



## Improvements in Essential Electrical and Physical Properties of Phenol Formaldehyde Resin by Incorporation of Modified Coal Tar Pitch

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**Abstract:** Phenol-formaldehyde (PF) resin is used here for making thermosetting composites along with environmentally friendly coal tar pitch(CTP). These PF-CTP composites are made with dual objectives of using environment-friendly CTP to improve the electrical and physical properties of PF resin and to reduce cost of PF resin for final applications. The composites are prepared by a two-step method using standard compression molding technique.

Comparing the properties of the samples containing varying amount of CTP with pure PF resin as the reference sample, significant improvements in electrical properties like surface resistivity, volume resistivity and dielectric strength are observed with the increase in amount of CTP. The waterproofing tendency also improved as the amount of CTP is increased. The best properties are observed for the thermosetting composition with 40 phr of CTP.

### Introduction

The phenol-formaldehyde resins(PF resins) represents one of the oldest class of polymers. Their advantage include very low manufacturing costs, excellent chemical and thermal stability, favourable combustion behaviour, fire retardance and low toxicity of combustion products [1-3]. PF resins are high value products, particularly because of their resistance to hydrolysis [4].

These are widely used as molding powders, impregnating resins, casting resins, binders, impregnants in surface coatings and in adhesives [5]. They are mainly used as thermosets and also as electrical insulating materials in various electrical applications. The chemical structure of phenolic resins is very complex. Phenolic resins are classified as resoles and novolacs, based on the synthetic conditions. The novolac resins require a crosslinking agent for its curing in contrast to resoles which are cured thermally. The properties of the final product are dependent on various parameters like choice of material, curing method, processing technology etc. [6].

Here it may be noted that for desired performance, the resin needs to be modified because unmodified phenolic resin lack in various properties which limits its applications. Much research has been conducted to improve the properties of phenolic resin by structural modifications as well as by making compositions [7]. In

order to improve the electrical and physical properties of PF resin, coal tar pitch(CTP) which has been modified to reduce its carcinogenic contents [8], is used as filler in making thermosetting compositions.

CTP is the residue produced by distillation of coal tar [9,10]. Some of the polycyclic aromatic hydrocarbons(PAHs) present in the CTP have been found to be carcinogenic or mutagenic [11-19]. Benzo(a)Pyrene[B(a)P] is one of the strongest carcinogens among various PAHs [20-21]. Thus genuine efforts have been made for using CTP in which B(a)P is reduced by different methods for various value added applications.

In the present work, the attempt has been made to study the possibility of using environmental-friendly CTP, which is a thermoplastic material [22-24] as one of the components of some known polymeric composites which are thermosets.

The process adopted for the present work included the blending of modified pitch with PF resin to improve properties of PF resin. In this study, firstly, a fusible thermosetting composition is prepared by heating CTP with PF resin together at 130°C for two hours. This fusible composition is cooled and dried. After drying it is crushed and sieved so as to mix it properly with cross-linking agent to make the thermosetting composition by compression molding technique [25]. This also results in the reduction of the cost of PF resin when it is used alone in similar applications. The thermosetting sheets prepared by varying quantity of CTP in the blend are studied for physical and electrical properties.

## Results and Discussion

The various PF-CTP composites (Table 1) are evaluated for water absorption, dielectric strength, volume and surface resistivity, the results of which are shown in Figure 1-4. These composites are also tested for glow-wire test and the results are shown in Table 2.

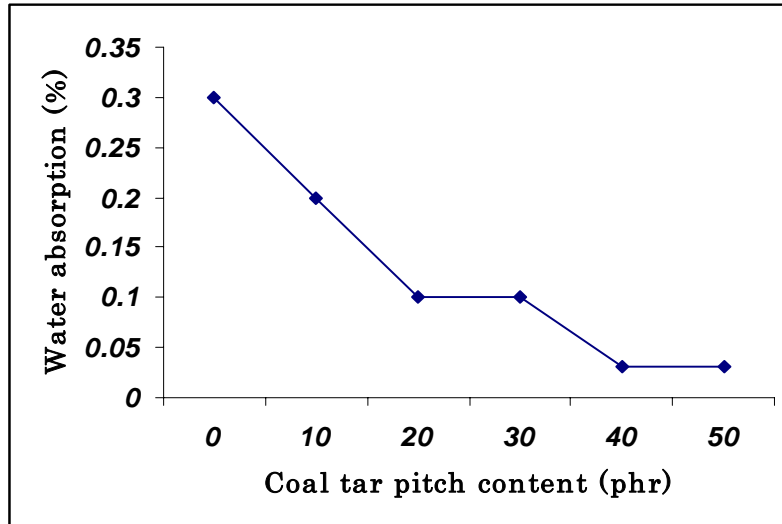
**Tab. 1.** Various compositions of PF-CTP composites.

