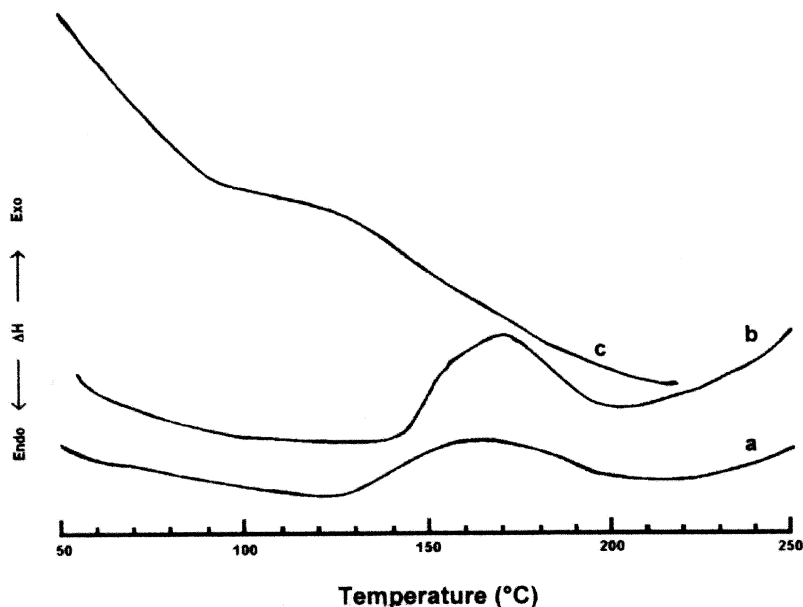Figure 8 illustrates the results of lap shear (Al-Al), T-peel (Al-Al), and rubber-to-metal peel (Al-NBR) strength of adhesive joints prepared with nitrile-epoxy films. The strengths of adhesive joints prepared with unmodified nitrile-epoxy film and nitrile-epoxy film containing 15 wt% of BPA and 15 wt% of HMBPA and having different concentrations of the hydroxyl methyl group (BPA/CH$_2$O mole ratio) are compared in Figure 8. The addition of 15 wt% HMBPA-c (BPA/CH$_2$O mole ratio 1:3) to the nitrile-epoxy film results in lap shear strength 2.64 times higher, T-peel strength 2.66 times higher, and rubber-to-metal peel strength 7.63 times higher than the joints prepared using adhesive film without HMBPA. An important aspect of the results in Figure 8 is that the adhesive performance of the nitrile-epoxy film with HMBPA is better than with BPA, and the hydroxyl methyl group in HMBPA has an influence in enhancing the adhesive properties. Another aspect of the results in Figure 8 is the higher strength, which occurs with HMBPA-c (BPA/CH$_2$O mole ratio 1:3).

It is well known that epoxy resins have great affinity for chromic-acid-etched aluminium surfaces with the ability to attach to the oxide
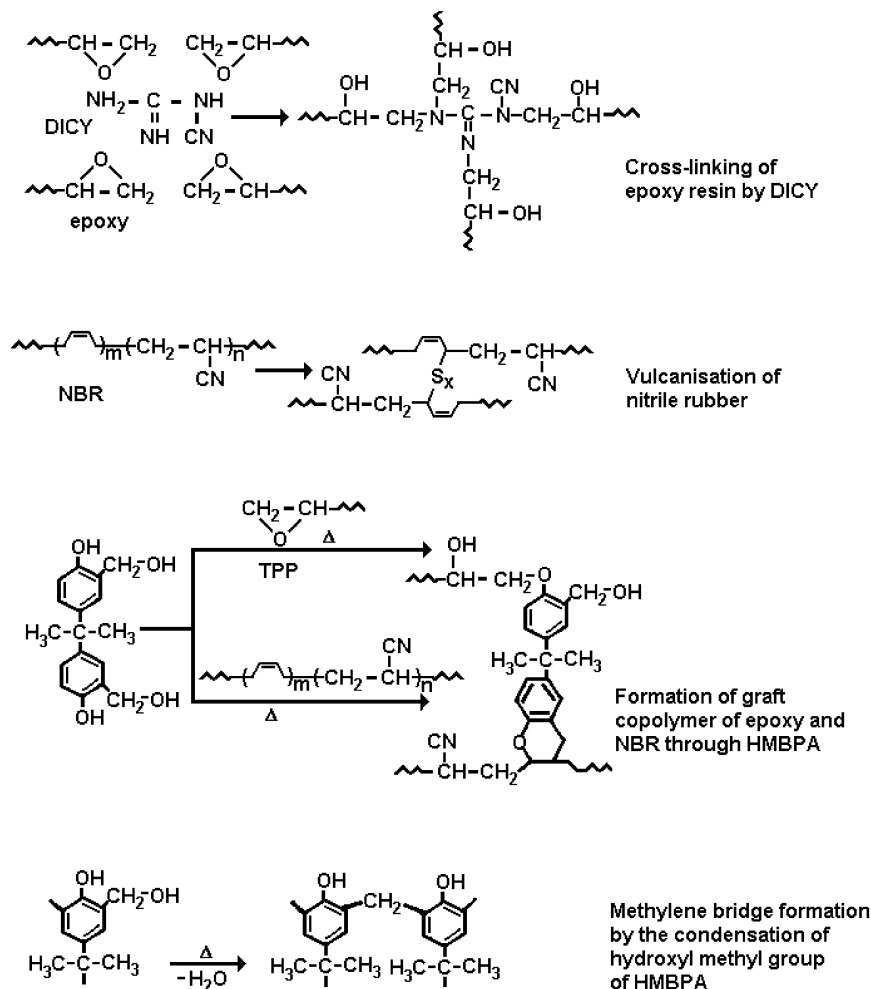
FIGURE 6 Possible chemical reactions of the nitrile-epoxy adhesive film during cure.

