Highlights

1. A combination of phenolic resin with cross-linking polymer divinylbenzene (DVB) is introduced with dodecylbenzene sulfonic acid (DBSA)-doped polyaniline complex to make a thermosetting conductive composite.
2. It is shown that phenol-DVB complex can be polymerized catatonically in the presence of acid doped-PANI without any additional catalyst.
3. It is reported that the new structure of phenol-DVB resin, effectively reduced the de-doping of PANI, rendering high electrical conductivity.
4. The combination of phenol-DVB also increases the flexural modulus of the prepared composites.

Graphical Abstract

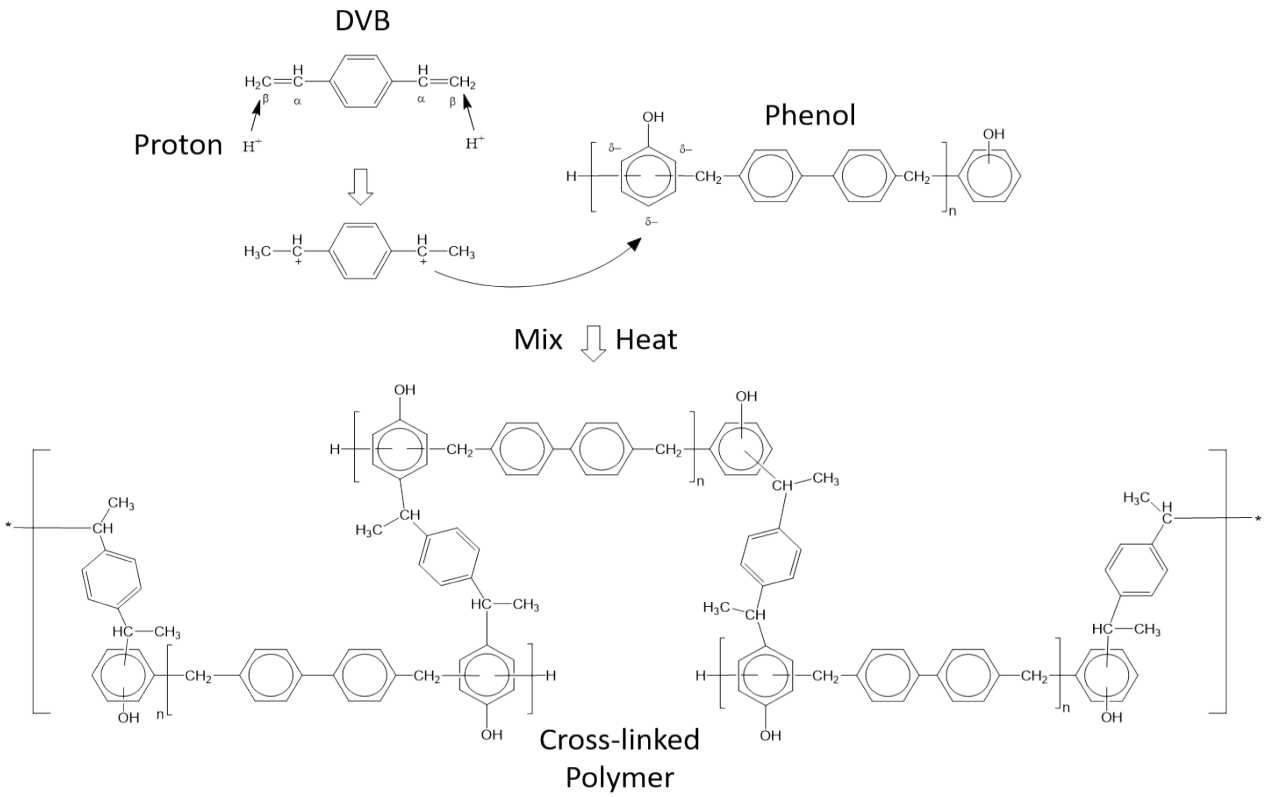

Figure 1- Plausible curing mechanism of phenol-DVB in the presence of protonic acid.

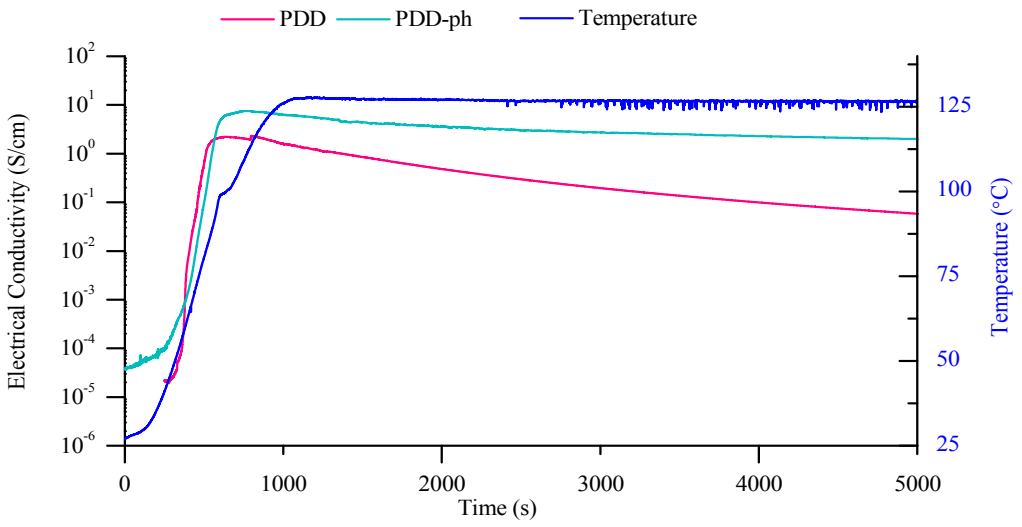

Figure 2. Reduced de-doping of polyaniline in presence of phenol-DVB structure confirmed by in-situ electrical conductivity measurement.

Reduced De-Doping and Enhanced Electrical Conductivity of Polyaniline filled Phenol-Divinylbenzene Composite for Potential Lightning Strike Protection Application

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Abstract: Phenolic resin was mixed with a cross-linking agent divinylbenzene (DVB) to prepare a polyaniline-based electrically-conductive thermosetting polymer composite. It has been shown that this Phenol-DVB mixture can undergo cationic polymerization in the presence of the dodecylbenzene sulfonic acid (DBSA)-doped polyaniline (PANI). Composites with different weight ratios of phenolic resin and DVB were mixed with a fixed weight of DBSA-PANI (i.e. 30 wt. %). Increasing the phenol content in the resin system was found to improve the electrical conductivity of the composite to almost 2700%. This improvement has been assigned to the reduced de-doping of polyaniline in phenol-DVB resin. Active sites of phenol effectively attached to the β carbon of DVB and reduced the proton subtracting species of DVB, leading to reduced de-doping of PANI. This behavior was studied through various characterization techniques including differential scanning calorimetry (DSC), FT-IR spectroscopy and Scanning Electron Microscopy (SEM). Electrical conductivity measurement, mechanical properties, and in-situ electrical conductivity measurements were performed to find the

optimized properties of the composite. Optimized composites prepared with the composition of 30 wt. % DBSA-PANI and 70 wt. % of phenol-DVB (50 wt. % each), have shown electrical conductivity of 0.20 S/cm and a flexural modulus of 2.1 GPa, which is a significant improvement in the flexural properties of polymer based-thermosetting composites with similar electrical conductivity. This material can be a potential candidate for the lightning strike protection of fiber reinforced plastics.

1. Introduction

Since the discovery of conductive polymers, researchers have looked for applications in thermoset composites. Polyaniline (PANI) is slowly gaining the reputation of a multifunctional material that is used in various applications such as capacitors, sensors, electromagnetic shielding, etc. [1–7]. PANI has advantages such as easy synthesis, availability, low cost, and tuneable electrical properties [8]. However, it has some severe disadvantages including bad processability and de-doping [9–11]. The bad processability of PANI can be effectively solved by mixing it with other processable polymers [12]. Hence, PANI is regularly mixed as a filler with other polymers (matrices) to prepare useful products. These matrices can be thermoset or thermoplastic resins [13–15].

Thermoset polymers are of particular interest to the aerospace industry. Many researchers have attempted to mix conductive polymers like PANI with aerospace grade commercial epoxies. While they are able to get some conductivity into the composites, the full potential of the conductive thermoset composite ~~was~~ is yet to be realized. An extensive survey was ~~done~~ conducted by Perrin et. al. The survey reported electrical conductivity values in order of 10^{-2} -10^{-6} S/cm [16]. This range of electrical conductivity may be good enough for some applications, like static dissipation and EMI shielding, but not for more challenging applications such as lightning strike protection of carbon fiber reinforced plastic (CFRP) materials, where high electrical conductivity is needed.

