

DEVELOPMENT OF HIGH TEMPERATURE OVERWRAP COMPOSITE REPAIRS FOR PIPELINES

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ABSTRACT

Resin formulations consisting of a cyanate ester resin (CER) as the base material, a cobalt catalyst, a nanofiller and various thermoset additives, such as benzoxazines, phenolic and epoxy were investigated as a potential candidate matrix for high temperature composite materials suitable for use as overwrap repairs. All of the samples investigated in the present work displayed moderately large exotherms, indicative of unreacted functional groups after curing at 100°C for 16 hrs. Nonetheless, the reactive diluents in CER all appeared to have advanced the cure to some extent. Cure conversions for the unmodified CER formulation is about 64.5%, while each of the blends modified with a reactive diluent had higher cure conversions, with up to 84.1% for the benzoxazine modifier. Only the benzoxazine modified CER and the unmodified CER formulations passed the thermal stability test, which demanded measured weight loss of no more than 5% at 250°C over a period of 1000 hrs. The weight loss in an air circulating oven for the two resin formulations was measured to be less than 3%, which was vastly superior to the rest of the formulations, which registered at least 7% and up to 9.5% weight loss under the same ageing conditions. Visual inspection of the samples further revealed that the integrity of the unmodified CER and benzoxazine modified CER samples was maintained after the thermal ageing, while the rest of the resin formulations revealed either gross cracking due to resin shrinkage, or expansion due to formation and evaporation of water. Hence the unmodified, and the benzoxazine modified, CER formulations appeared to hold the greatest promise as a candidate resin for a composites to be used in elevated temperature pipeline overwrap repairs.

1 INTRODUCTION

Composite overwrap repairs provide a cost effective and versatile remedy for metal pipes that are damaged by corrosion or have deteriorated due to ageing. Depending on the application, some of these pipes typically operate at temperatures well in excess of 100°C, some reaching close to 250°C. While there are a number of composite overwrap repair products available on the market that claim to withstand high service temperatures in or near the targeted range, they also generally require high temperature cure profiles which can be logistically challenging in the field and unfavourable from the standpoint of safety.

Cyanate ester resins (CER) are well known for their high glass transition temperatures, which could be as high as 400°C, plus their superior thermal stability at these high temperatures [1-6]. This behaviour is attributed to their highly aromatic structure containing nitrogen heteroatoms which further confer thermal stability. A schematic representation of the basic structure of a cyanate ester resin and its polymerisation mechanism is shown in Figure 1.

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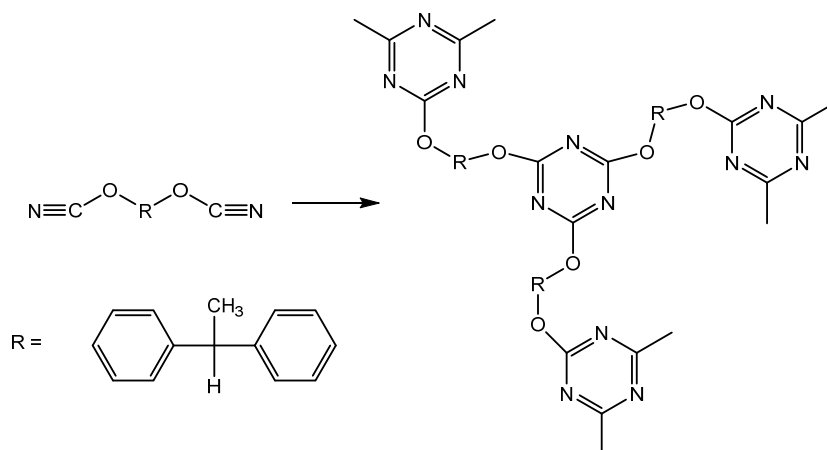


Figure 1: Generic representation of the polymerisation mechanism of cyanate ester resin illustrating the hetero-aromaticity of the developing network responsible for enhanced thermal stability.