layer by chemical interaction [27] and to provide strong metal-to-adhesive interfacial bonding. Therefore, the increase in adhesive properties of the nitrile-epoxy film by the incorporation of HMBPA can be explained by the increase in cohesive strength of the adhesive layer and the changes in the blend morphology (discussed later). Bikerman [28] has postulated that failure of the adhesive joint in most cases is cohesive because of the various levels of heterogeneity and weak links.
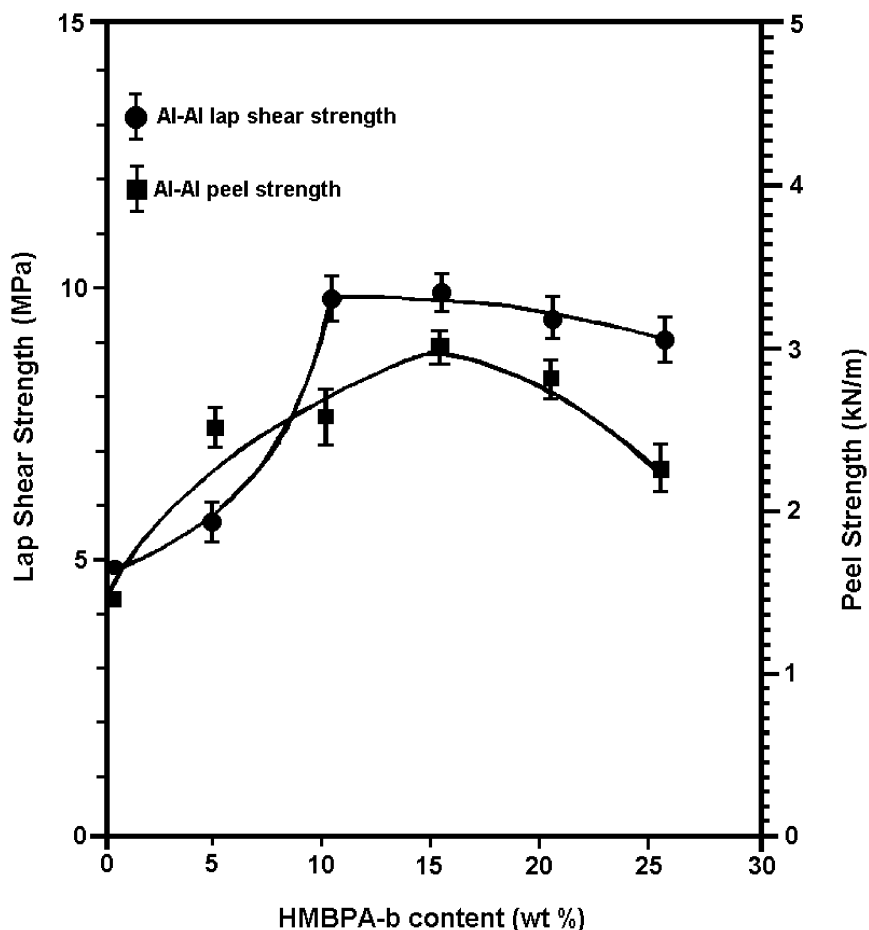
FIGURE 7 Dependence of lap shear strength and T-peel strength on the concentration of hydroxyl methyl derivative of bisphenol A (HMBPA-b) in the nitrile-epoxy film adhesive (NBR/epoxy resin 50/50 wt/wt).

A plausible explanation for the increase in joint strength by the incorporation of HMBPA is the strengthening of the weak link where failure begins [29]. The difference in solubility parameter and the lack of chemical reactivity between epoxy resin and NBR are the reasons for weak link, which result in low adhesive properties for the unmodified (F1) and BPA-modified (F2) nitrile-epoxy adhesive films. The molecular factor responsible for the increased joint strength by the addition of HMBPA is the in situ formation of a copolymer network at
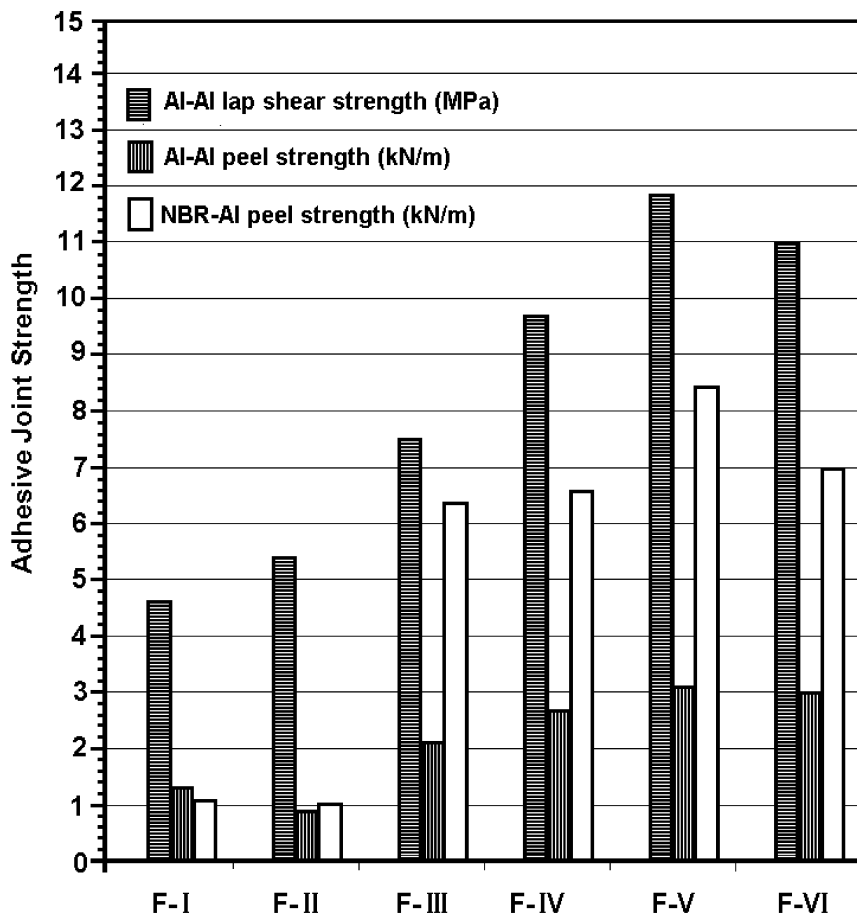
FIGURE 8 Effect of BPA and various HMBPA having different hydroxyl methyl content on the adhesive joint strength of the nitrile-epoxy film. F-I, unmodified film. F-II, film with 15 wt% BPA. F-III, F-IV, F-V, and F-VI, films with 15 wt% HMBPA-a, HMPBA-b, HMBPA-c, and HMBPA-d, respectively.

the NBR/epoxy interphase region through the reactions of hydroxyl methyl groups of HMBPA during the curing process.