Yokozeki et al. and Hirano et al., reported that a PANI-based composite could help to withstand a lightning strike [17,18]. Kumar et. al. recently reported that a Polyaniline-based adhesive layer on top of fiber reinforced plastic (FRP) structures successfully suppressed lightning-induced damages. They used 0.25-0.40 mm thick layer of PANI-DBSA/DVB composite and tested it against a simulated lightning strike of 100 kA intensity. In this work, the authors reported high residual strength of

protected CFRP but also reported small local damage to the PANI-LSP layer. Further work is a logical step to improve the electrical and mechanical properties of PANI-DBSA/DVB composites to achieve an improved all-polymeric PANI-LSP layer [19]. Kumar et. al. have proposed that a change in electrical conductivity could lead to different damage behavior of CFRP from lightning strikes [20]. They also reported that through-thickness electrical conductivity of PANI-based CFRP composites could be tuned by controlling de-doping of PANI [21]. The de-doping phenomenon is attributed to thermal degradation and to the high affinity of the un-polymerized DVB to the protons. De-doping is significantly enhanced in the presence of more doped DBSA-PANI complex as explained in detail in ref. [22]. Thermal doping of PANI in the presence of protonic acid is a straightforward and effective way to impart electrical conductivity in the material [23,24]. However, the doping bond between PANI and the protonic acid can be broken by other proton subtracting species [21]; therefore, such composites cannot be exploited to their full potential [25].

Other than de-doping of PANI, another disadvantage of PANI is that it hinders the polymerization of many commercial resins, i.e., epoxy and DVB. This is defined as a scavenging property of PANI [26,27]. For example, the high weight content of polyaniline is detrimental to the curing of commercial bisphenol type epoxies as shown in **Figure 1**. To explain the disadvantage of PANI scavenging in the curing of epoxies, authors tried to cure the complex of bisphenol type F epoxy (RE-303S-L), hardener (KAYAHARD GPH-65) and catalyst (curezol C17Z) with and without DBSA-PANI (30 wt. %). The DSC curve of both the specimens confirms that large amounts of PANI is detrimental to the curing of the epoxy.

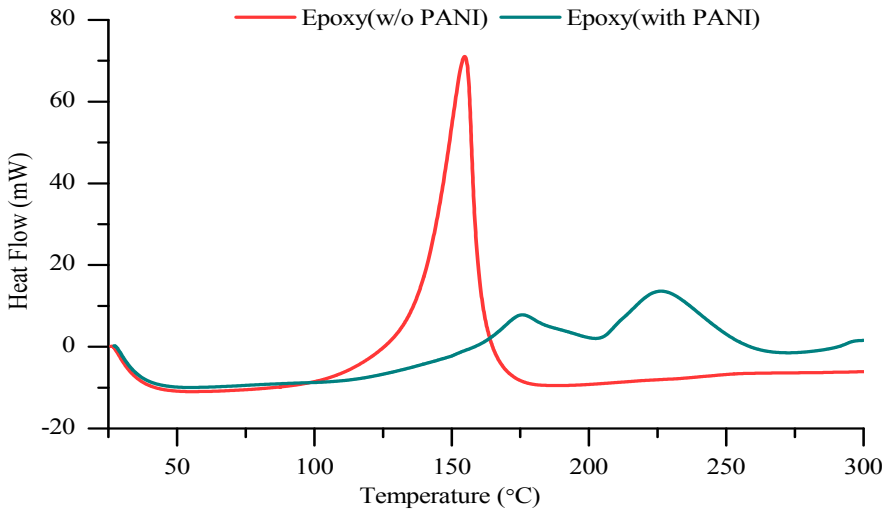


Figure 1- Curing hindrance of epoxy in the presence of DBSA-PANI.

In the present research, authors have tried to solve both problems as mentioned above by replacing bisphenol type epoxy with DVB in combination with Phenol-based (KAYAHARD GPH-65) hardener. Mori et al. reported that phenol resin could be modified with vinyl components and the modified complex could be cured using protonic acids [28,29]. They showed that this unique combination of phenol resin and a cross-linking agent, DVB, creates a new polymer which can undergo cationic polymerization. As per the knowledge of authors, for the first time, phenol-DVB resin is utilized to synthesize PANI-based conductive composites.

The novelty of the present work is that researchers used a combination of phenolic resin with divinylbenzene (DVB) cured in the presence of DBSA-PANI complex, obtaining a good curing property and a relatively good electrical conductivity of the thermoset composites. A pure phenol resin cannot be cured with DBSA-PANI and a pure DVB resin led to de-doping of PANI. Therefore, the combination of Phenol and DVB provided the needed synergic balance. In this work, efforts have been made to discover the best resin composition for optimized mechanical and electrical properties by keeping DBSA-PANI amount constant but changing the ratio of phenol and DVB. Concerning electrical, mechanical, and rheological properties, an ideal composition of the resin is proposed.

2. ~~Experimental~~ Methodology

2.1 Chemical materials ~~supplies~~

The following chemicals were purchased from different commercial producers, polyaniline (PANI) in its emeraldine base form, from Regulus Co. Ltd., Divinylbenzene (DVB) of 80% technical grade from Sigma Aldrich Co. and dodecylbenzene sulfonic acid (DBSA) from Kanto Chemical Co. Inc. Bisphenol-F type epoxy RE-303S-L and phenol-based hardener KAYAHARAD GPH-65 were purchased from Nippon Kayaku Co. Ltd., and curezol C17Z catalyst was procured from Shikoku Chemical Corporation. All chemicals were used as received, without any modifications.

2.2 Plausible chemical reaction

Plausible cationic polymerization of Phenol-DVB in the presence of a protonic acid like camphor sulfonic acid (CSA), dodecylbenzene sulfonic acid (DBSA), and p-toluene sulfonic acid (PTSA) is shown in **Figure 2**. A proton-donating acid is utilized to cure the mixture of Phenol-DVB. The protons react with the vinyl group of DVB and the α carbon atom becomes carbonium ion. This carbonium ion reacts with the δ bond of the active phenol point. By electrophilic substitution reaction, curing of Phenol-DVB takes place at a higher temperature. Literature suggests that cationic polymerization and doping of PANI can occur simultaneously [30]. PANI-based composites were fabricated without any additional curing agent while using DBSA as the dopant and curing agent at the same time. The thermal doping mechanism of polyaniline with DBSA has been studied extensively in the literature; therefore, it has been omitted in this work [31,32].

