

THERMOMECHANICAL PROPERTIES OF TOUGHENED PHENOLIC RESOL RESIN

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ABSTRACT

Changes in thermal and mechanical properties of polyvinylbutyral (PVB) modified phenolic resole resin were studied. The DSC and TGA studies show that an increase in PVB content results in a reduced thermal stability at temperatures above 360 °C, but causes little change in thermal properties at temperatures below 300 °C. The izod impact strength of cast moulded resin is maximum with PVB content of 10 phr. The PVB modified phenolic system possessed discrete spheres of PVB evenly dispersed in a phenolic resin matrix at low thermoplastic content. However, at higher concentrations, phase inversion resulted, and the morphology consisted of discrete spheres of phenolic resin embedded in a PVB matrix. A decreased in hydroxyl peak intensities (3497-3362 cm⁻¹) and broadening of ether peak (1275-1200 cm⁻¹) are more prominent when compared with the unmodified blend, due to cure reactions and with the increased amount of PVB in the blend film.

INTRODUCTION

Phenolic resins have been a staple product of the synthetic polymer industry for the past 90 years [3]. These resins have been used extensively in the production of moulded plastics, wood products, and aerospace components [2]. In constructing aerospace components, the most important use of phenolic resins is in the manufacturing of high performance composites [1].

Phenolic resins and powders have found diverse applications in filament winding, sheet moulding compounds, honeycomb structures, prepregs, and resin transfer moulding [5]. In these applications, phenolic resins are used as matrices to protect and reinforce the fibres contained within the composite structure. Phenolics have found wide utilization in these fields due to their strength retention at elevated temperatures and low fire, smoke, and toxicity properties. However, the used of phenolics has historically also been limited due to lack of understanding regarding their mechanical properties and fracture mechanics, as well as health concern [6]. While the above-mentioned, thermoset resins have high material strength and high interfacial strength with

reinforcing fibres, they show low ductility, resulting in low failure toughness. Thus the resins are sometimes modified to improve the performance of the composites [4]. The elastomers widely used in the modification of thermosets are: carboxyl terminated butadiene acrylonitrile (CTBN), vinyl terminated butadiene acrylonitrile (VTBN), polyurethane, polyvinyl butyral (PVB) [7]. The elastomer particles, dispersed in a resin, regulate the fracture mode and prevent brittle fracture of the resin by inducing plastic deformation at the tips of propagating cracks and lowering the stress around the crack tip below the critical point. Hence enhanced impact properties and fracture toughness can be obtained.

Phenolic resin brittleness has significantly limited their widespread applications. High performance composites used for structural applications required excellent mechanical properties [8]. The high degree of anisotropy and laminar structures of most fibre-reinforced composites mean that delamination is one of the most prevalent life-limiting damage modes as it causes catastrophic reduction in stiffness and other mechanical properties [8]. The improvement of interlaminar adhesion and thereby toughness is therefore essential for the efficient performance of composites of brittle matrices. Recently many attempts have been made to improve the toughness of phenolic resins [10]. It is well known that small amounts of elastomer can significantly improve the fracture toughness of phenolic resins, by forming discrete rubbery particles that are chemically bonded to the matrix. Improvement in toughness is generally accompanied by a relatively small loss of thermo-mechanical properties. A review of the literature indicates that both chemistry and thermodynamics play an essential role in determining the final properties of these elastomer/phenolic blends. Thermodynamics includes issues of miscibility and phase separation. Initially, the elastomer must be able to dissolve in the polymerizing monomer system. However, complete miscibility is also undesirable because a certain degree of elastomer phase separation of the rubber before gelation of the matrix is one of the crucial requirements for effective matrix toughening. A perfect miscibility of the elastomer in the matrix leads to a diluent effect rather than a toughening effect. The balance between phase separation and polymerization steps depends on the solubility of the elastomer in the matrix, the initial fraction of elastomer and cure conditions. In the absence of chemical bonding, only Van-der-Waals attractive forces or the hydrogen bonding type of forces are present and not much toughening can be expected [9].