Figure 8 reveals that the nitrile-epoxy film without HMPBA gives low peel strength in vulcanisation bonding of NBR-to-aluminium, with NBR/adhesive interfacial failure. The nitrile-epoxy film produces strong adhesion to aluminium, and the heat supplied during the vulcanization process of the rubber converts the adhesive into a

mechanically strong film. So it appears that the low peel strength of the NBR/adhesive/aluminium joint of the unmodified and BPA-modified nitrile-epoxy film (Figure 8) can be attributed to the weak NBR/adhesive interfacial strength. The dramatic improvement in peel strength of the rubber/adhesive/aluminium joint, with a transition from rubber/adhesive interfacial failure to the bulk of the rubber by the incorporation of HMBPA into the adhesive film, can be attributed to the formation of a chemical link at the rubber/adhesive interface. HMBPA is able to act as a reactive interfacial agent and reinforce the interphase between NBR and epoxy phases by in situ reactive compatibilization [30, 31], leading to better stress transfer across the interface that enhances the joint strength. A few studies have recently reported [32, 33] that the concentration of functional groups in the reactive compatibilizer (interfacial agent) is very important and that an optimal concentration of functional groups exists in this additive in order for it to play an effective role as compatibilizer. The degree of compatibilization is dependent on the areal density of the interfacial agent and the extent of formation of copolymer at the interfacial region [34]. Results in Figure 8 reveal that the degree of enhancement of joint strength is strongly dependent on the hydroxyl methyl group content in HMBPA. The reduction in joint strength with HMBPA-d, having a higher concentration of hydroxyl methyl groups (BPA/CH_2O mole 1:4), is believed to be the result of a higher crosslinking and an inferior stress distribution pattern.

Addition of fillers to the nitrile-epoxy film was examined as another means to improve the cohesive strength of the adhesive layer in order to enhance the joint strength. Kinloch et al. [35] showed that addition of rigid particulate fillers to rubber-modified epoxy resin further increases the fracture toughness. Our previous studies [18] have revealed that addition of silica filler improves the performance of a nitrile rubber/phenolic resin blend and the strength maximum occurs at 30 wt% of filler concentration. Figure 9 illustrates the effect on the performance of the adhesive bonded joint of the addition of silica, alumina, and aluminium fillers, at 30 wt%, in the nitrile-epoxy adhesive film. It is found that joint strength (shear strength) increases with filler addition, and the improvement is better with aluminium filler than with alumina and silica. Somewhat similar trends are observed in the lap shear strength by the addition of the same filler content in the nitrile-epoxy film containing 15 wt% HMBPA-c, but there is a marginal decrease in peel strength. We believe that the effect of filler on the joint strength is connected with the nature and composition of the adhesive polymer, filler, and the magnitude of interfacial interaction between them. Filler purity, surface area,
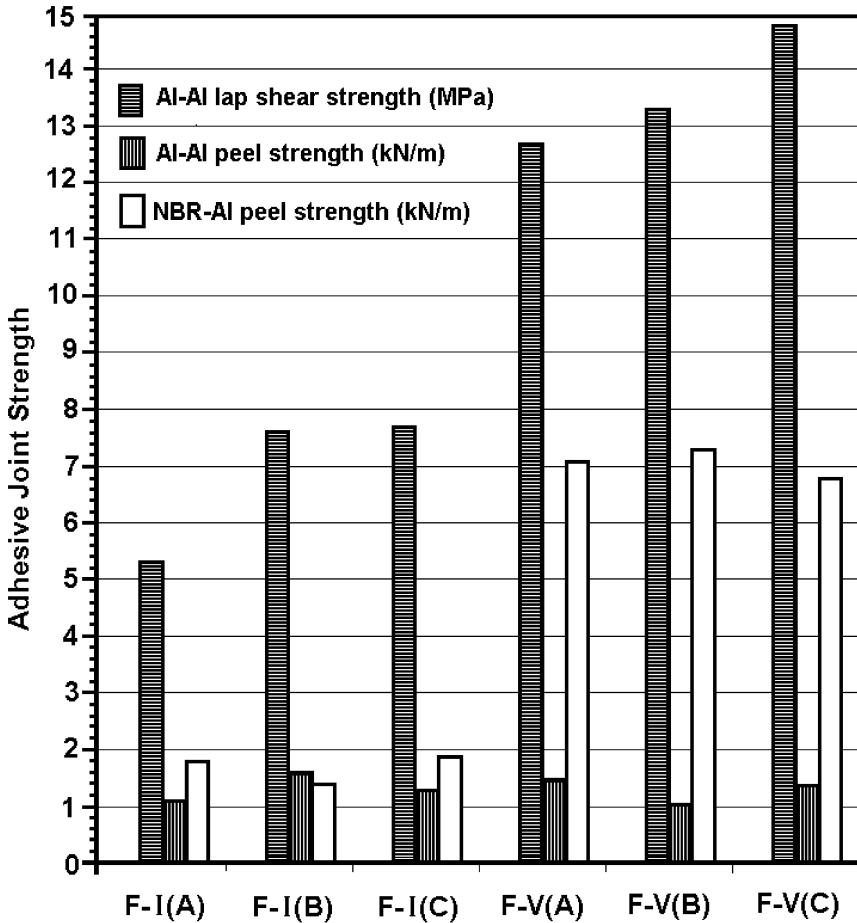
FIGURE 9 Change in the joint strength by the addition of various fillers in the nitrile-epoxy (NBR/epoxy resin 50/50 wt/wt) adhesive film. (Filler concentration 30 wt%). F-I, nitrile-epoxy film without HMBPA. F-V, nitrile-epoxy film with 15 wt% HMBPA-c: (A) Silica filler, (B) Alumina filler, and (C) Aluminium filler.

porosity, surface chemical characteristics, particle size and shape, thermal properties (coefficient of thermal expansion and thermal conductivity), percentage of filler content in the polymer, the dispersion and distribution of filler in the polymer, interfacial interactions, and the properties of the interphase region all influence the strength of the particulate-filled polymer composite [36]. The adhesive poly-

mers, which hold the particulate filler and serve as a means of load transfer, strongly influence the strength properties.