S.No.	Materials Ratio PF:CTP	Weight of PF resin (g)	Weight of CTP (g)	Weight of Hexamine (g)
1	100:0	100	0	10
2	100:10	100	10	10
3	100:20	100	20	10
4	100:30	100	30	10
5	100:40	100	40	10
6	100:50	100	50	10

### *Effect of CTP on Water Absorption*

CTP is used in water proofing applications because of its water resisting properties which arises due to the presence of non-polar groups in it. As seen from Figure 1, it is observed that as the CTP content increases from 0 to 50 phr in PF-CTP composites, the water absorption decreases from 0.3 % to 0.03 %. Thus, 90 % reduction in water absorption is observed for the composite where 50 phr of CTP is present. Thus water resisting property of CTP has significantly enhanced the water

resisting property of PF resin. Water absorption behavior of the composites is one of the important criteria for the evaluation and selection of components, especially, those meant for electrical applications. Thus, the composites of PF-CTP are transformed in the form of sheets that can be effectively used for waterproofing applications. Thus, the composites have become impervious in nature.



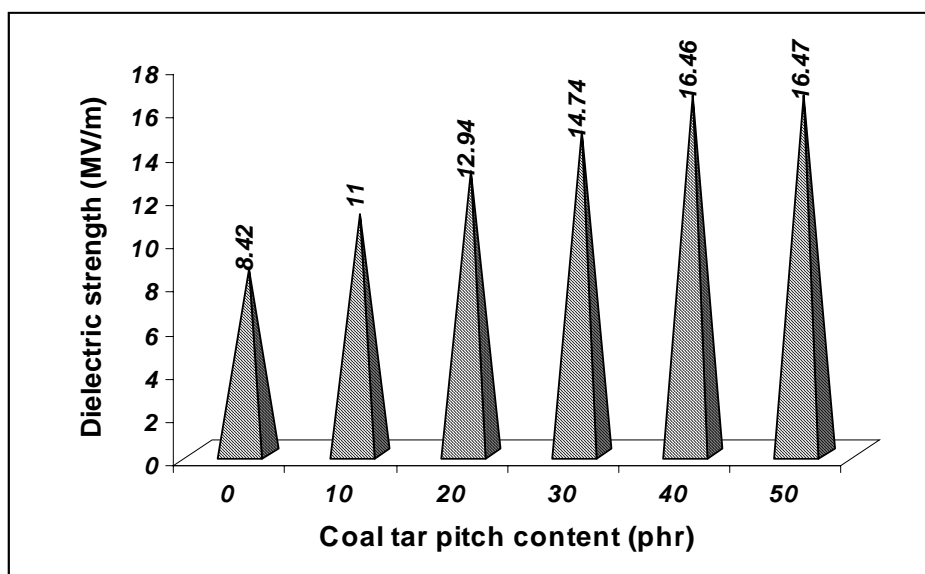
**Fig. 1.** Effect of CTP content on water absorption of PF-CTP composites.

#### *Effect of CTP on Electrical Properties*

Results of different electrical properties are described below:

##### *-Dielectric Strength*

As seen from Figure 2, the dielectric strength of the composite material has increased significantly as the CTP content increases.