In this study, the thermo and mechanical properties of cast phenolic resole resin modified with polyvinyl butyral (PVB) were studied. The property enhancement achieved in the phenolic resin by adding elastomer was compared with the unmodified resin. The optimum izod impact property and % improvement in impact toughness was determined for the modified phenolic resin. Changes in thermal properties of modified phenolic resin were studied as a function of PVB contents.

EXPERIMENTAL METHOD

The phenolic resin to be tested in this study is a resole type manufactured by Changshu South-east Plastic Co. Ltd., Jiangsu, China under the trade name NR 9430. If required, a catalyst from Changshu Plastic by the trade name of C-100 which consist of p-Toluene Sulfonic and Sulfuric acid is used to enhance the curing process. The phenolic resole resin is a liquid with density of 1.20 g/cm³. The elastomer employed was PVB by Solutia Inc. Singapore Pte. Ltd. under the trade name of BUTYVAR B-90 which has butyral and hydroxyl content of 80.0 % and 18.5-20.5% respectively.

Table 1: Physical properties of phenolic resole resin

Properties	Phenolic Resole NR 9430
Non-volatiles, %	> 70
Viscosity,cps@ 25 °C	400 ~ 700
pH	6.5 ~ 7.5
Pot life , minutes @10phr C-100	> 20.0

Table 2: Physical properties of polyvinyl butyral

Properties	BUTYVAR B-90
Volatiles, max %	5.0
Molecular weight, (weight average in thousands)	70 ~ 100
Ostwald Solution Viscosity, cp.	13.0 ~ 17.0
Specific gravity	1.10

Blending of Phenolic Resins with PVB

Phenolic resin was blended with PVB at various levels i.e. 0, 1.0, 5.0, 8.0, 10.0, 20.0, 30.0 parts per hundred weight of resin (phr) using IKA LR 2000 chemical reactor / stirrer at 30 °C at low 250rpm for 2 hours. The toluene and ethanol solvent and air bubbles were removed in a vacuum oven at room temperature.

Preparation of cast resin

Cast resins of thickness approximately 3.2 mm were prepared on aluminium mould waxed with a release agent. About 8% of catalyst was added. To remove the solvents, cast resins were cured for 12 hours at 50 °C for and 12 hours at 80 °C. The cast resins were 12.0 mm wide, 15.0 mm long and 3.0 mm thick.

Infrared spectroscopy of the blended resin

The chemical interaction between phenolic resole and the PVB resin was studied by infrared spectroscopy. The spectra of the phenolic resole / PVB blend at different levels were recorded directly using PERKIN ELMER's Fourier Transform infrared spectrometer by ATR techniques without the need to prepared KBr pellet.

Scanning electron microscopy analysis on blended resin

The study on the effect of elastomer modification on the resin blends were done by using LEO Field Emmission Scanning Electron Misroscope (FESEM) at magnifications of 50000 x. Non-etched specimen surfaces were coated with a thin layer of platinum by ion sputtering to provide a conductive surface and scanned.

Thermal and mechanical properties of the modified cast resins.

The thermal properties of the resins were examined in a nitrogen atmosphere from room temperature to 500 °C with a heating rate of 10 °C/min using differential scanning calorimeter (DSC) from METTLER TOLEDO. Samples (5-10 mg) were hermetically sealed in aluminium pan and placed in a DSC cell together with an empty aluminium pans as a reference and the heated at programmed heating rate with continous nitrogen purge at flow of 10 ml/ min. Using METTLER TOLEDO thermogravimetric analyser (TGA) in a nitrogen atmosphere, the thermal degradation and the residues at 500 °C were investigated. The heating rate used was 10 °C/min. Samples (4-6 mg) were placed in alumina crucible and heated from room temperature to 900 °C with continous nitrogen purge. Izod impact test was conducted on the cast resin specimen with type A notch and at an angle of 45° using CEAST RESIL Pendulum Impactor according to ASTM D 256 guidelines. With an impact velocity of 3.46 m/s, a 2 joule hammer was impacted on to the specimens to obtain the izod impact resilience data.

RESULTS AND DISCUSSION

Infrared analysis

Figure 1 presents the possible reaction scheme between PVB modified phenolic resole resin.