Mechanical Properties

In general, it is known that the cohesive strength of the adhesive affects the joint strength. To verify this statement, standard tensile test is performed on the cured bulk adhesive films and the stress-strain curves are recorded. The stress-elongation curves in Figure 10 show that NBR/epoxy (50/50 wt/wt) blend displays low tensile strength (σ_b) and high elongation (ε_b) which suggests that NBR is the continuous phase. Addition of HMBPA gives rise to a significant increase in tensile strength and modulus with a decrease in elongation at break. It is found that the modulus and tensile strength increases, while the elongation at break decreases progressively as the CH_2O/BPA mole ratio used for the preparation of HMBPA is increased (increased hydroxyl methyl content). It is evident from Table 2 that hardness, the relative cross-link density of the rubber network (ν_e), and the energy-absorbing efficiency (indicated by the area under stress-strain curve) of the blend increases as the hydroxyl methyl content of HMBPA increases. It is observed that the highest energy absorbing efficiency (toughness) is obtained for the film (F-V) containing HMBPA-c (CH_2O/BPA mole ratio 3:1) that shows the higher adhesive performance. Even though there is an increase in tensile strength and modulus for the film containing HMBPA-d (F-VI), there is a decrease in adhesive performance due to the decrease in energy-absorbing efficiency. The results can be interpreted by the chemical reactions of HMBPA with epoxy and NBR, which are strongly influenced by the hydroxyl methyl content in HMBPA.

Because of the incompatible nature of epoxy resin and nitrile rubber, their mixture results in a two-phase morphology with a weak interface due to the lack of chemical reactivity between them. Results in Figure 10 and Table 2 imply that HMBPA crosslinked the rubber and increased the NBR/epoxy interfacial adhesion, which has been confirmed from the dynamic mechanical analysis and morphological investigation.

Figure 11 shows the storage modulus, E^1, and damping, tan δ, of the cured nitrile-epoxy films with and without HMBPA. The storage modulus, E^1, gradually decreases as the temperature increases, and there is a drastic reduction of E^1 and an increase of the tan δ value to a maximum near the rubber's glass transition temperature (Tg_R) region, which is close to that of the pure NBR ($Tg - 21°C$) that is shifted to higher temperature for the HMBPA-modified blend. E^1 is increased
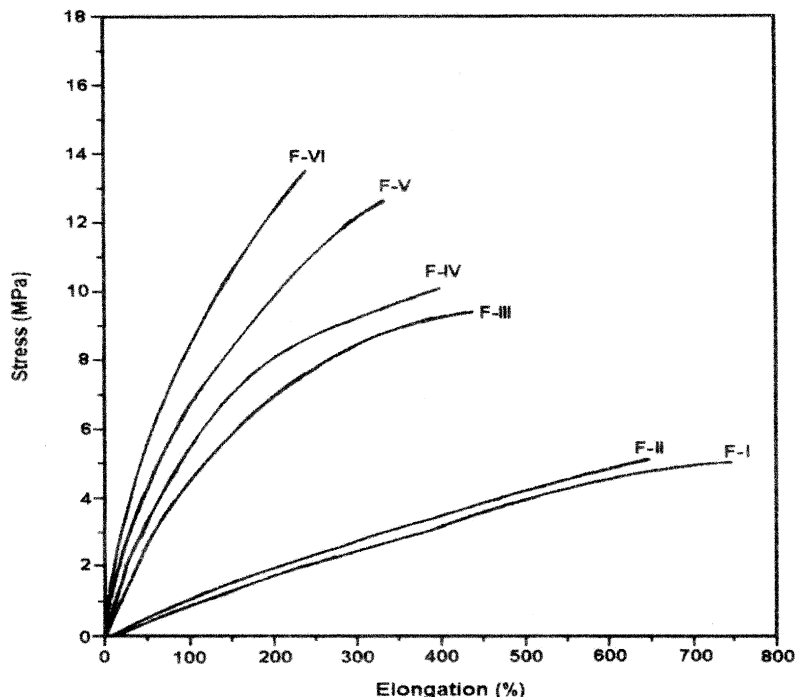
FIGURE 10 Stress elongation curves for cured nitrile-epoxy films. (NBR/epoxy resin 50/50 wt/wt). F-I, unmodified film; F-II, film with 15 wt% BPA. F-III, F-IV, F-V, and F-VI, films with 15 wt% HMBPA-a, HMBPA-b, HMPBA-c, and HMBPA-d, respectively.

and tan δ decreased and shifted to higher temperature for the HMBPA-modified nitrile-epoxy film due to the higher stiffness introduced into the film by the phase mixing and crosslinking of the rubber [37, 38]. HMBPA is able to act as a reactive interfacial agent and reinforce the interface between the rubber and epoxy phase by the reaction of HMBPA with NBR and epoxy during the cure (Figure 6). The copolymer formed by the reaction of HMBPA with NBR and epoxy may coexist with the NBR phase, which shifted the rubber glass transition (TgR) to higher temperature for the HMBPA-modified blend. The glass transition of epoxy (ETg) increased very marginally by the reaction of HMBPA (ETg, without HMBPA, 99.2°C, with 15 wt% HMBPA-c, ETg, 101.5°C).