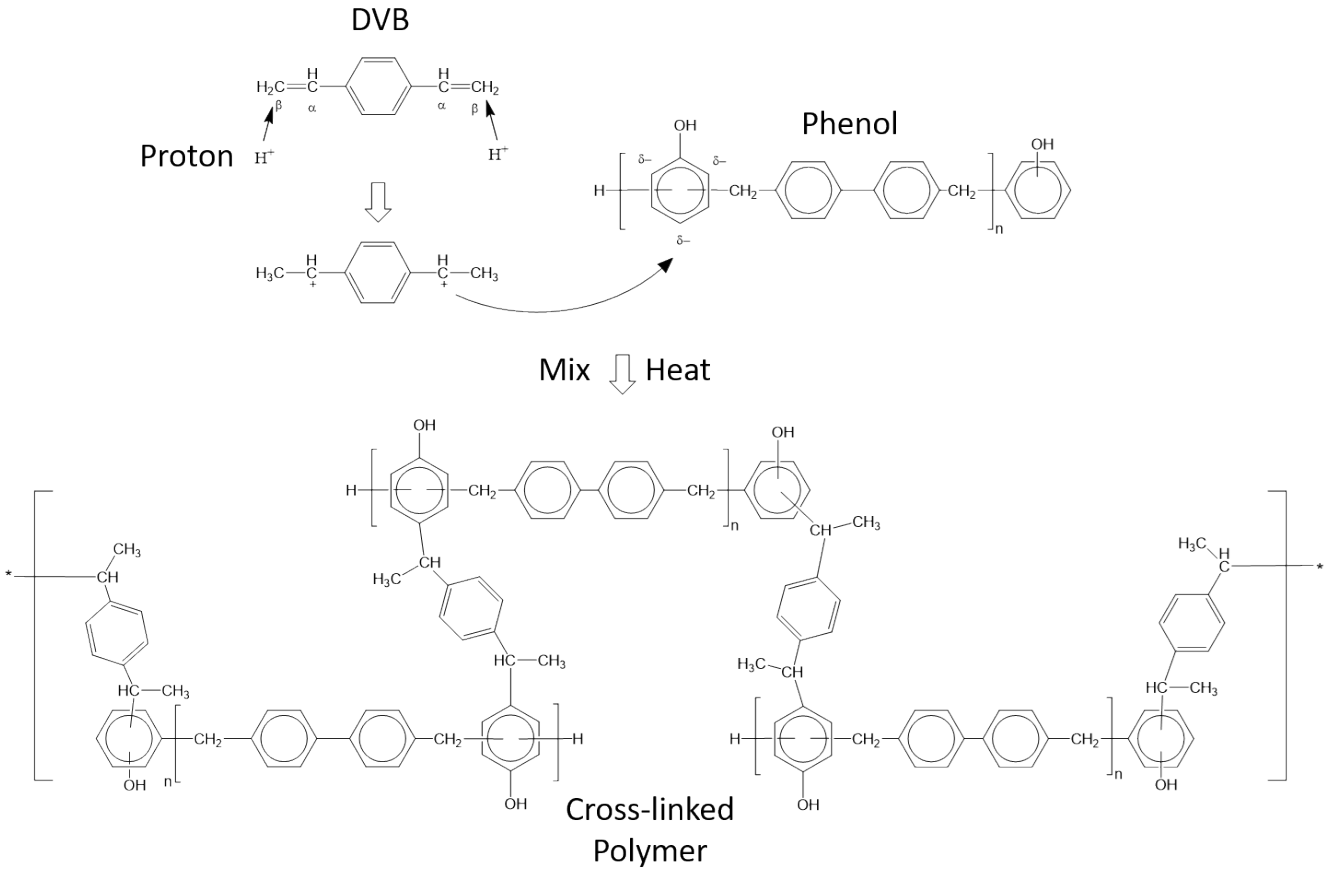


Figure 2- Plausible curing mechanism of phenol-DVB in the presence of protonic acid.

2.3 Specimen preparation

Semi-doped polyaniline is necessary for desired electrical, mechanical and rheological properties of the PANI-based composites as explained in previous work by authors [33]. PANI was thermally semi-doped with DBSA in a weight ratio of 1:2 (which is equivalent to the molar ratio of 1:0.6) to obtain the emeraldine salt form of PANI via controlled thermal doping process. Phenol and DVB in different ratios were mixed using a centrifugal mixer. Firstly, the phenol hardener (KAYAHARD GPH-65) flakes were ground into fine powder with mortar and pestle. The powder was then added into different amounts of DVB at room temperature and mixed thoroughly using a centrifugal mixer to obtain a paste-like homogeneous mixture. Then, the Phenol-DVB mixture and semi-doped DBSA-PANI complex were moved into a cold pot (mixing cup surrounded by a cooling gel), which was specially designed for the centrifugal mixer and utilized to avoid undesirable exothermic curing. The complex was mixed thoroughly and poured into a mould (50 mm × 12.5 mm × 2 mm). The mould was kept in the hot press with a curing profile of one hour at 130° C under 3 MPa pressure. The pressure was applied after the

gelation of the resin started at around 100° C. In this work, the amount of DBSA-PANI complex was kept constant, and the ratio of phenol and DVB was varied as shown in **Table 1**. The nomenclature of the specimens shown in **Table 1**, where PDD-ph stands for PANI-DBSA/phenol-DVB resin. This nomenclature will be followed hereafter in this paper.

Table 1. Variation in weight ratios of DVB and Phenol with a fixed amount of DBSA-PANI

Specimen	PANI		DBSA		DVB		Phenol*	
	Molar ratio	Wt. ratio	Molar ratio	Wt. ratio	Molar ratio	Wt. ratio	Molar ratio	Wt. ratio
PDD	1	10 %	0.6	20 %	5.54	70 %	0	0 %
PDD-ph-1	1	10 %	0.6	20 %	4.75	60 %	0.52	10 %
PDD-ph-2	1	10 %	0.6	20 %	3.96	50 %	1.03	20 %
PDD-ph-3	1	10 %	0.6	20 %	3.17	40 %	1.55	30 %
PDD-ph-4	1	10 %	0.6	20 %	2.77	35 %	1.80	35 %
PDD-ph-5	1	10 %	0.6	20 %	2.38	30 %	2.06	40 %
PDD-ph-6	1	10 %	0.6	20 %	1.58	20 %	2.58	50 %

* Molar ratio of the constituents are normalized with respect to molar ratio of PANI.
* KAYAHARD GPH-65 is a polymer resin with no certain molecular weight, the molar ratio is calculated by the hydroxyl equivalent weight: 195~205(g/eq).

2.4 Experimental techniques

Differential scanning calorimetry (DSC) analysis was conducted using a DSC-60 Plus (Shimadzu Co. Japan). FT-IR spectra of all specimens were obtained by the IRAffinity-1S spectrometer (Shimadzu Co. Japan). For electrical conductivity DC measurement, the specimens were polished using a grinding machine. Electrodes made of aluminium tape were attached to the polished side via conductive silver adhesives. The silver adhesive was dried completely at 60° C before measurement. DC electrical resistance was measured using 3522-50LCR meter (Histester, Hioki E.E. Corporation, Ueda, Japan). Mechanical properties were measured using Instron-5582 UTM machine. A flexural bending test was performed in a 3-point bending configuration. At least five specimens were tested for both electrical and mechanical property measurement. Scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS) was employed with a JSM-7900F (JEOL, Japan). Viscosity was measured using Viscometer TV-25 Type H (Toki Sangyo co. ltd.), at 10 rpm speed with a 3 × R9.7 cone.

3. Results

3.1 DSC Analysis

DSC analysis was performed to understand the reaction mechanism during doping of PANI and curing of phenol-DVB, and the results are shown in **Figure 3**. As explained in the literature, the doping extent of DBSA-PANI significantly affects the curing mechanism of some of the resins [33]. A fixed amount of DBSA-PANI with the same doping extent was used to prepare all the specimens. Three distinct peaks can be seen during the temperature sweep from 25°C to 300°C. The first peak is around 95°C and can be assigned to the joint peak of the DBSA-PANI complex doping and the cationic polymerization of the phenol-DVB resin.

A shoulder-like peak appears with an increased amount of phenol in the composite. This could be due to the effect of the phenol content in the resin and curing of phenol-DVB. The second peak, around 140°C -170°C, is the radical polymerization of remaining DVB. It can be observed that this peak shifts to a lower temperature with decreased DVB content. The third peak is attributed to the decomposition of the dopant DBSA. From DSC analysis, it can be inferred that with increased phenol content in the composite, exothermic reaction reduces, as indicated by reduced intensity of first joint peak. With the shifting of the second peak toward a lower temperature, it can be inferred that polymerization time required for the complete curing of the resin reduces with increasing phenol content. This finding bolsters the idea that DVB is highly prone to the scavenging behavior in the presence of doped polyaniline [22].

DSC of cured specimens was also conducted to find out the cure percentage after a fixed curing time of 1 hour at 130°C. DSC curves for cured specimens are shown in the **Figure 3**. High residual uncured peaks were observed with high content of DVB. Residual DSC peaks suggest that DVB was not able to cure completely within the specified curing profile. With the addition of phenol, almost complete curing of the resin is observed. Complete curing directly affects the mechanical properties of the composites as it will be confirmed in the next few sections.

It should be noted that the first peak is a joint peak of doping of PANI and cationic polymerization of the resin. Therefore, to calculate total curing percentage, heat flow for 30 wt.% of DBSA-PANI is

subtracted from the total heat flow as shown in **Table 2**. An assumption was made that there was no coupling reaction between doping and curing. 100 wt.% of DBSA-PANI gave 85 J/g doping heat.