REACTION WITH PHENOLICS

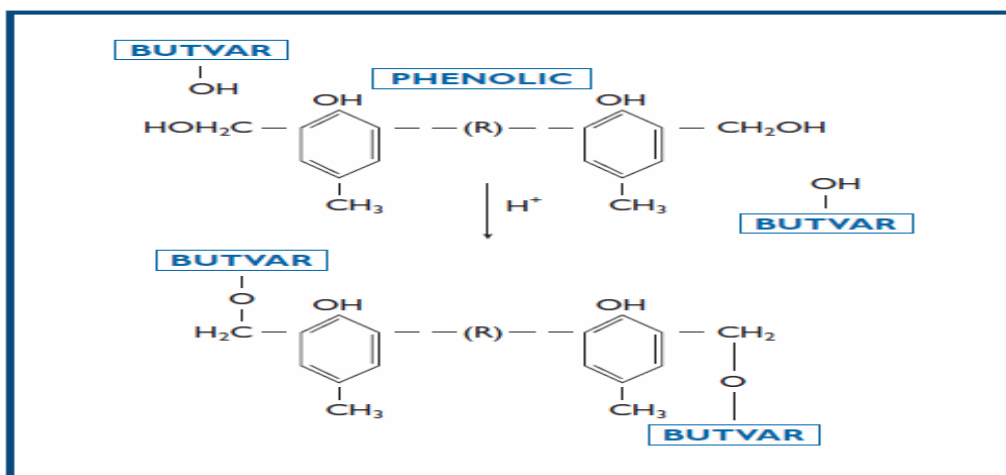


Figure 1: Chemical reaction between PVB (Butyvar) and phenolic resole resin.

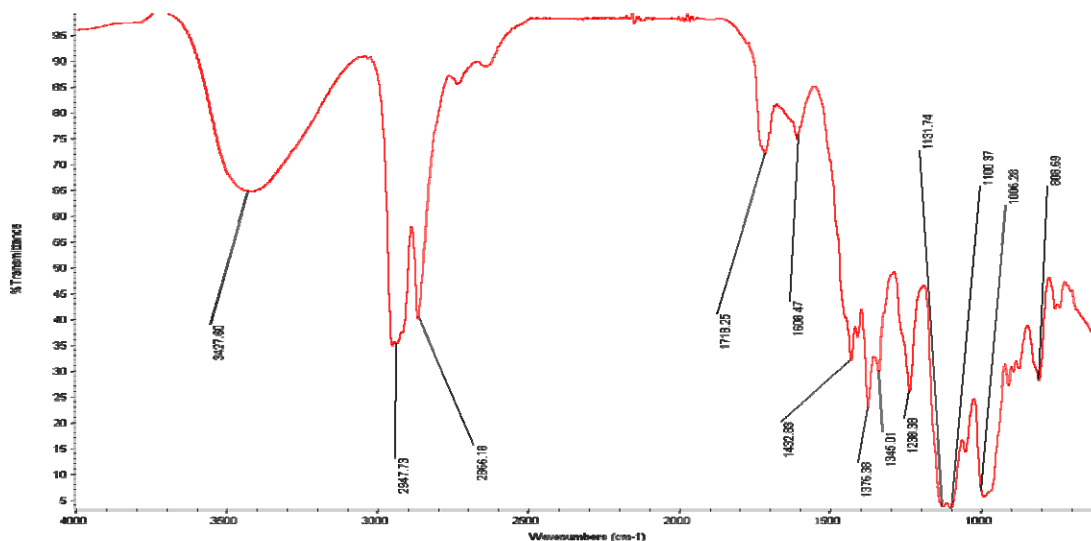


Figure 2: FTIR Spectra of unmodified phenolic resole resin after curing

From figure 2, it can be seen that when there is no PVB, an increased in hydroxyl peak intensities ($3497\text{-}3362\text{ cm}^{-1}$) and broadening of ether peak ($1275\text{-}1200\text{ cm}^{-1}$) due to cure reactions at high temperature. The peak associated with methylene groups ($2967\text{-}2871\text{ cm}^{-1}$) also become visible due to the etherification reactions. C. Nirmal et al. [8] in his work on modification of phenolic resole with hydroxyl terminated polybutadiene (HTPB) explains that in phenolic / resole blends, the etherification reaction between the methylol groups always prevails at $120\text{-}130\text{ }^{\circ}\text{C}$ and as the cure reaction progress at higher temperatures, further cross-linking take place at $160\text{ }^{\circ}\text{C}$.