While research on understanding the reaction mechanism is continuing, CER cure is broadly understood to occur via a cyclotrimerisation reaction that forms very thermally stable cyclic cyanurates. Polymerisation is thermally activated, however this is typically catalysed using a transition metal carboxylate in the presence of an active hydrogen co-catalyst such as a phenol [7]. The challenge with CERs is the comparatively high temperatures required to achieve full cure, often well above 180°C , compared with the more reactive epoxy resins. This is particularly relevant, given that the objective of this work was to develop a low temperature curing resin system that was also thermally stable to high temperatures.

Hence, this work involved investigating the thermal stability of CER with different combinations of resin modifier and reactive diluents. The addition of phenolic, benzoxazine and epoxy were investigated for enhanced processability (*i.e.* reactivity) without potentially compromising thermal stability or other desirable properties. All resin formulations were cured at 100°C , which was taken for the present work as the highest practical temperature used for a field overwrap repair.

2 EXPERIMENTAL

2.1 Materials

The CER formulations described in Table 1 are a mixture of CER and blended formulations containing different compositions of thermoset resins. Unmodified CER was also studied as the baseline formulation. The thermoset resins considered in this study were phenolic, benzoxazine, epoxy TGOPE/Resorcinol and epoxy TGOPE/D4-Si/Resorcinol, while a cobalt acetylacetonate - Co (III) - catalyst, and a nanofiller, were added at concentrations of 0.3wt% and 33wt% of each resin formulation, respectively. TGOPE and D4-Si are tri and tetrafunctional epoxy resins, respectively, while resorcinol is a curing agent.

2.2 Formulation

CER and the reactive diluent (*i.e.* phenolic, benzoxazine, epoxy TGOPE/D4-Si or epoxy TGOPE) were mixed in a pre-heated oil bath at 80°C . When the CER and resin modifier mixture became a clear yellow liquid, the catalyst was added and stirred until it was dissolved and a clear green liquid emerged. The nanofiller was then gradually added in small portions while stirring until it was completely and evenly dispersed. When mixing was completed, the formulations were degassed at 80°C under full vacuum for 5 to 10 mins followed by a final cured at 100°C for 16 hrs.

Differential scanning calorimetry (DSC) was employed to gain an insight into the level of cure, while the weight loss resulting from continuous exposure to heat ageing was used as a measure of thermal stability of the resin formulations. Both thermogravimetric analysis (TGA) as well as oven heating were used to carry out this measurement.

Table 1: Cyanate ester resin formulations investigated in the current work.

Resin Formulation	CER (wt. %)	Resin Modifier (wt. %)
CER	100	-
CER/Phenolic	80	20 Phenolic
CER/Benzoxazine	80	20 Benzoxazine
CER/Epoxy 1	80	20 TGOPE/D4-Si/Resorcinol
CER/Epoxy 2	80	20 TGOPE/Resorcinol

2.3 Level of cure

DSC analyses were conducted using a Mettler Toledo DSC 3 for the uncured and cured resin to investigate the effects of cure temperature on cure conversion. Analysis was performed on ~10 mg resin samples in a 20 mL min⁻¹ nitrogen gas stream. Samples were heated from 30 to 350°C at a heating rate of 10°C min⁻¹. The total energy was recorded and the degree of cure conversion, α , was calculated as per equation 1 below:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad \dots (1)$$

where ΔH_T is the total enthalpy of reaction measured at a certain heating rate for an unreacted sample, and ΔH_R is the residual heat of the reaction for the isothermally cured sample for a prescribed amount of time.

2.4 Thermal stability

TGA was performed using a Mettler Toledo TGA 2 for preliminary assessment of thermal stability of the resin formulations. Each sample was heated from 30 to 700°C at a heating rate of 10°C min⁻¹ in an oxidative air environment, simulated with a 30 mL min⁻¹ air stream. Sample weight loss was monitored as a function of time.

A similar set of samples were further subjected to more rigorous thermal ageing process by placing the samples, which were cured in aluminium moulds, in an air circulating oven at 250°C for up to 1000 hrs. The resin samples were weighed every 24 hrs in first 3 days then every 10 days or so to monitor weight loss over time.