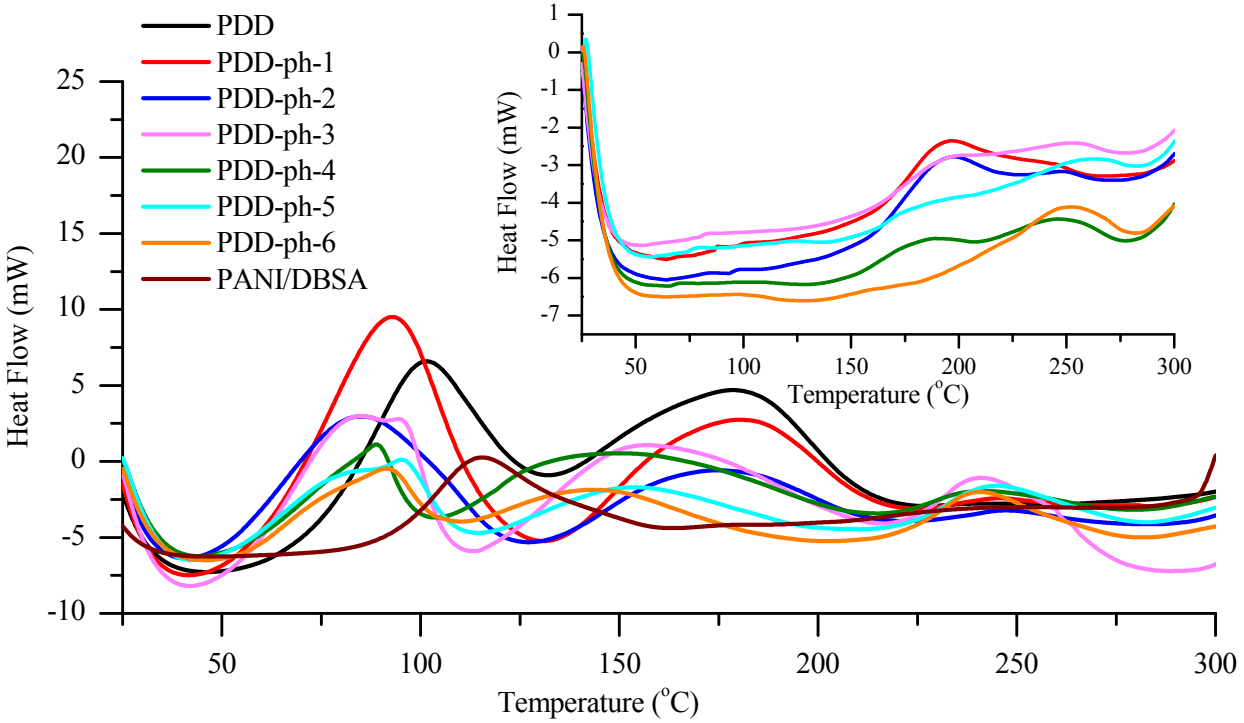


Figure 3. DSC analysis of phenol-DVB resin with respect to the various content of phenol. (inset is the DSC curve for the cured specimens)

Table 2. Percentage cure change with respect to the various content of phenol.

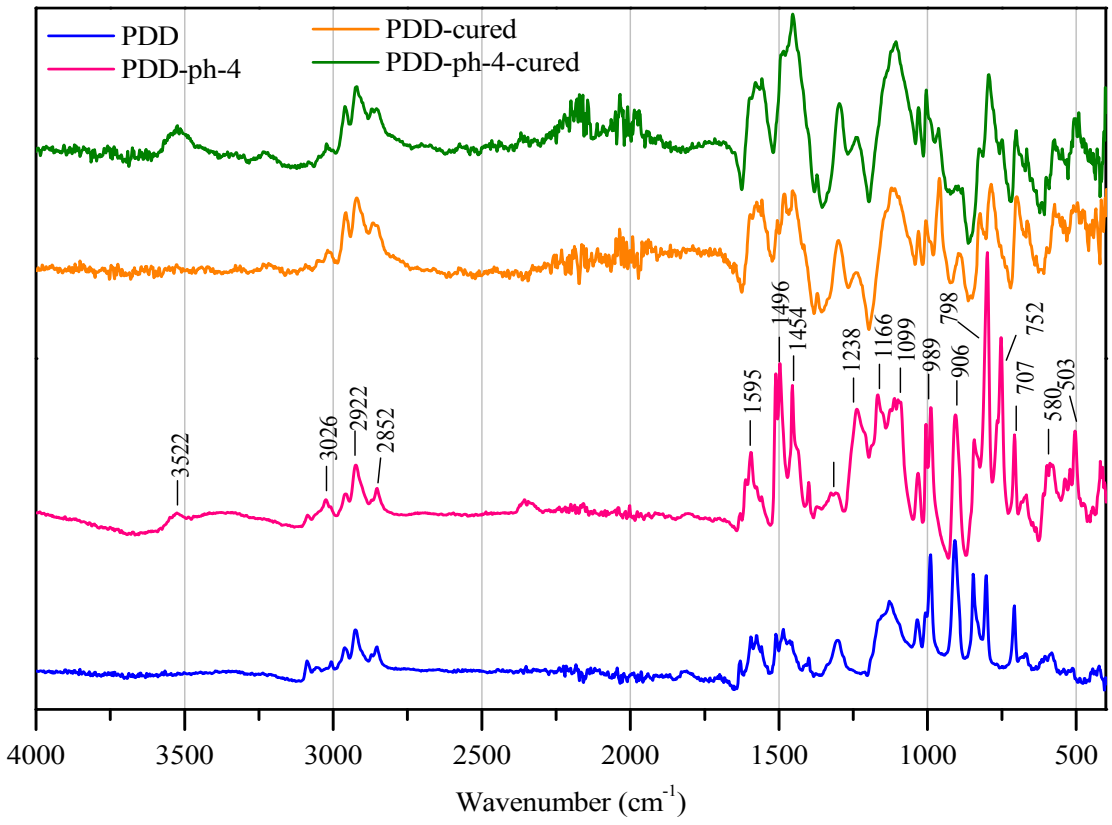
	Heat flow (uncured resin) (J/g)	**Heat flow (cured resin) (J/g)**	**Heat flow for 30 wt. % PANI doping (J/g)**	**% Cure**
PDD	196.97	41.12	25.80	75.97
PPD-ph-1	245.54	65.36	25.80	70.26
PPD-ph-2	190.72	32.12	25.80	80.52
PPD-ph-3	153.97	18.23	25.80	85.78
PPD-ph-4	141.13	17.23	25.80	85.06
PPD-ph-5	107.18	6.45	25.80	92.07
PPD-ph-6	80.11	3.25	25.80	94.02

3.2 FT-IR spectroscopy

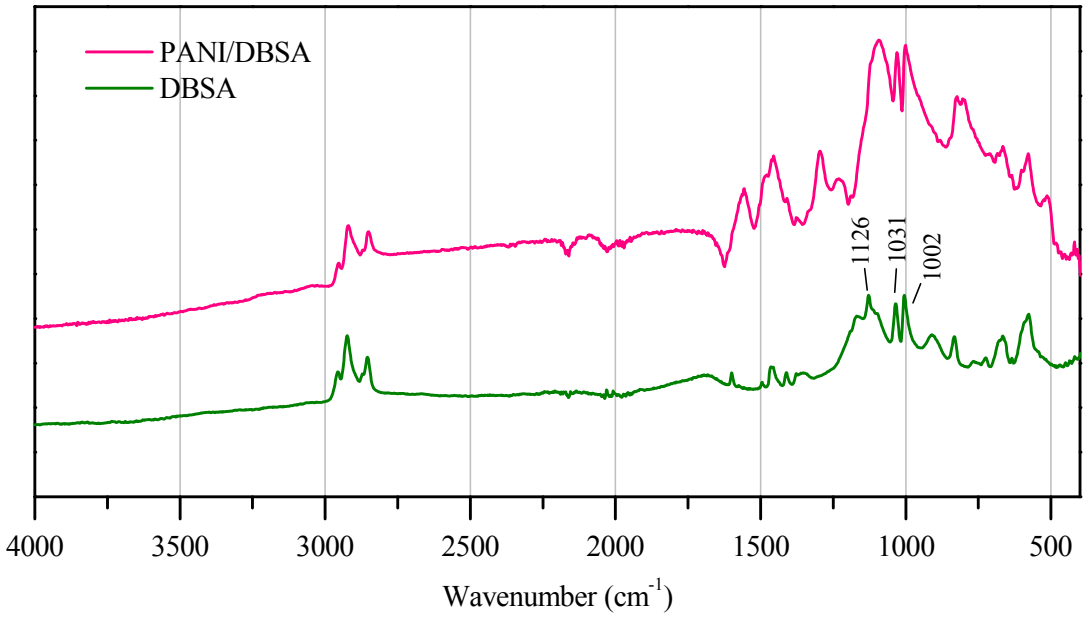
FTIR characterization of the uncured PDD & PDD-ph-4 and cured PDD & PDD-ph-4 was performed to study the reaction mechanism of PDD-phenol composite with results shown in **Figure 4**. Several

characteristic peaks could be observed in all spectra. For instance, peaks around 3100 cm^{-1} to 2800 cm^{-1} corresponded to the C=C-H asymmetric stretching vibration and C-H stretch vibration; peaks around 1600 cm^{-1} to 1400 cm^{-1} were due to the C-C=C stretching vibration of the benzene skeleton of quinone (N=Q=N) and benzene (N-B-N) rings in polyaniline; peaks observed around 1200 cm^{-1} to 1000 cm^{-1} were observed and can be identified in the DBSA spectra as shown in **Figure 4** (b), which could be contributed to the S=O stretching vibration shifting, which is a doping bond; peaks around 990 cm^{-1} and 910 cm^{-1} were the absorption of =C-H bend vibration in DVB monomer; peaks around 800 cm^{-1} to 700 cm^{-1} corresponded to C-H of ortho-disubstituted and meta-disubstituted benzene rings, which were abundant in the PDD-ph-4 due to the phenol product structure.