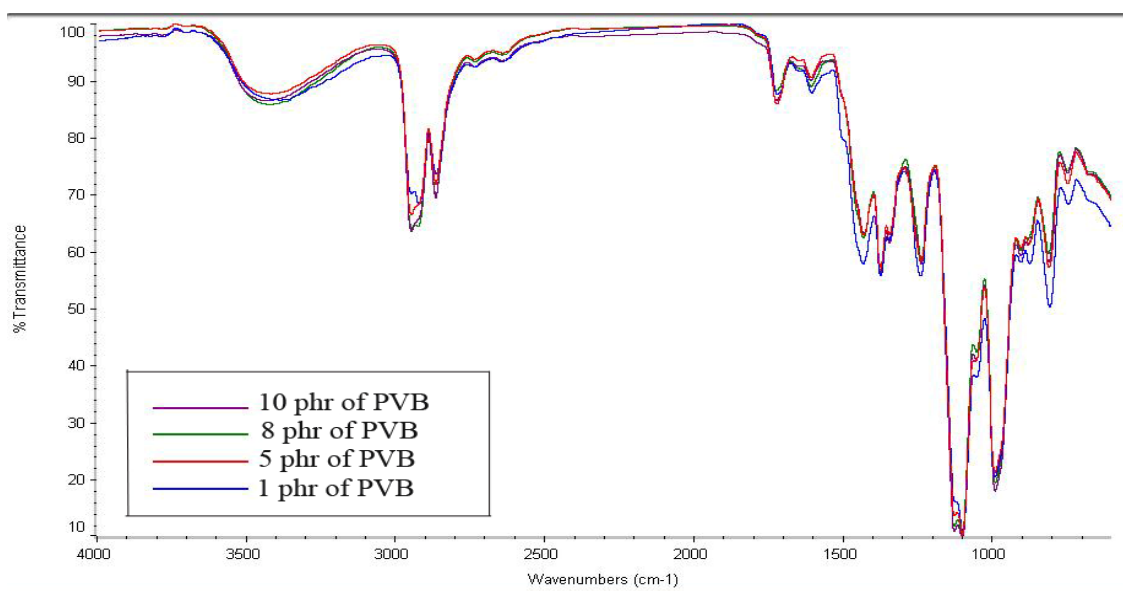


Figure 3: Overlays of FTIR Spectra for PVB/ Modified Phenolic Resins

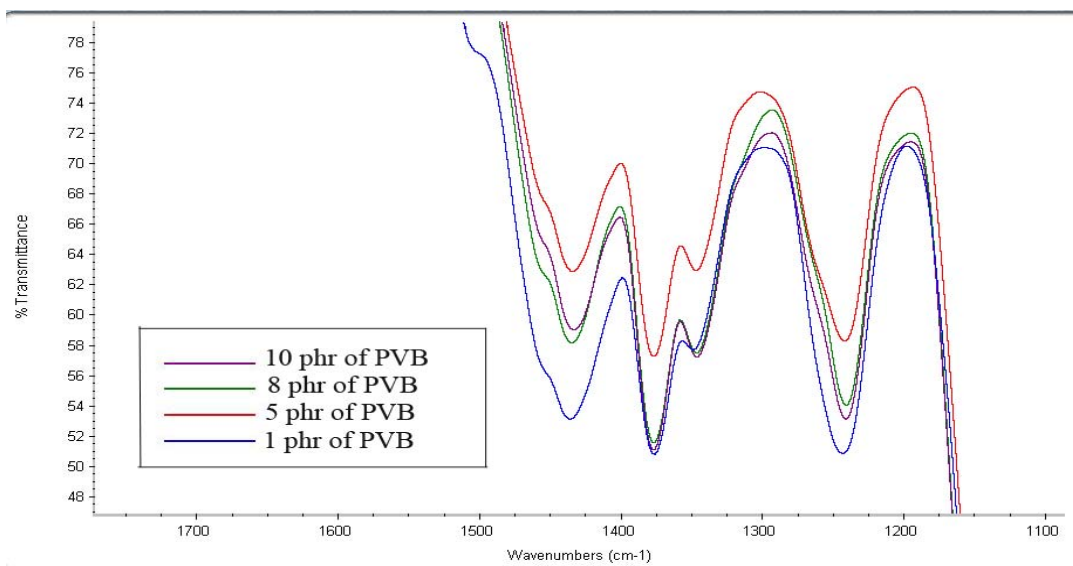


Figure 4: Overlays of FTIR Spectra for PVB/ Modified Phenolic Resins

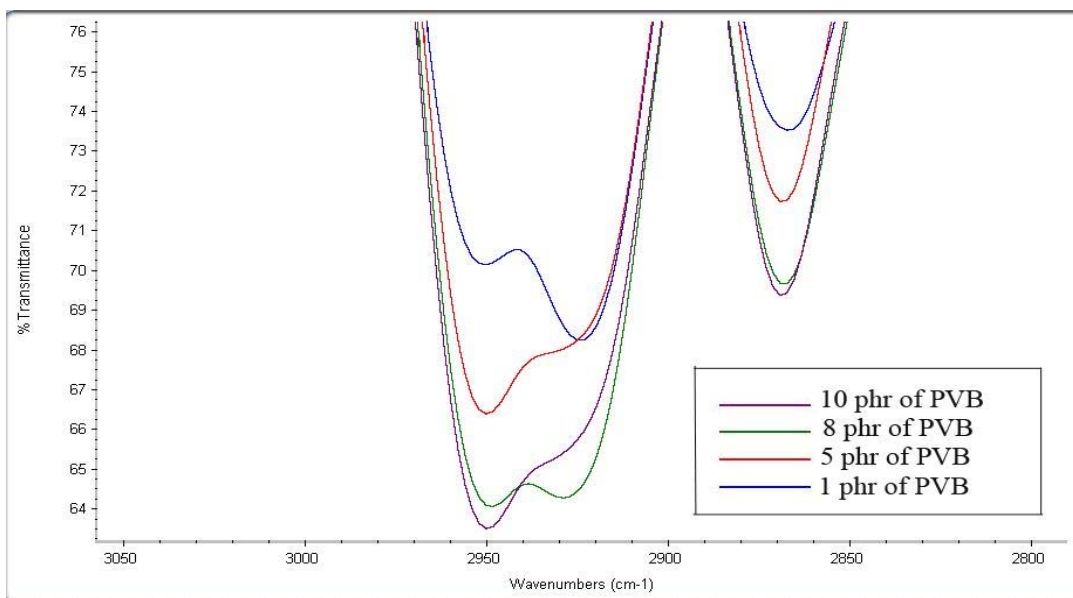


Figure 5: Overlays of FTIR Spectra for PVB/ Modified Phenolic Resins

In the case of phenolic / resole/ PVB blends, from figure 3, it can be seen that after blending with PVB, a decreased in hydroxyl peak intensities ($3497\text{-}3362\text{ cm}^{-1}$) and from figure 4, broadening of ether peak ($1275\text{-}1200\text{ cm}^{-1}$) are more prominent when compared with the unmodified blend, due to cure reactions and with the increased amount of PVB in the blend resin.

The peak associated with methylene groups ($2967\text{-}2871\text{ cm}^{-1}$) from figure 4 were declining compared to the unmodified blend, with the increased in PVB contents in the modified resin. This is due to the declining of etherification reactions as explained by C. Nirmal et al [8] in his works.

SEM analysis

Changes in morphology of PVB / modified phenolic resin were studied. The PVB modified phenolic system possessed discrete spheres of PVB evenly dispersed in a phenolic resin matrix at low elastomer content. However, at higher concentrations, phase inversion resulted, and the morphology consisted of discrete spheres of phenolic resin embedded in a PVB matrix.