It is clear that interfacial coupling between the NBR and epoxy phases occurs as the hydroxyl methyl group is introduced into BPA, and better adhesion and compatibility between the two phases results

TABLE 2 Energy Required for Break, E_b (Area Under the Stress-Strain Curve), Hardness and Relative Network Density, ν_e, of Rubber in the Nitrile-Epoxy Blend (NBR/Epoxy Resin 50/50 wt/wt)

Sample designation of the film	E_b (J/ mm^3)	Hardness (Shore A)	Network chains (mole/mL)
FI	0.22	32	9.2
F1(A)	(0.375)	(49)	(36.0)
F1(B)	(1.24)	(39)	(22.4)
F1(C)	(2.28)	(40)	(16.0)
F II	0.187	29	8.1
F III	0.268	34	10.9
F IV	0.287	38	11.8
F V	0.292	38	13.1
F V (A)	(0.311)	(66)	(63.0)
F V (B)	(0.940)	(64)	(34.9)
F V (C)	(1.54)	(52)	(19.2)
F VI	0.223	42	13.9

F I−unmodified film, F II−film with 15 wt% BPA, F III, F IV, F V, F VI−films with 15 wt% HMPBA-a, HMBPA-b, HMBPA-c, HMBPA-d, respectively. Figures in parenthesis with 30 wt% fillers A) silica, B) alumina, C) aluminium.

as the hydroxyl methyl concentration in HMBPA is increased. The copolymer formed by the reaction of HMBPA with epoxy and NBR forms interphase junctions (illustrated schematically in Figure 12), which serve as bridges for stress transfer and improve the interfacial strength, hence the toughness [39, 40]. In addition, there can be intimate interpenetration of the NBR and epoxy networks due to the reactive coupling of HMBPA that can result in the formation of a graft IPN [41]. Increasing the hydroxyl methyl content in HMBPA beyond a certain level does not lead to any enhancement in toughness but to a decrease due to the increased crosslinking of the rubber.

The influence of silica, alumina, and aluminium fillers on the mechanical behaviour of nitrile-epoxy film with 30 wt% filler is shown in Figure 13. It is evident from Figure 13 and Table 2 that incorporation of fillers into the nitrile-epoxy film increases the modulus, tensile strength, hardness and cross-link density and decreases the percentage of elongation at break and is in the order silica > alumina > aluminium. The fillers increase the toughness (energy required for break) of the nitrile-epoxy film and are in the order aluminium > alumina > silica. For a fixed percentage of filler content, the lower-particle-size alumina is expected to give higher mechanical properties because of the availability of higher contact surface for the
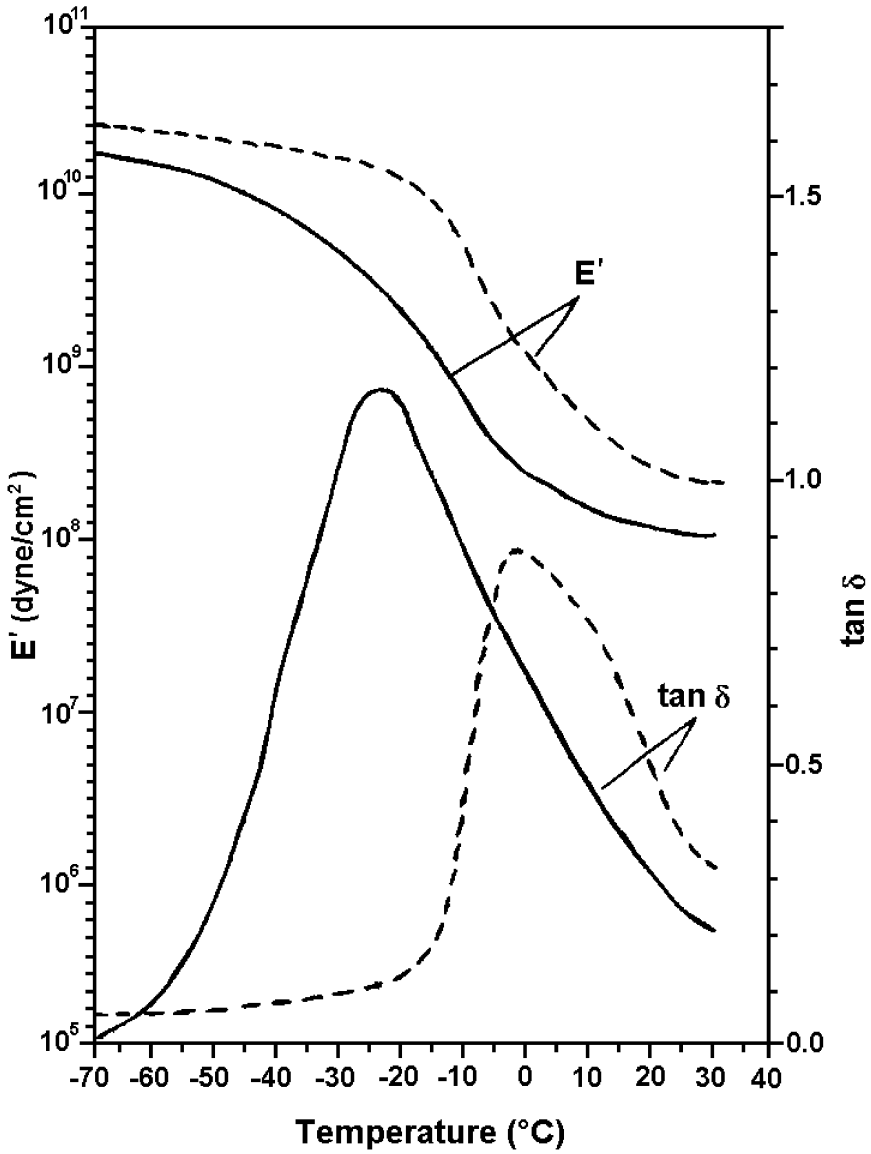
FIGURE 11 Dynamic mechanical data for the cured nitrile-epoxy film (———) without HMBPA, and (– – –) with 15 wt% HMBPA-c.