By comparing PDD and PDD-ph-4 spectra we can easily identify the difference due to the adding of phenol. A broad, but weak, peak at 3522 cm^{-1} and a medium peak at 1238 cm^{-1} could be observed in the uncured PDD-ph-4 spectra, which corresponded to the O-H stretching vibration and bending vibration of phenol, respectively. The same broad peak could be observed in the cured PDD-ph-4 spectra, which indicates the existence of -OH groups after curing.



(a) FT-IR spectra for uncured/cured PDD and PDD-ph-4 specimens



(b) FT-IR spectra for semi-doped PANI/DBSA and pure DBSA specimens

Figure 4. FT-IR of composite specimens and raw materials.

3.3 Electrical Conductivity

The electrical conductivity value of the composites is shown in **Figure 5**. Almost 2700 % improvement in the electrical conductivity of the composite with the same content of conductive filler (30 wt. % DBSA-PANI) is achieved with the addition of phenol. This range of electrical conductivity was reported with the 50 wt. % of DBSA-PANI and 50 wt. % DVB in the literature [25,34,35]. Therefore, we can infer that a unique combination of phenol-resin is highly efficient for better electrical properties. With increased electrical conductivity at the same PANI content, we can have an extra amount of structural component (i.e. resin) to increase the mechanical properties of the composites for practical structural applications of electrically-conductive composites. The combination of high electrical conductivity as well as mechanical properties is in high demand in order to maximize the potential multi-functionalities of electrically-conductive composites.

It is known that the β-carbon of DVB has a high proton affinity compared to polyaniline and hence causes the de-doping of PANI. In phenol-DVB resin, the β-carbon of DVB is utilized to initiate phenol-DVB cationic polymerization as explained in **Figure 2**. High electrical conductivity in this system can be attributed to the change in the structure of the polymer. The proton-subtracting species of DVB,

reacted first with phenol, drastically reduces the presence of these proton-subtracting sites. In the absence of proton-subtracting species, PANI retained its electrical conductivity by avoiding de-doping. It should be noted that the authors used only 30 wt. % of DBSA-PANI, but were still able to achieve the same level of electrical conductivity which was only possible with 50 wt.% of DBSA-PANI in the case of pure DVB resin [8,35,36].

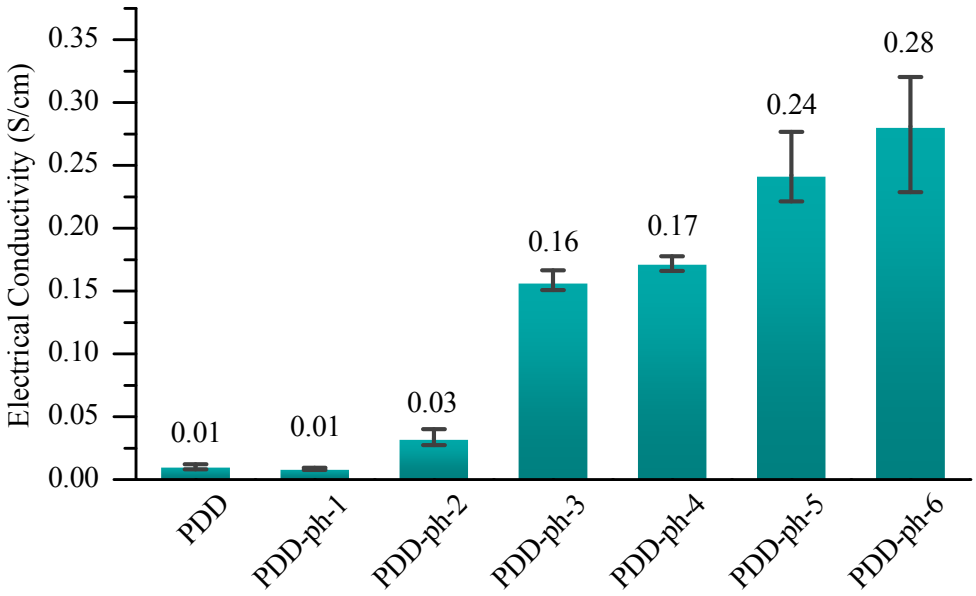


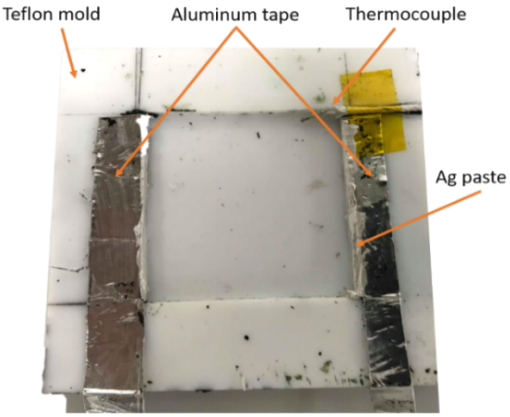
Figure 5. The electrical conductivity of phenol-DVB resin with respect to the various content of phenol.

3.4 In-situ electrical conductivity measurement

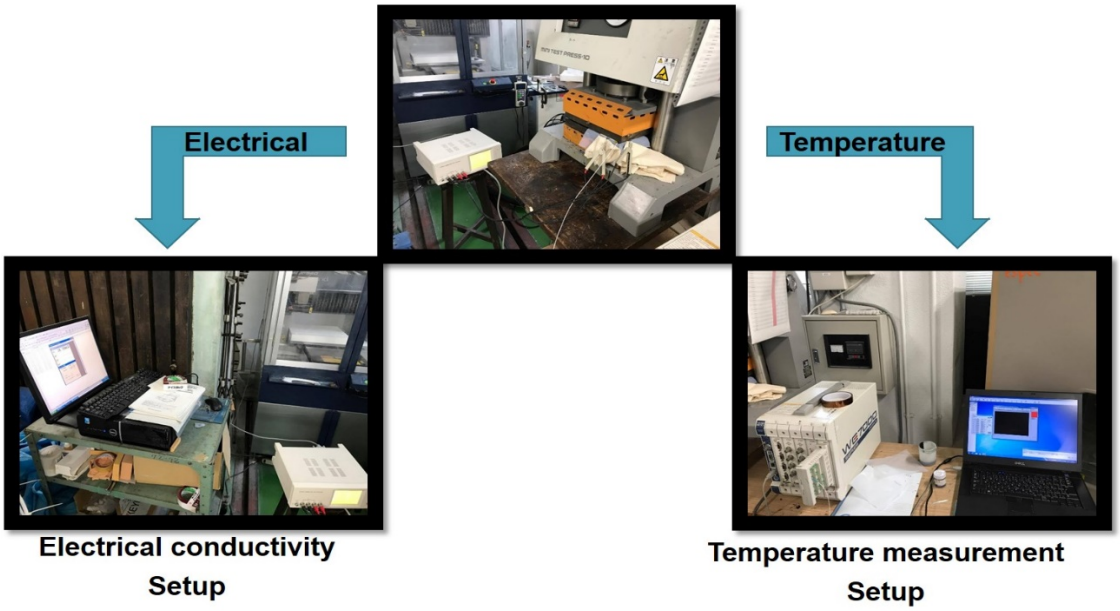
An innovative technique was utilized to measure the in-situ electrical conductivity of the composite during the transition from its uncured state to a fully cured state. The uncured resin was poured into a mould, which is attached to conductive aluminium tape at two opposite ends as shown in **Figure 6**. To reduce contact resistance between resin and aluminium electrode, electrically-conductive silver adhesive was applied to the tape, i.e. on the measuring sides. It is also important to understand that silver adhesive should be in a semi-dried state to minimize contact resistance with increasing temperature. Resistance measurement setup was connected to the computer and resistance was recorded using Hioki LCR software. Simultaneously, the temperature of the specimen was also measured using a thermocouple connected to the WE7000 data logger equipment. The specimen was inserted between

two hot-plates of the hot press. Proper electrical insulation was provided by applying Teflon sheets between the specimen and the hot press plates. The temperature was raised to 130°C at the rate of 10°C/minute and then kept for 5000 s.