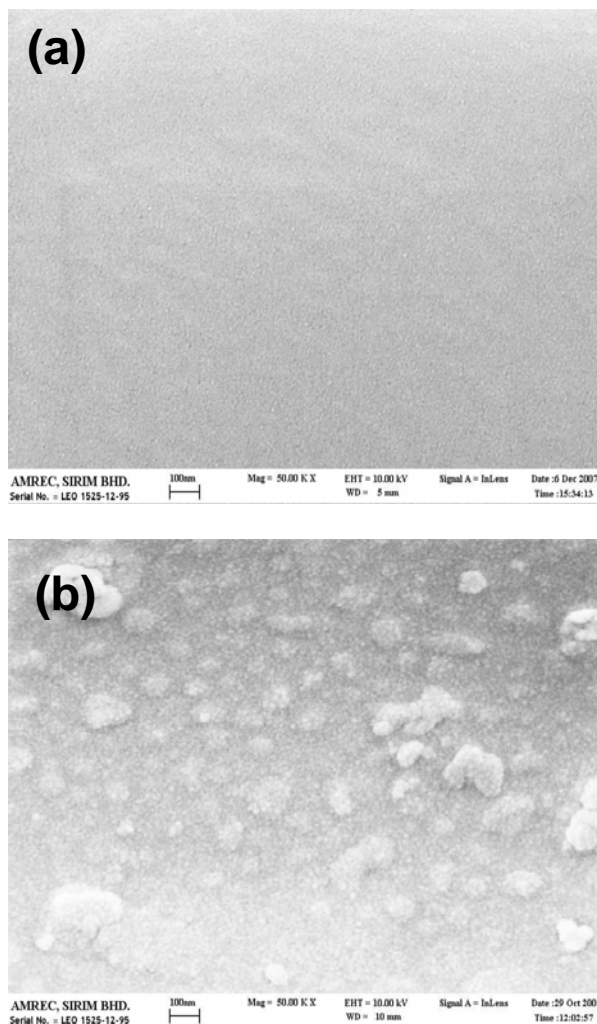


Figure 6: (a) SEM micrograph of PVB at 50k x. (b) SEM micrograph of phenolic resole at 50k x.

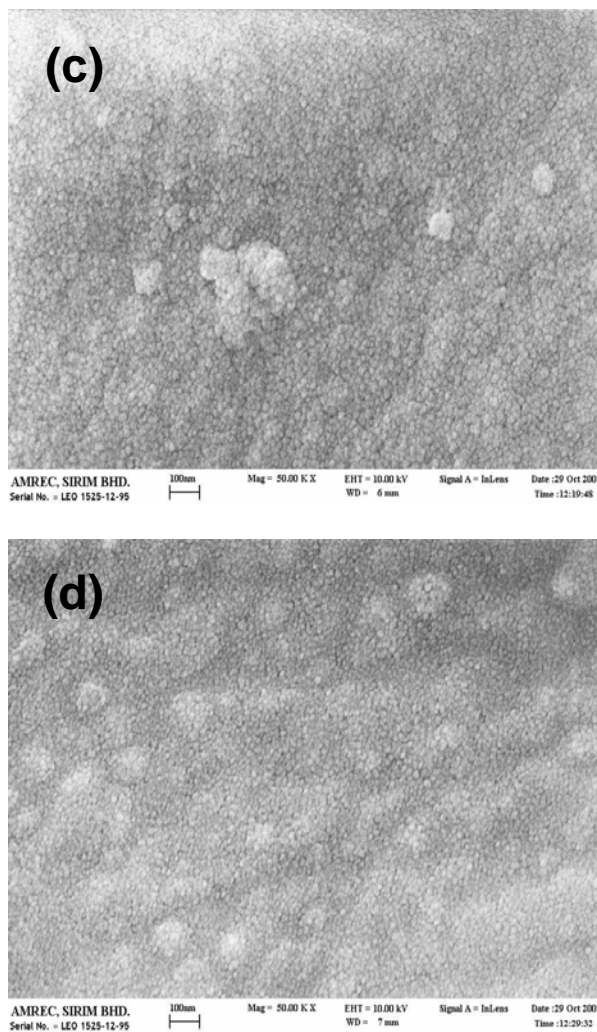


Figure 7: (c) SEM micrograph of 5 phr PVB/ resole at 50k x. (d) SEM micrograph of 10 phr PVB / resole at 50k x.