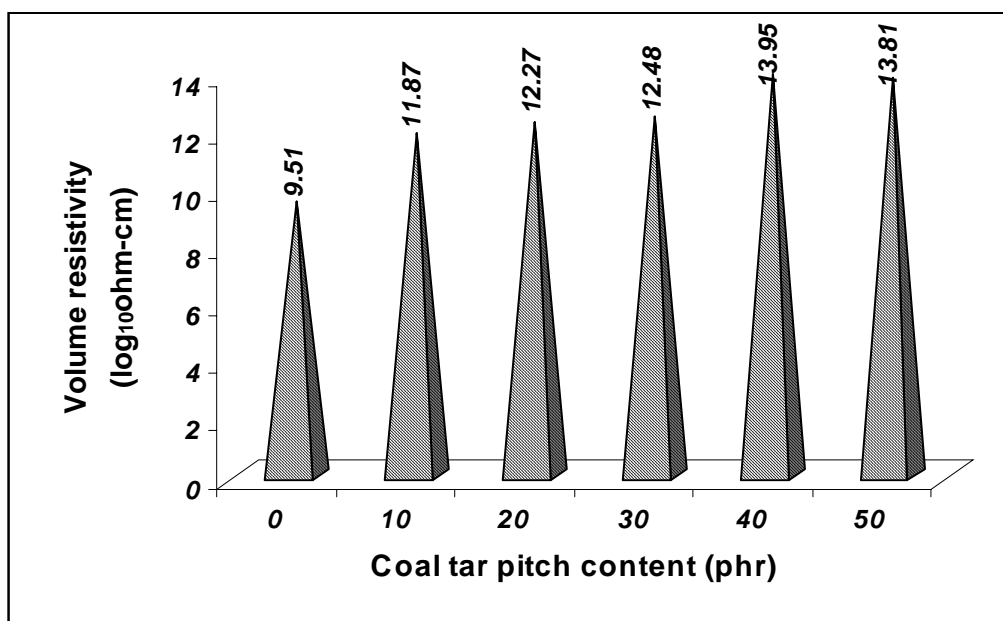


**Fig. 2.** Effect of CTP content on dielectric strength of PF-CTP composites.

The increase in value is from 8.42 MV/m for reference sample which is actually PF cross-linked with hexamethylenetetramine, to 16.46 MV/m for the composition in which 40 phr CTP is added i.e. almost 100% rise in dielectric strength on addition of CTP is observed. On further increasing the CTP content to 50 phr the dielectric strength remained almost same i.e. 16.47 MV/m.

#### -Volume Resistivity

It can be clearly seen from Figure 3 that volume resistivity values increase from 9.51 (in units  $\log_{10}\text{ohm-cm}$ ) for reference sample to 13.95 (in units  $\log_{10}\text{ohm-cm}$ ) for a sample in which 40 phr of pitch is added. However, beyond CTP content of 40 phr, the composite does not show any further increase in volume resistivity.

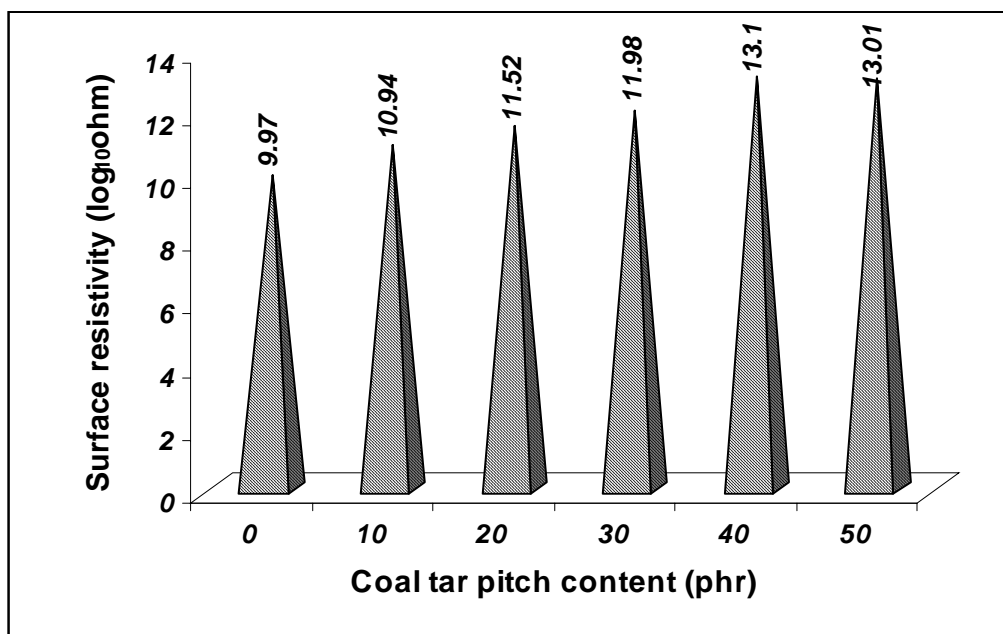


**Fig. 3.** Effect of CTP content on volume resistivity of PF-CTP composites.

#### -Surface Resistivity

The trend in values of surface resistivity of the composites is depicted in Figure 4, where it is seen that surface resistivity improved gradually from 9.97 (in units  $\log_{10}\text{ohm}$ ) for reference sample to 13.10 (in units  $\log_{10}\text{ohm}$ ) for the composition in which 40 phr of CTP is added. But once the CTP content is raised beyond 40 phr there is no further increase in surface resistivity. The major factor affecting surface resistivity is humidity i.e. formation of continuous film of moisture on the surface of insulator. The presence of PAHs (nonpolar) in the CTP provides resistance to the formation of a continuous film on a clean surface. Hence, as content of CTP which is water resisting in nature increases, surface resistivity also increases.