For in-situ electrical conductivity measurement, 50 wt. % of DBSA-PANI was added to two specimens: Phenol-DVB and DVB resin. The in-situ electrical conductivity of both specimens was calculated using resistance recorded during curing profile and the dimensions of the mould. Results are shown in **Figure 7 (a)**. It was observed that the electrical conductivity of the composite suddenly increased almost six orders between 60-100°C. This perfectly matches with the doping temperature of PANI discussed in section 3.1.



(a)



(b)

Figure 6. (a) Specimen holder preparation (b) In-situ electrical conductivity measurement setup.

Reduction in the electrical conductivity with respect to time was observed in both cases. The reduction of electrical conductivity with curing time can be assigned to the de-doping of PANI. However, the rate of de-doping in the case of phenol-DVB, was significantly lower compared to the rate of de-doping in only DVB case. This further emphasizes our hypothesis that the phenol-DVB structure helps reduce de-doping of polyaniline.

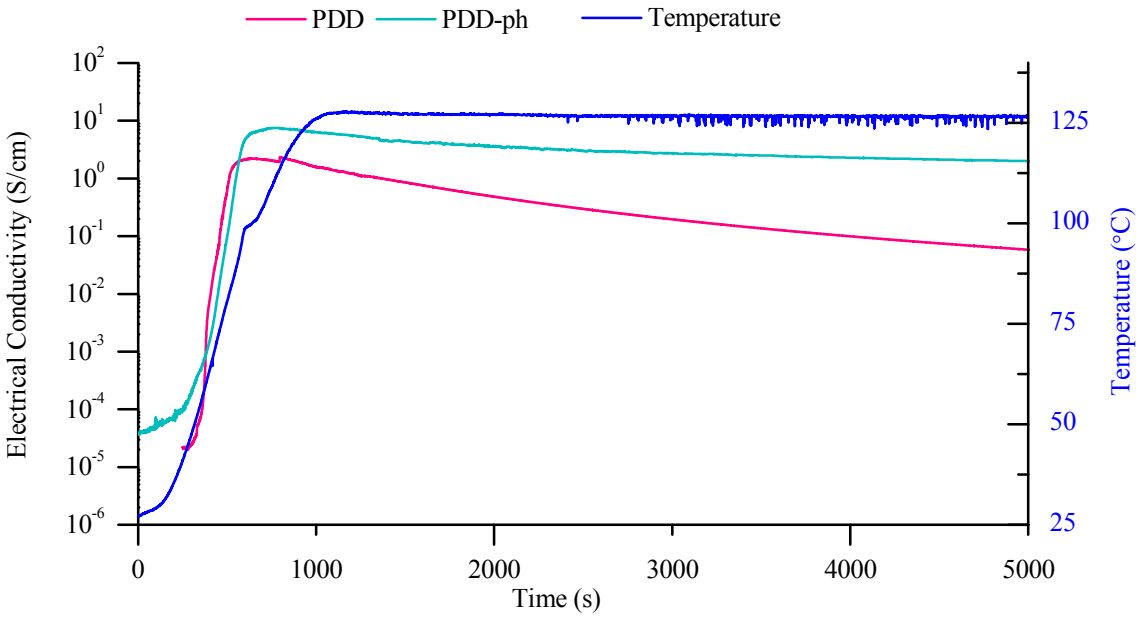


Figure 7 (a). Change in in-situ electrical conductivity of PDD and PDD-ph resin with respect to curing time.

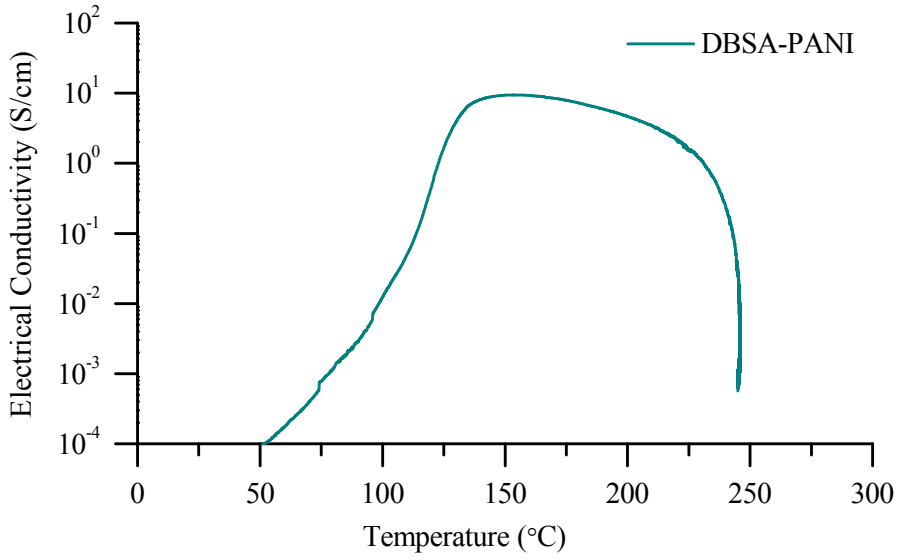


Figure 7 (b). In-situ electrical conductivity of DBSA-PANI as function of temperature.

Electrical conductivity of a pure DBSA-PANI complex, with respect to temperature, from room temperature to 250 °C is shown in **Figure 7(b)**. The temperature change rate was 10 °C/min. The highest electrical conductivity is observed between 120°C and 230 °C. Literature suggests that polyaniline can be made electrically conductive by many techniques; however, thermal doping is one of the easiest ways to make PANI electrically conductive by doping in the presence of a protonic acid. Thermal DBSA-PANI doping is an acid-base reaction between the acid ends of DBSA with base sites of polyaniline (amine and imine) [37]. With increased temperature, positively charged PANI chains are driven away from each other by electrostatic repulsion. It is postulated that the complete doping temperature can change depending on the agglomerate size and dispersion state of PANI. It is also postulated that alkyl side groups (from protonic acids) are reversibly substituted on the PANI backbone through Coulombic attraction [24]. Once all the available sites of substitution are filled, the thermal doping process stops. This could be the reason, why electrical conductivity first increased up to 120°C and then starts decreasing due to deprotonation or decomposition of electronic chains of PANI. The sudden drop in electrical conductivity after 230°C can be assigned to the degradation of DBSA and degradation of the electronic chain of PANI. Such continuous electrical conductivity of DBSA-PANI with respect to temperature is reported for the first time.

3.5 UV-vis spectroscopy

UV-vis spectroscopy is a very useful methodology to study the electronic structure of PANI. To understand the different de-doping process in both ~~the~~ cases, we also performed the UV-vis spectroscopy of PDD and PDD-ph resins with 50 wt. % of DBSA-PANI in them. Specimens were subjected to thermal treatment for 2 hr at 130°C. UV-vis spectra were taken after 0, 10 and 120 minutes. The UV-vis spectra obtained for resin PDD and with PDD-ph are shown in **Figure 8**. The UV-vis spectra of PDD and PDD-ph shows the characteristic peaks of the Emeraldine Salt (ES) form of PANI. One broader peak at around 830 nm and one shoulder-like peak at 430 nm can be observed in the plots. The free carrier tail is visible after 1000 nm in both specimens. Presence of a free carrier tail at 0 min is due to the semi-doped state of PANI, which is usually absent in an un-doped state of PANI.

The degree of doping of PANI can be determined by studying the joint peak of PANI and DBSA around 400-420 nm. The bifurcation of the joint peak at 400 nm corresponds to the detachment of DBSA from PANI. The overlapping of π-π* peaks at 350 nm and 420 nm, which represented PANI and DBSA respectively, indicates doping while their separation indicates de-doping. Formation of a distinct peak in PDD after a 2-hr thermal treatment clearly shows the de-doping of PANI. There is no such separation of the peak at 400 nm wavelength, in the case of PDD-ph specimen. This confirms that there is less de-doping of PANI in PDD-ph resin.