Thermal analysis

Figure 8 shows the thermal properties of modified phenolic resins with different PVB contents measured by DSC after cure. Thermal degradation only start to occurs after 360 – 400 °C for all samples, but the peaks associated with thermal degradation move towards lower temperatures with increasing PVB contents. The TGA studies show that thermal degradation processes start at around 100 °C for all samples but profound different differences with PVB content can be found above 350 °C. The DSC and TGA studies show that an increase in PVB content results in a reduced thermal stability at temperatures above 350 °C but causes little change in thermal properties at temperatures below 300 °C. Works by T.J Kang et al [4] showed the same trends even with PVB content up to 66.7 phr.

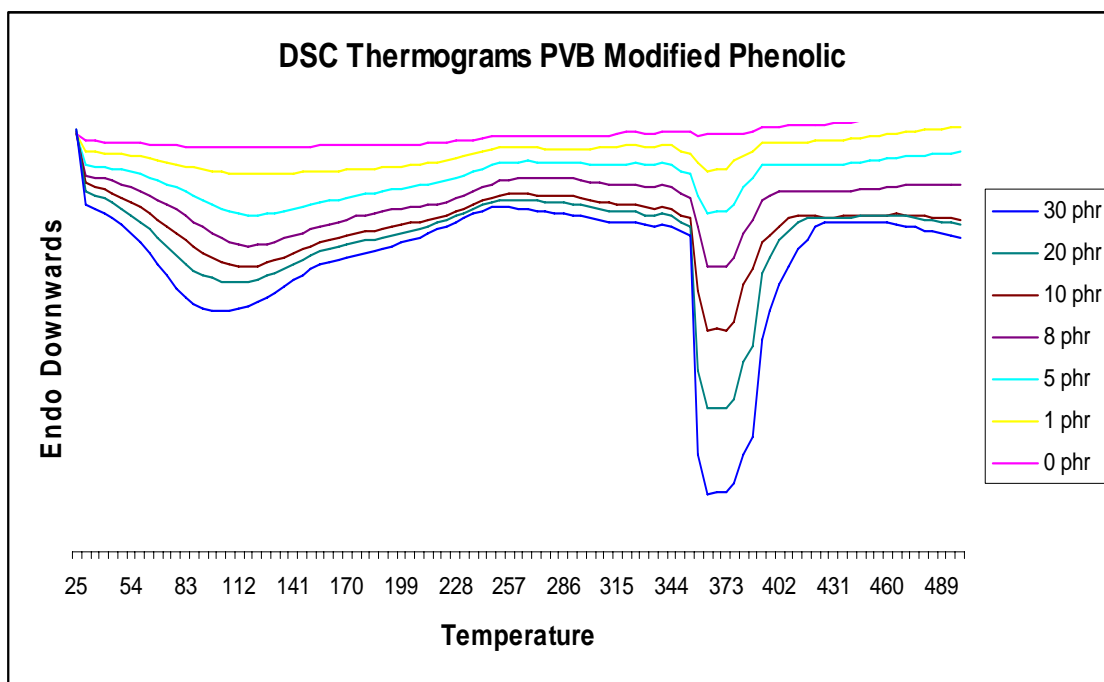


Figure 8: DSC Thermograms of PVB modified phenolic resins after curing with different level of PVB content.