Volume and surface resistivity measurements are often used to check the uniformity of an insulating material, either to determine the uniformity of processing or to detect trace impurities which affect quality of the material. Lesser the imperfections, the better insulator the material is; so in our case the increase in value of resistivity shows the perfection of the composite material formed as CTP content increased.



**Fig. 4.** Effect of CTP content on surface resistivity of PF-CTP composites.

#### -Glow-Wire Test

It can be seen from Table 2 that the PF-CTP composites prepared withstand the glow-wire test. No flames and glowing are observed in the reference sample as well as the composites. Only slight fumes are visible when the CTP content is raised beyond 20 phr till 50 phr, indicating that the composite formed are highly electrically stable.

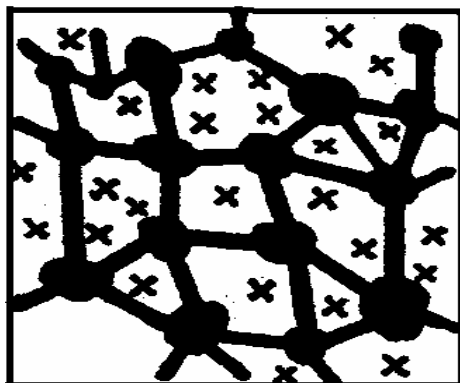
**Tab. 2.** Results of Glow-wire test of PF-CTP composites.

S.No.	Materials Ratio PF:CTP	Observations
1	100:0	No glowing, No fumes, No flame
2	100:10	No glowing, No fumes, No flame
3	100:20	No glowing, No fumes, No flame
4	100:30	No glowing, Slight fumes, No flame
5	100:40	No glowing, Slight fumes, No flame
6	100:50	No glowing, Slight fumes, No flame

The improvement in electrical properties of PF resin can be explained by the entrapment of CTP in the voids of interlocked chain formed due to cross-linking in the PF resin. The mechanism which can effectively explain the properties of CTP-PF composites is shown in Figure 5 which shows that the cross-linking takes place between PF molecules leading to a structure which, according to Houwink, can be equated to a sponge and is termed an isogel. In these voids of sponge CTP is entrapped. Similar work has also been explained by Robitschek and Lewin [26].

The study of morphology and other properties of these composites have been well explained in a separate study carried out by the authors where they have shown that there has been no deterioration of mechanical properties of PF resin due to addition

of CTP[27]. On comparing these values with that of the minimum requirements for the phenolic molding compounds for electrical applications it is found that these are much higher than the requirements as is given in ASTM D700. CTP molecules are entrapped in the lattices of this crosslinked structure.



**X** = CTP                      ● = PF resin

**Fig. 5.** The possible structure of CTP-PF.

Due to the non-conductive nature of CTP and also due to the insulating nature of PF resin, the composite of PF-CTP showed enhancement of electrical properties of PF resin and the sheets made from them can be used for electrical purposes like in switch boards, insulating casing etc.

## Experimental Part

### Materials

Modified CTP [8] (having Softening Point of 118.3°C, Coking Value of 53.9 %, Toluene Insolubles content as 43.1 % and Quinoline Insoluble content as 13.7 %) was used for the study. PF resin(Novolac grade) with gel time of 70 s & density of 1.5 g/cm<sup>3</sup> was obtained from the Cosmos International, India. The cross-linking agent i.e. hexamethylenetetramine used in the compositions was obtained from s.d.fine-Chemicals Ltd, India.

### Apparatus/Instruments used

Santec compression molding machine of 30 ton capacity procured from Santec House, Pitampura, Delhi, India.

Elite Mixer procured from Elite, India.

AC High voltage test set procured from Rectifiers & Electronics, Delhi, India with 100kV capacity is used for evaluating dielectric strength.

Million Meghommeter(IE make) bearing model no.MMO-20H was used for testing surface and volume resistivity.

Ammeter Glow wire tester(0-200 amps) from Sensors, India was used for carrying out glow-wire test.

## Methodology

### -Preparation of composites

The PF-CTP composites were prepared by a two-step procedure. In first step, the mixture with various ratios of PF resin & modified CTP was heated at 130°C with constant stirring for two hours and poured hot once the blending is complete.