3 RESULTS AND DISCUSSION

3.1 Residual Cure

The DSC results are summarised in Figure 2 where it shows all the samples displaying residual exotherms, which indicates incomplete cure. This was not unexpected given the lower than typical cure temperatures used, however it is evident from the smaller pre- and post-cure enthalpies (see Table 2), that the reactive diluents did indeed have a positive effect on the curing process. It may be inferred that the use of the reactive diluents had advanced curing at 100°C. Table 2 quantifies this by calculating cure conversions, which for the unmodified CER formulation is about 64.5%, while each of the blends modified with a reactive diluent had higher cure conversions, with up to 84.1% for the benzoxazine modifier.

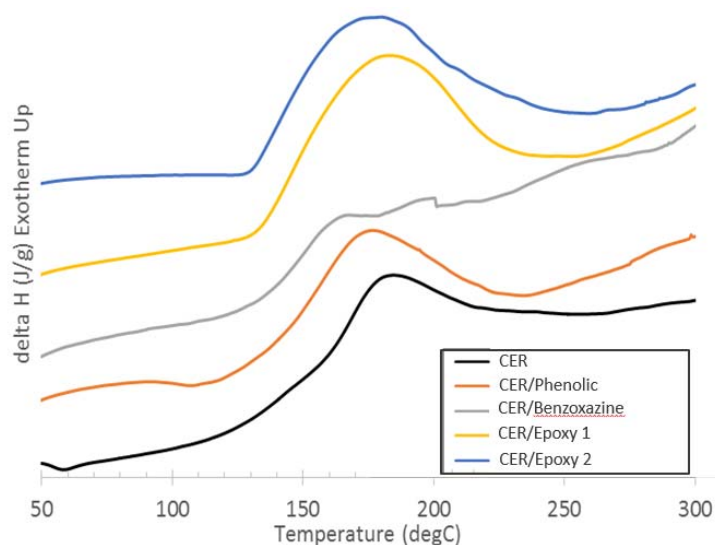


Figure 2: DSC thermograms of the CER formulations after curing at 100°C for 16 hrs.

Table 2: Enthalpy (ΔH) of the curing exotherm of the CER formulations after curing at 100°C for 16 hrs.

Resin Formulation	ΔH (J/g) (pre-cure)	ΔH (J/g) (post-cure)	Cure Conversion (%)
CER	415.0	147.4	64.5%
CER/Phenolic	370.6	84.2	77.3%
CER/Benzoxazine	447.8	71.1	84.1%
CER/Epoxy 1	434.0	105	75.8%
CER/Epoxy 2	537.9	112.3	79.1%

3.2 TGA Analysis

The raw thermograms from the TGA analyses are shown in Figure 3. The plots clearly illustrate the better thermal stability of the CER formulations that did not contain any resin modifier. The unmodified CER formulation appears to have the greatest thermal stability, as determined by the onset temperature of weight loss, followed by the benzoxazine and phenolic blends. This result suggests that adding of resin modifier would disrupt the thermal stability of CER, presumably due to the ether bonds present in the CER/phenolic and CER/benzoxazine formulations, as they require less energy to break at high temperatures. This in turn leads to a lower temperature at which 10% weight loss is recorded (*i.e.* $T_{10\%}$) while for unmodified CER there are more triazine rings which could have been responsible for the higher $T_{10\%}$ that was recorded. A similar trend was reported by Wang *et al.* [8] in their thermal study of benzoxazine with bismaleimide/cyanate ester. The $T_{10\%}$ values recorded for each sample are shown in Table 3.