Interphase 1
(Epoxy network
coexist with
epoxy-HMBPA-NBR)

Interphase 2
(NBR network
coexist with
epoxy-HMBPA-NBR)
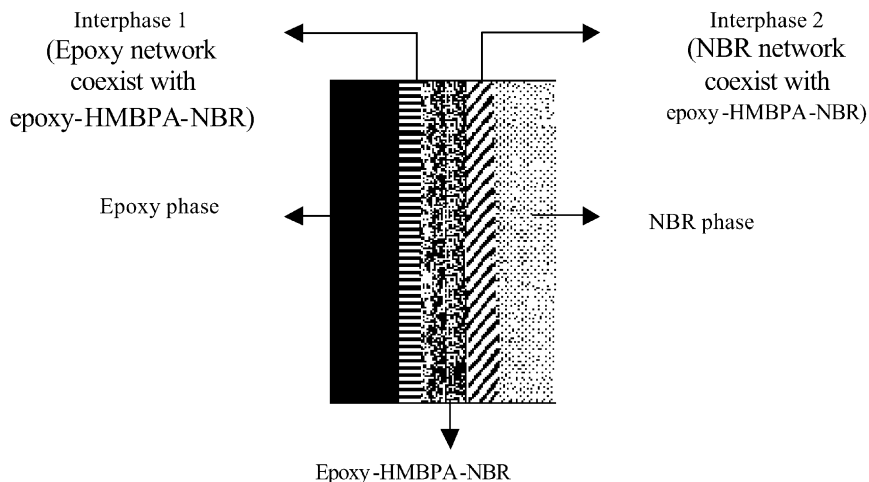
Epoxy phase

NBR phase

Epoxy-HMBPA-NBR

FIGURE 12 Schematic diagram describing the interfacial coupling between NBR and epoxy phases through HMBPA.

filler−polymer interaction. But it can be noted that the difference in mechanical properties produced by the fillers has no relation to the particle size since the chemical and physical nature of the fillers, wettability of the fillers by the adhesive polymer, adhesion bond at the polymer-filler interface, properties of the polymer-filler interphase region, and many other factors are responsible for the mechanical characteristics of the filled polymer composites [36]. The degree to which the polymer is adsorbed on to the filler surface is largely responsible for the adhesion interactions and properties of the polymer−filler interphase region, which significantly influence the mechanical properties of the filled polymer system.

Thermal Properties

Thermal stability of the cured nitrile-epoxy films was studied by TGA. In Figure 14, the thermogravimetric curves of unfilled and filled nitrile-epoxy films without and with HMBPA are compared. It may be analysed from the thermogravimetric curves that incorporation of HMBPA into the nitrile-epoxy adhesive film introduces a certain amount of thermal stability. The NBR/epoxy resin blend starts degrading at a lower temperature in comparison with the HMBPA-modified NBR/epoxy resin blend. This may be attributed to the increase of crosslinking in the polymer network by the reactions of
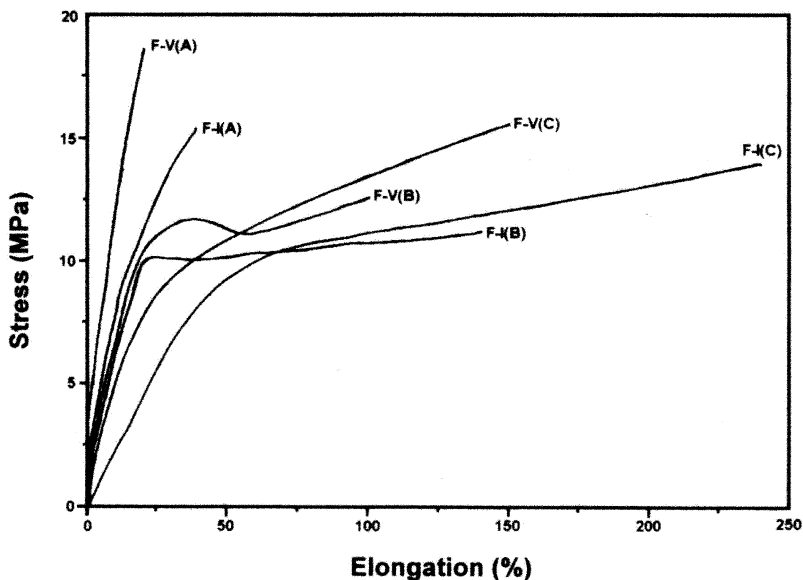
FIGURE 13 Stress-elongation curves for cured nitrile-epoxy adhesive films. (NBR/epoxy resin 50/50 wt/wt/). Filler content 30 wt%. F-I, nitrile-epoxy film without HMBPA. F-V, nitrile-epoxy film with 15 wt% HMBPA-c. (A) Silica filler, (B) Alumina filler, and (C) Aluminium filler.

HMBPA with epoxy and NBR. Increased thermal stability with the increase of crosslinking is simply because more bonds will have to be broken before the total network breakdown occurs [42, 43]. It is observed from TGA thermograms that incorporation of fillers into the adhesive film provides a modest improvement in thermal stability. Fillers improve the thermal stability of the nitrile-epoxy film in the order silica > alumina > aluminium. The improved thermal stability might be due to the inorganic-organic interactions. The chemical groups of the polymer matrix can interact with the surface hydroxyl of fillers, present as silanol on silica and as aluminol on the alumina and aluminium surfaces [44]. The results indicate that the filler-matrix interaction in silica-filled nitrile-epoxy composite is greater compared with alumina and aluminium filled nitrile-epoxy composite.