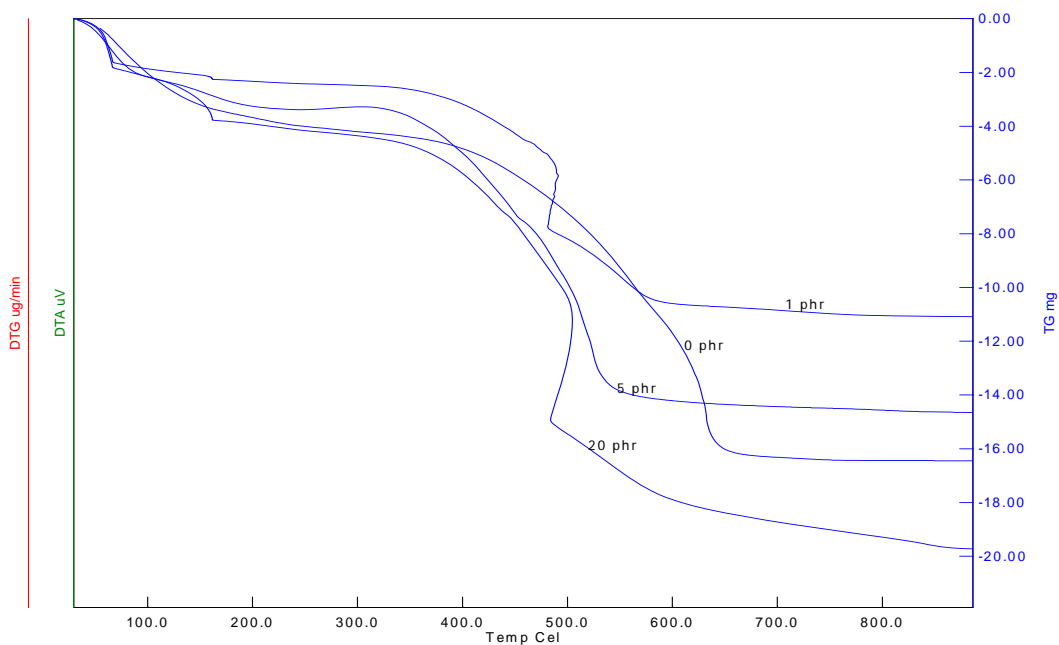


Figure 9: TGA Thermograms of PVB modified phenolic resins after curing with different level of PVB content.

From figure 8, it can be seen that, the DSC thermograms showed two endothermic peaks. The first broader peak corresponds to the transition of phenolic resins. The transition is associated with bridging of methylene to dimethylene ether bridge as demonstrated by C. Nirmal et al [8]. The peak declined endothermic ally with the increased in PVB contents. The second endothermic peak is less broad corresponds to the completion of ether bridging at higher temperatures, where the hydroxyl and methylol groups would be converted to water and formaldehyde.

Mechanical analysis

From table 3, it can be seen that the impact resilience of cast specimens reach peaks at 10 phr with max resilience of 17.03 J/m² compared to unmodified phenolic resin at 0 phr. The impact properties start to drops from 20 phr onwards. The overall toughening trends have been shifted to the lower PVB contents as also demonstrated by T.J. Kang et al [4]. The impact toughness of the 10 phr PVB modified phenolic resole showed 25 % improvement compared to unmodified phenolic resole.

Table 3: Impact resilience of modified PVB phenolic resole.

Item Tested	Temp. tested	(PVB / Phenolic blend ratio)						
		30phr	20phr	10phr	8phr	5phr	1phr	0 phr
Impact Resilience (J /m ²) max.	23 °C	11.56	13.11	17.03	16.45	14.88	13.50	13.59

Impact test results demonstrate better how the addition elastomers materials can improved the impact toughness of the phenolic resin. In the case of composite laminates, other factor have also to be considered such as interfacial strength which plays an important role in determining the mechanical and impact properties of the compositions.

CONCLUSION

To improve the toughness of phenolic resole resin, PVB has been added to phenolic resin from 0 phr to 30 phr. Changes in morphology and thermal properties as well as mechanical properties of the modified resin were studied as a function of PVB content and compared with unmodified resin. The PVB modified phenolic resin systems possessed discrete spheres of PVB evenly dispersed in a phenolic resin matrix at low elastomer content. However, at higher loadings, phase inversion resulted, and the morphology consisted of discrete spheres of phenolic resin embedded in a PVB matrix. The thermal stability decreased with PVB content at temperatures above 350 °C but showed little change below 300 °C. PVB modified phenolic resin achieved a maximum / optimum impact resilience at 10 phr @ 17.03 J/m² with 25% improvement in impact toughness compared to unmodified resin.

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