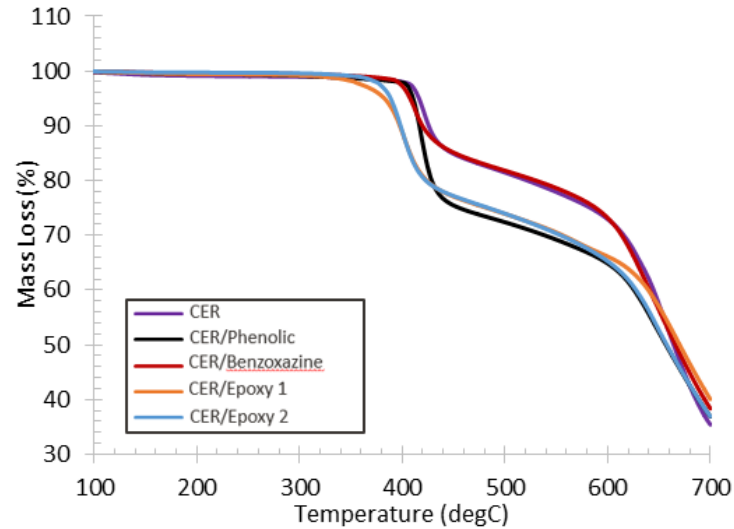


Figure 3: Raw TGA thermograms showing the weight loss as a function of temperature.

Table 3: Temperature at which 10wt% weight loss was recorded for the resin formulations.

Resin Formulation	T _{10%} (°C)
CER	425.7
CER/Phenolic	416.7
CER/Benzoxazine	419.7
CER/Epoxy 1	397.3
CER/Epoxy 2	398.3

3.3 Thermal ageing

To better evaluate the durability of the resin formulations under intended field conditions, a separate set of samples cured at 100°C for 16 hrs were placed in an air circulating oven at 250°C for at least 1000 hrs. The resin samples were cured and aged in aluminium moulds in an attempt to mimic the in-service environment where the exposure to elevated temperature largely comes from a metal pipe with only one surface exposed to a potentially oxidative air atmosphere. Figures 4(a) – (e) show the samples after 1000 hrs and visually illustrate the varying degrees of resistance to elevated temperature of each resin formulation. Particular attention is drawn to Figures 4(a) and (c) which show the CER and the CER/Benzoxazine networks appearing to be the least affected systems during exposure, apart from the darkening of the resin, which all five resins underwent during the ageing process. There is much less surface cracking or macro-degradation over the course of the ageing process for these two resins concerned, with the benzoxazine modified CER formulation being particularly unaffected. In contrast, the CER/Phenolic resin formulation (Figure 4b) has expanded substantially out of the mould, most likely due to formation and evaporation of water, a by-product of the phenolic condensation reaction [9,10]. The CER blends containing epoxy resins illustrated in Figures 4(d) and (e), on the other hand, exhibited significant shrinkage, resulting in gross cracking with also a decidedly dull appearance, evident of surface degradation. This comparison, albeit qualitative, nonetheless provided an indication of the superiority of the CER/Benzoxazine formulation.

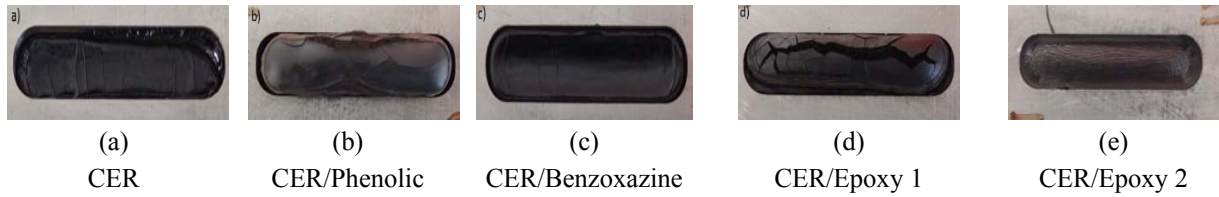


Figure 4: Photographs of the resin samples after about 1000 hrs in an air circulating oven at 250°C.