The temperature dependence of thermal expansion coefficient for the nitrile-epoxy film without and with HMBPA is shown in Figure 15. HMBPA has the effect of reducing the thermal expansion coefficient due to the increasing crosslinks in the polymer network. The thermal expansion coefficient versus temperature plots of unfilled and filled
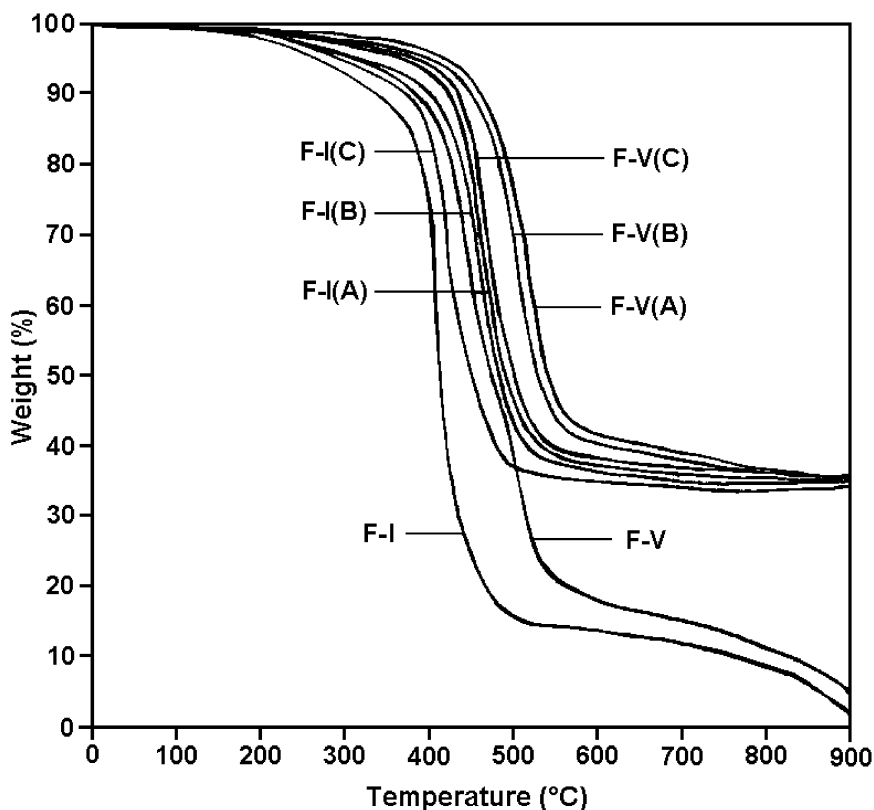
FIGURE 14 Thermogravimetric curves (10°C/min) of the cured nitrile-epoxy films. (NBR/epoxy resin 50/50 wt/wt). F-I, nitrile-epoxy film without HMBPA. F-V, nitrile-epoxy film with 15 wt% HMBPA-c. (A) Silica filler, (B) Alumina filler, and (C) Aluminium filler. Filler content 30 wt%.

films is displayed in Figure 15. The thermal expansion coefficient increases with temperature and shows a steplike change at the glass transition temperature. Filler addition decreased the thermal expansion coefficient of the film as polymers have coefficients of thermal expansion greater than inorganic fillers.

Phase Morphology

The tensile fractured surface of cured nitrile-epoxy films with and without 15 wt% BPA, HMBPA-a, HMBPA-b, HMBPA-c, and HMBPA-d
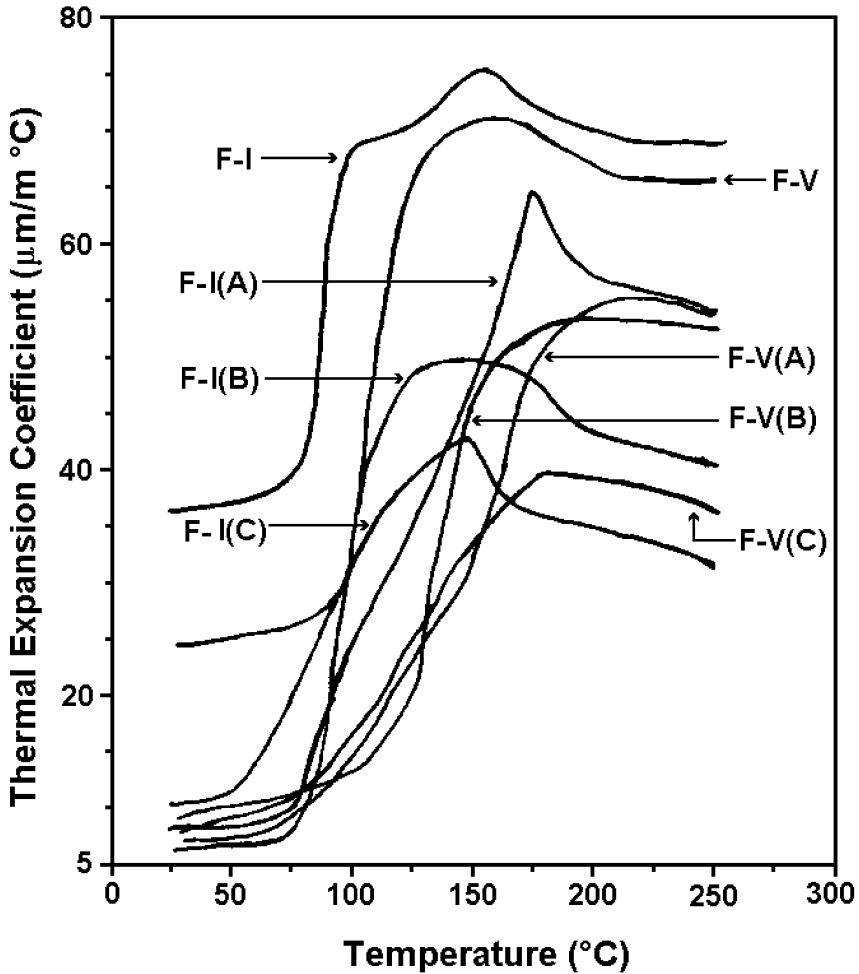
FIGURE 15 Thermal expansion coefficient for cured nitrile-epoxy films. (NBR/epoxy resin 50/50 wt/wt). F-I , nitrile-epoxy film without HMBPA. F-V, nitrile-epoxy film with 15 wt% HMBPA-c. (A) Silica filler, (B) Alumina filler, and (C) Aluminium filler. Filler content 30 wt%.

were examined using the scanning electron microscope. These results are shown in Figure 16 (F-I to F-VI). As seen in Figure 16, phase separation is present in the cured nitrile-epoxy films and the fractured surface of the unmodified NBR/epoxy resin blend contains irregularly dispersed domains and crack phase boundaries. The low mechanical properties of the NBR/epoxy resin blend is due to the poor stress

transfer under loading because of the poor interfacial phase adhesion. The results in Figure 16 reveal that inclusion of HMBPA in the blend changed the morphologies, and the trend indicates that the size of the separated phase diminishes with the increase of hydroxyl methyl content in BPA. The morphology becomes a co-continuous phase structure for higher hydroxyl methyl content. The semicontinuous or co-continuous phase structure observed in blends containing HMBPA