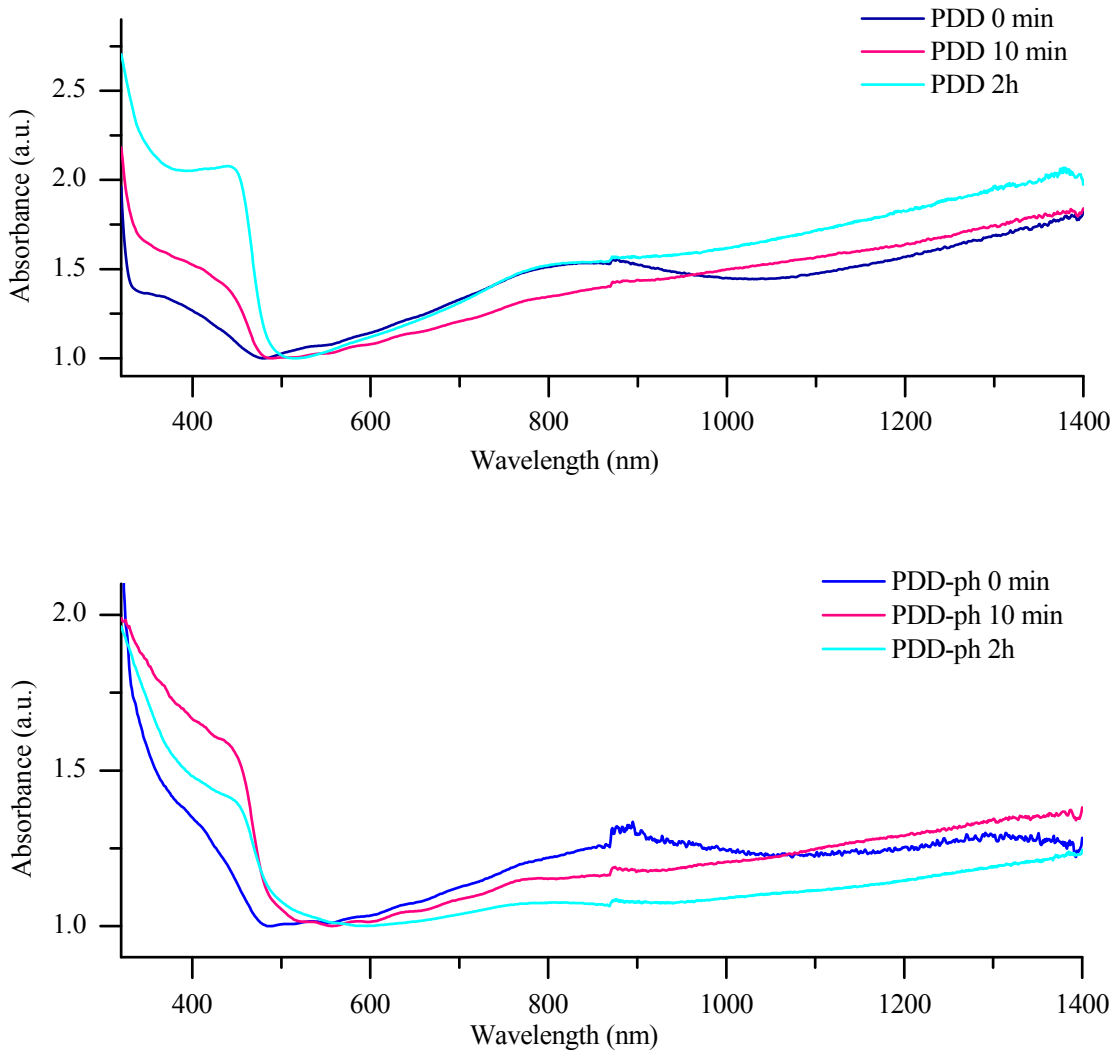


Figure 8. UV-vis spectra to check de-doping of PANI in DVB and phenol-DVB resin with respect to curing time.

3.6 Flexural Properties

Flexural properties of PDD-ph composites were investigated using a 3-point bending test, and the results are shown in **Figure 9**. Interestingly, flexural modulus increases, but strength decreases with increased phenol content into the composite. However, in the case of pure PDD, the flexural strength was low compared to PDD-ph-1. This could be due to the fact that the cationic polymerization of DVB is difficult to control; therefore, PDD specimens undergo fast exothermic reactions causing porosity in the specimens that lead to some defects. This eventually results in low flexural strength of pure PDD. However, with addition of just 10 wt. % phenol (PDD-Ph-1), the quality of the specimen improved significantly. With the addition of phenol, the rate of cationic polymerization of resin subsided, which led to a good quality of the final specimen. The attachment of the vinyl group of DVB to the activated site of the phenol enables the curing to proceed without gas formation, which helps to avoid porosity. The flexural modulus increased from 1.79 GPa to a maximum of 2.15 GPa with the addition of phenol in DVB. This increased modulus can be attributed to the complete curing of the resin in the absence of scavenging of DVB polymerization.

On the other hand, flexural strength was found to be decreasing with the reducing DVB content. This suggests that the cross-linking polymer DVB is very effective for enhancing the strength of phenol resin. It can be concluded that complete curing of resin resulted in improving the flexural modulus of the composite, but it also increased the brittleness. Nevertheless, optimum mechanical properties seem to have been achieved in the cases of PDD-ph-3 and PDD-ph-4 specimens.

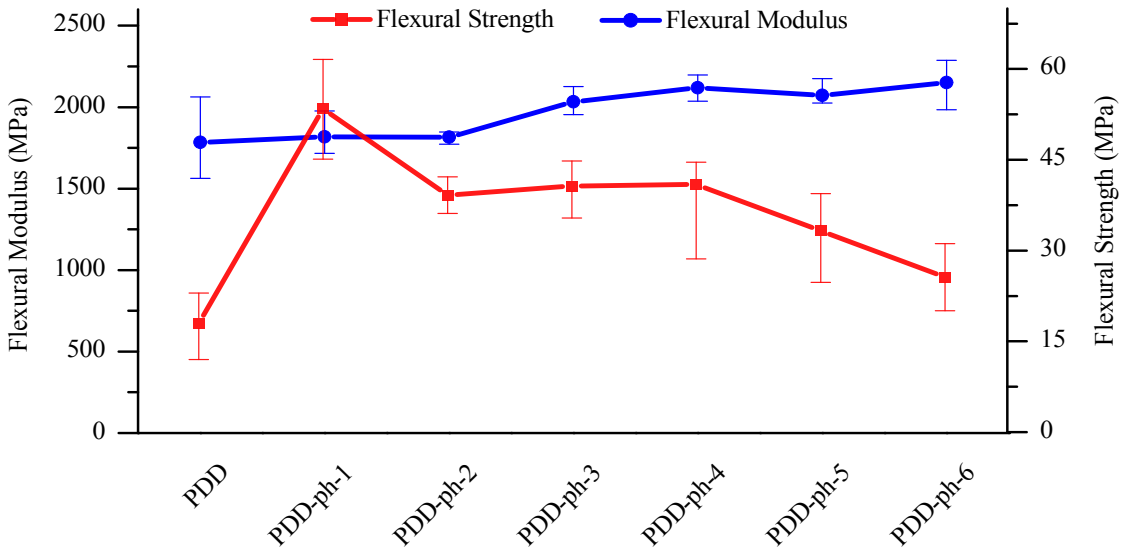


Figure 9. Flexural properties of PDD-ph composites with respect to phenol content.

3.7 Morphology of the composite

Scanning electron microscopy (SEM) was employed to study the morphology of the composites. The specimens were observed without platinum coating due to the conductive property of PANI, as shown in **Figure 10** (a), (b) and (c). For conventional SEM observation, nonconductive materials should be coated with an ultrathin coating containing conducting metals to prevent the charge problem [38]. However, a highlighted phenomenon was observed during the experiment, demonstrated by an electrical charge problem on the specimen surface when using a relatively high electrical voltage. Interestingly, as shown in the figure, the highlighted area expanded with the increasing phenol-to-DVB ratio, from which it can be concluded that the highlighted areas correspond to tiny nonconductive phenol agglomerates.

To better explain the conclusion of the SEM photographs, the element mapping performed by EDS was utilized to study the dispersion of polyaniline. Through analyzing the components of raw materials, nitrogen could only be found in polyaniline molecular chains. Therefore, the N mapping via EDS was performed and the results are shown in **Figure 10** (d), (e) and (f). Good dispersion of N can be observed in graphs (d) and (e), which indicate the well-dispersed polyaniline. The dispersion of polyaniline was also found not varying with the change of phenol content. Nevertheless, it is easy to see that there were still some blank spaces without N in graph (f), which interestingly corresponds to the highlighted area in graph (c). It can be concluded that the polyaniline is well dispersed in phenol-DVB resin.