The mass loss due to heat ageing was tracked and plotted as a function of exposure time in Figure 5. The plot provides supporting quantitative information to the above observations that the unmodified CER and the benzoxazine modified CER resin networks exhibited superior thermal resistance at 250°C compared with the rest of the resin formulations. They both lost under 3wt% over the course of 1000 hrs, compared with CER/Phenolic and CER/Epoxy 2 at approximately 7wt%, and CER/Epoxy 1 at approximately 9.5wt%. Clearly the use of benzoxazine as a resin modifier did not deleteriously impact weight loss, unlike the phenolic modified CER, which exhibited superior thermal resistance after relatively short heat exposure times, but displayed a drastic increase in weight loss with further ageing.

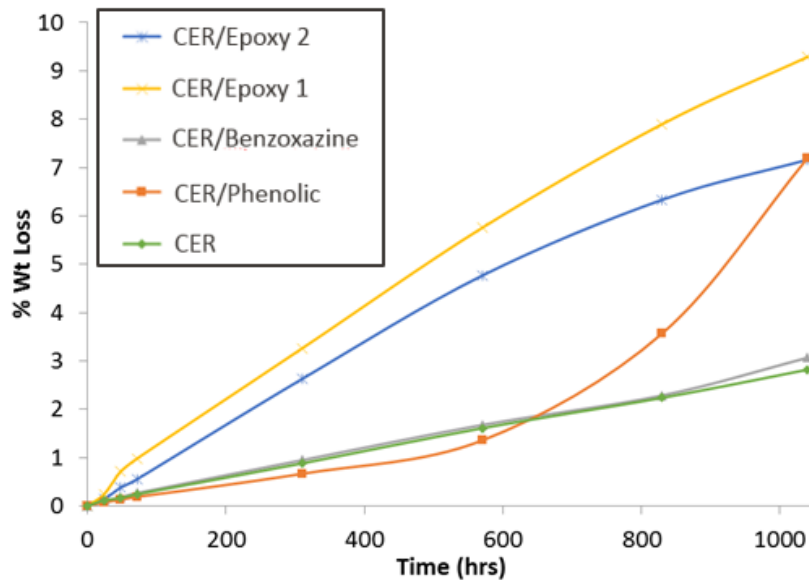


Figure 5: Weight loss as a function of time at elevated temperature in an air circulating oven.

The significant weight loss measured for the epoxy and phenolic modified CER formulations would correlate with the observed volume expansion via the formation and evaporation of water in the CER/Phenolic resin formulation and resin shrinkage in the CER/Epoxy resin formulations. These thermal ageing results hence further confirm the deleterious impact of epoxy resins on the thermal stability of CER.

4 SUMMARY AND CONCLUSION

All of the CER-based resin formulations investigated in the present work displayed moderately large exotherms, indicative of unreacted functional groups after curing at 100°C for 16 hrs. Nevertheless, all the reactive diluents, *viz.* phenolic, benzoxazine and epoxy, in CER all appeared to have advanced the cure to some extent. Cure conversions for the unmodified CER formulation is about 64.5%, while each of the blends modified with a reactive diluent had higher cure conversions, with up to 84.1% for the benzoxazine modifier. Only the benzoxazine modified CER and the unmodified CER formulations passed the thermal stability test, which demanded measured weight loss of no more than 5% at 250°C over a period of 1000 hrs. The weight loss in an air circulating oven was recorded for the two resin

formulations to be less than 3%, which was vastly superior to the rest of the formulations, which registered at least 7% and up to 9.5% weight loss under the same ageing conditions. Despite all the samples turning darker, visual inspection of the samples further revealed that the integrity of the unmodified CER and benzoxazine modified CER samples was maintained after the ageing process. This contrasts the observation recorded for the rest of the resin formulations which revealed gross cracking due to resin shrinkage for the epoxy formulations, and expansion due to formation and evaporation of water for the phenolic formulation.

Based on the results of this work, the unmodified, and benzoxazine modified, CER formulations have the greatest potential to be processed and applied in the field without compromising its thermal stability. Hence, following on from this stage of the work, glass fibre fabric prepregs based on the shortlisted resin formulations would be produced to demonstrate the applicability of the repair system in the field, and to provide sufficient materials for a field trial. The outcomes of this next phase of work would be published elsewhere in the near future.

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