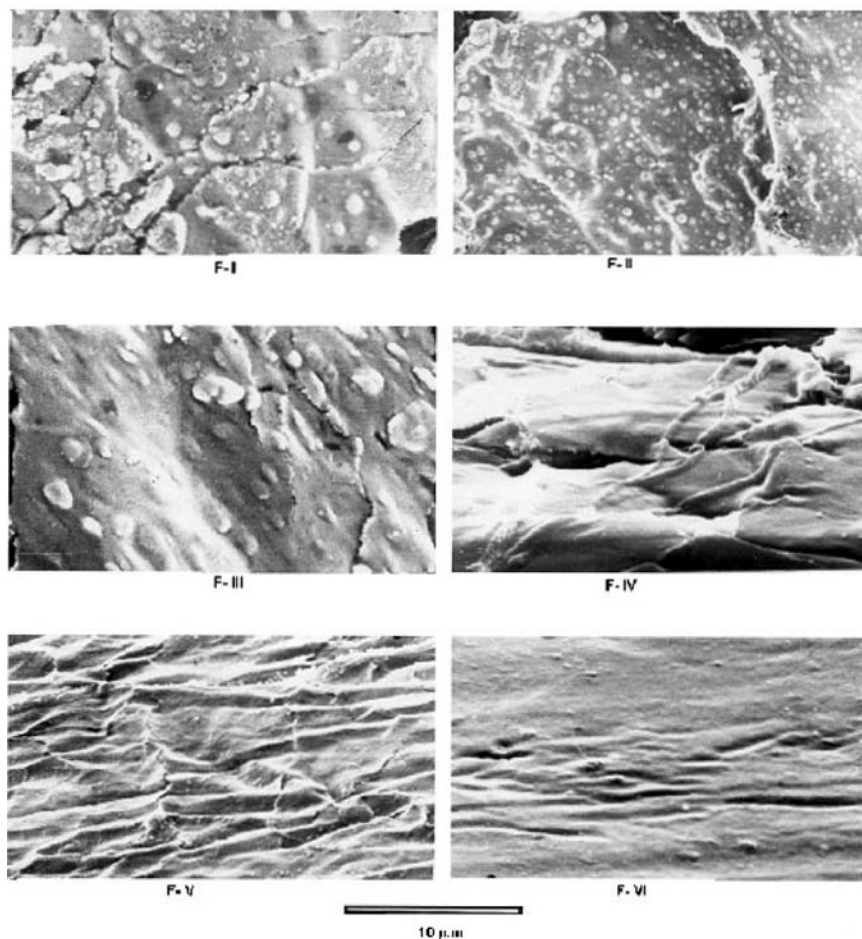**FIGURE 16** SEM micrographs of tensile-fractured surface of cured nitrile-epoxy adhesive films. F-I, unmodified film. F-II, film with 15 wt% BPA. F-III, F-IV, F-V, and F-VI, films with 15 wt% HMBPA-a, HMBPA-b, HMBPA-c, and HMBPA-d, respectively.

can be attributed to better compatibilization due to the formation of NBR-HMBPA-epoxy copolymer. The in situ-formed copolymers due to the occurrence of the chemical reactions of HMBPA with NBR and epoxy resin tend to reside along the interfacial region, preventing coalescence through stabilising the interface, and thus the morphology becomes co-continuous. The in situ-formed copolymers anchor the phases to generate strong interfacial adhesion to transmit the applied force between the component phases, which enhances the mechanical properties [45].

CONCLUSIONS

This work demonstrates the ability of hydroxyl methyl bisphenol A (HMBPA) to function as a reactive interfacial agent (compatibilizer) in a nitrile rubber (NBR)/epoxy resin blend. The synthesis of HMBPA with different hydroxyl methyl content and the effect of incorporating HMBPA on the adhesive, mechanical, thermal, and morphological properties of the NBR/epoxy resin adhesive film without and with filler addition is presented. Based on our results, the following conclusions are drawn.

1. NBR/epoxy resin blends can be modified with HMBPA to obtain films with better adhesive properties. Film adhesive containing 15 wt% of HMBPA having an optimal hydroxyl methyl content exhibited higher adhesive joint strength. The increase of joint strength achieved by the incorporation of HMBPA may mainly be attributed to the effect of chemical bond formation of HMBPA with NBR and epoxy resin, leading to better stress transfer.
2. With the addition of HMBPA into a film of an NBR/epoxy resin blend, ultimate tensile strength, modulus, and toughness increased and the elongation at break decreased. Strong bonding between NBR and epoxy resin created by the insertion of cross-linking by HMBPA within the NBR phase and in the NBR-epoxy resin interphase is probably the main factor that influenced the mechanical properties.
3. Additionally, HMBPA exhibited significant influence on the thermal properties of the nitrile-epoxy adhesive film, which could be attributed to the interfacial and crosslinking reactions involving HMBPA. HMBPA has the effect of enhancing thermal stability, reducing thermal expansion coefficient, and increasing the glass transition temperature of the rubber phase of the nitrile-epoxy blend.

4. Incorporation of HMBPA into the blend reduced the domain size, and the morphology became a co-continuous phase structure with the increase of hydroxyl methyl content in HMBPA, presumed to be caused by the reactive compatibilization and formation of a copolymer network at the NBR-epoxy resin interphase through the reactions of HMBPA.

5. Results showed that the mechanical and thermal properties of nitrile-epoxy adhesive film could be altered by the addition of fillers, which in turn affected the adhesive joint strength. For 30 wt% filler content in the nitrile-epoxy adhesive film with or without HMBPA, aluminium filler produced better adhesive joint strength compared with alumina and silica fillers. The properties of the filled adhesive are related to the physical and chemical nature of the constituents and the magnitude of filler-polymer interactions.

6. The present study suggests that a reactive interfacial agent (compatibilizer) of appropriate molecular structure and functional groups can be employed in immiscible polymer blends and filled polymer composites to solve problems concerning compatibilization of ingredients to achieve enhanced adhesive performance.

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