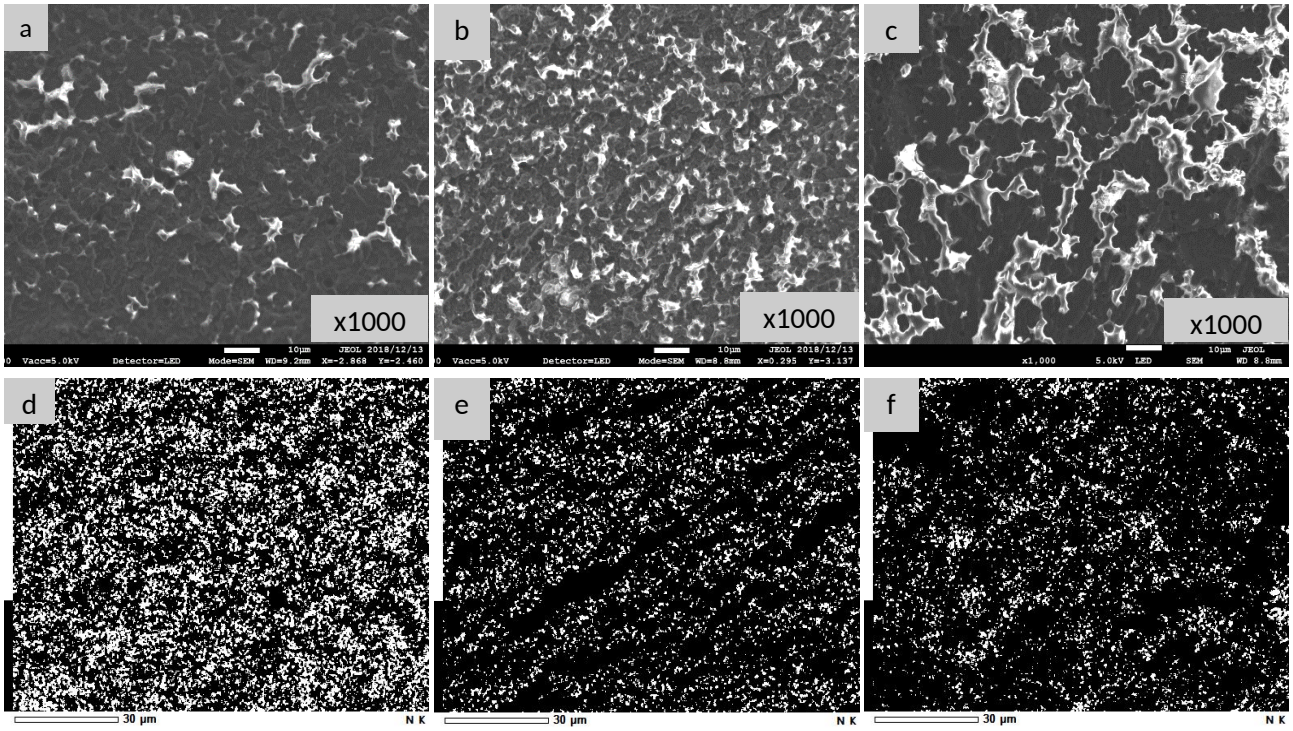


Figure 10. (a), (b) and (c) are SEM micrographs of PDD-ph-2, PDD-ph-4 and PDD-ph-6 respectively.(d), (e) and (f) are the corresponding EDS element mapping for N at the identical areas of (a), (b) and (c), respectively.

3.8 Rheological Properties

One of the primary potential uses of this resin system is for it to function as an electrically-conductive matrix of CFRP for lightning strike protection application. Therefore, proper impregnation of carbon fibers should be kept in mind while designing such a resin system. The phenol used in this work is in the form of yellowish solid flakes and the DVB is a low molecular weight (liquid) monomer. The mixture of phenol and DVB is a wax-like complex initially, but over an extended time period it changes to the more viscous form of phenol (solid) at room temperature. Therefore, it was observed that the viscosity of PDD-ph increased with the higher content of phenol in the mixture as shown in **Figure 11**. Viscosity in the case of PDD-ph-6 was measured at 0.5 RPM. Rotational speed of 10 RPM was used to measure the viscosity in all the other cases. Rotational speeds were chosen according to the maximum viscosity limit defined by the manufacturer at specific rotational speeds. Even at 0.5 RPM speed, the torque on the spindle reached to the 70 % of the allowable torque, hence the measurement was stopped mid-way in case of PDD-ph-5 and PDD-ph-6. Manufacturability of the composites became more difficult at higher loading of phenol. Therefore, from the analysis of rheological, electrical, and mechanical

properties, PDD-ph-3 and PDD-ph-4 seem to be excellent options to be used for impregnation of carbon fibers.

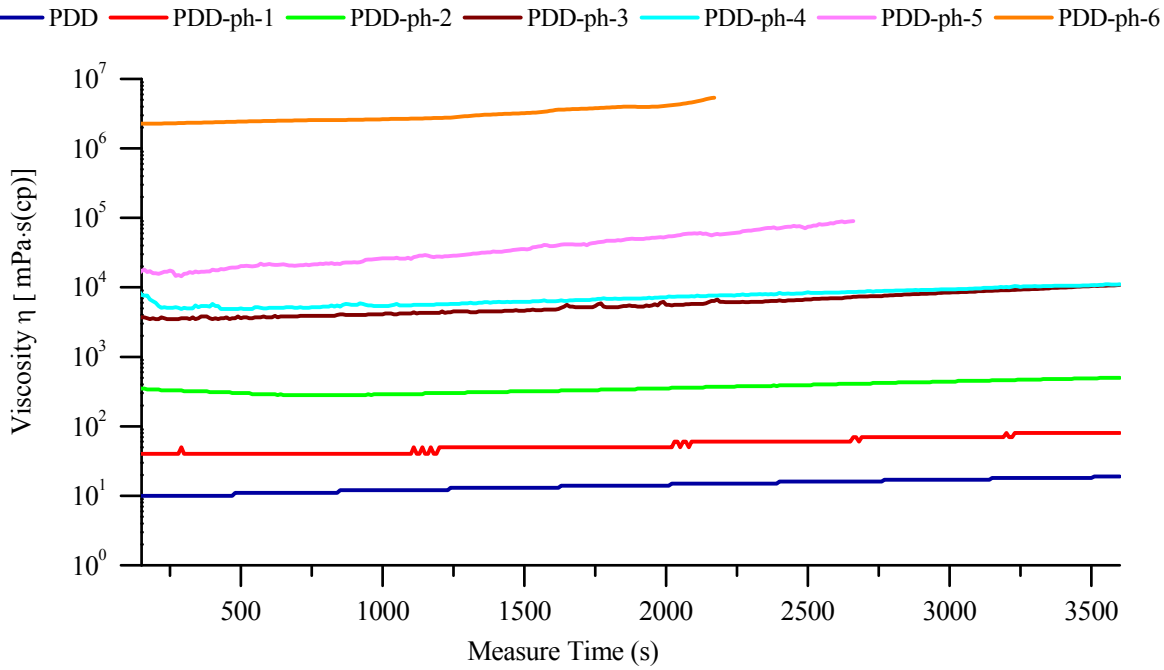


Figure 11. Rheological properties of PDD-ph composites with respect to phenol content.

4. Conclusion

A phenol-DVB complex was synthesized to be cured in the presence of semi-doped PANI. PANI was semi-doped with a protonic acid, i.e. dodecylbenzene sulfonic acid. Curing of phenol-DVB resin and complete doping of polyaniline was carried out using a single thermal treatment without any additional catalyst. It was found that due to the formation of a new structure between phenol and DVB, there are fewer number of proton-subtracting species in the system, which causes de-doping. The addition of phenol in DVB improves the electrical conductivity and flexural modulus of the material. An innovative method was utilized to measure the in-situ electrical conductivity of the composite with and without phenol. It is shown that the rate of de-doping is significantly high in the case of DVB-only resin. The reduced de-doping of the PANI is also corroborated by UV-vis spectroscopy. A good dispersion of polyaniline was observed using SEM and EDS element mapping. Optimal material composition, prepared with 30 wt. % DBSA-PANI and 70 wt. % of phenol-DVB, resulted in the achievement of electrical conductivity of 0.20 S/cm and a flexural modulus of 2.1 GPa as well as viscosity of 3600

mPa.s. There is a high potential that an electrically-conductive adhesive layer or conductive CFRPs with better mechanical properties can be prepared using this newly developed resin system.

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