This fusible thermosetting composition was cooled to ambient temperature and crushed to obtain homogeneous powder. This powder was homogenized in mixer along with the cross-linking agent i.e. hexamethylenetetramine [10 %(W/W) of PF resin] followed by sieving it through sieve of 300µm. Almost all the material passed through 300µm sieve.

This sieved powder was used for preparing the thermosetting sheets using compression molding technique at a temperature of 160°C and pressure of 21 MPa.

### Analysis

In order to investigate the effect of addition of varying amount of CTP to the PF resin on the physical and electrical properties, the samples were evaluated in triplicate. The results were found consistent and repeatable. Following are the details of the studies conducted for the present work.

### -Physical Property

#### *Water Absorption Test*

This test was carried out by following ASTM-D570. The specimens were precut as per specification and kept in oven at 50°C for 24 hrs. After this they were cooled in desiccator and soaked in cold water for 24 hrs at a temperature of 23 ± 2°C and relative humidity 55 ± 5%. Percent water absorption was calculated by following equation:

$$\% \text{ water absorption} = \frac{\text{Wet wt.} - \text{Dry wt.}}{\text{Dry wt.}} \times 100$$

Dry wt. = dry weight of the specimen,

Wet wt. = wet weight of the specimen after soaking 24hrs in cold water

### -Electrical Properties

#### *Dielectric Strength*

Test was conducted as per ASTM:D149-94. This test method covered procedure for determination of dielectric strength of solid insulating materials at commercial frequencies under specified conditions. The specimen with smooth surface of sufficient size to prevent flashover was used under the condition of test. Test specimen was conditioned according to procedure mentioned in D618.

Voltage was applied uniformly to the test electrodes from zero at the rate of 500 V/s until breakdown occurs. In nearly all cases the actual thickness of the test specimen was important. Thickness of the specimen after the test in the vicinity of the area of

breakdown is measured. Measurement is made at room temperature ( $25 \pm 5^\circ\text{C}$ ), using the appropriate procedure of test method D374.

The dielectric strength in kV/mm or MV/m at breakdown is calculated by the formula

$$\text{Dielectric strength} = \frac{\text{Dielectric Breakdown Voltage (kV)}}{\text{Thickness of sample (mm)}}$$

#### *Surface and Volume Resistivity*

Test was conducted as per ASTM:D257-93. This test method covered direct-current procedure for the determination of dc volume resistivity and surface resistivity. Specimens in form of circular discs with absolutely smooth surface were prepared by compression molding technique. Mercury metal electrode was used for the test. The specimens were conditioned in accordance with method D618.

Time of electrification for both surface and volume resistivity was 60s and the direct applied voltage is  $500 \pm 5\text{V}$ . Measurement is done with a suitable device having the required sensitivity and accuracy. Calculations are carried out using following formulas:

$$\text{Volume resistivity} = \rho_v = AR_v / t$$

where  $\rho_v$  = Measured volume resistance in ohms  
 $A$  = The effective area of measuring electrode for the particular arrangement employed  
 $t$  = Average thickness of the specimen  
 $A = \pi(D_1 + g)^2 / 4$

$$\text{Surface resistivity} = \Omega(\text{per square}) = P_s = P.R_s / g$$

where  $P = \pi D_0$   
 $R_s$  = measured surface resistance in ohms

#### *Glow Wire Test*

This test was carried out as per IEC Pub 695-2-1(1980). The suitable test specimen was cut from the sample. The glow-wire consisting of a loop of nickel/chromium (80/20) wire with 4mm diameter was connected with a thermocouple. This was electrically heated between 120-150A for 60s so as to maintain a temperature of  $650^\circ\text{C}$  and kept in horizontal plane. The tip of the glow wire was then brought into contact with the specimen for  $30 \pm 1$  s. After this period, they were separated and observation is recorded.

### **Conclusions**

From the study it has been established that it is possible to improve the electrical and physical properties of PF resin by processing it with CTP, which is a thermoplastic material to prepare thermosetting composites. Moreover, CTP even when it is used as filler can reduce the cost of PF resin. PF-CTP sheets prepared would be a preferred material with good insulating property and minimum water absorption. In fact, the PF-CTP composites will exhibit better properties than the PF resin alone. Thus, a novel method has been developed to prepare thermosetting compositions of PF resin with CTP that is modified by various methods to reduce its carcinogenic content.



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