Preparation of Phenolic Resin Complexes

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Date of acceptance 5/6/2005

Summary:

In this work, three types of complexed phenolic resins were prepared using various additives such as ($AlCl_3$, $FeCl_3$, $ZnCl_2$) and improving the aim of this work by modifying the phenol formaldehyde resins to high thermal resistance polymers and higher mechanical properties. This was attributed to chemical bonding between metal ions and polymeric phenol formaldehyde resins, the increasing in crosslinking which effects on thermal and mechanical properties of phenolic complexes as a function of temperature up to 1000 °C, the complexes could be used as insulators.

The complexes were characterized and tested by infra-red spectroscopy, thermogravimetry and mechanical properties for the phenolic resin complexes were measured the tensile strength, flexural strength, they were found that the higher thermal resistance and higher mechanical properties, therefore it was concluded that the phenolic complexes could be possibly used as insulation material and for other applications.

Introduction:

Phenols and oligomeric phenol compounds are weak acids and are able to form metal salts or complexes with metal ions. The reaction with Fe^{+3} ions, has been studied for analytical purposes with oligo (2-hydroxy-1,3-phenylene-methylene) (1).

The ability of p-tert-butyl alixarenes to transport metal ions through hydrophobic liquid membranes were reported by Izatt and coworkers (2).

Heat and flame resistant resins are obtained by the reaction of phenols and phenolic resins with metal halides (molybdenum trichloride, titanium trichloride, zirconium trichloride, tungsten trichloride), metal alcohols (aluminum trimethoxide, titanium tetramethoxide) or metal organic compounds (acetylacetones) (3). If such metal containing resins are subjected to high temperature, the decompose considerably slower than conventional resins.

Further, it is assumed that metal carbides are formed complexes with carbon atom of the resin. The resins are deeply coloured and may contain up to 20% of ionic bond metals.

Otherwise (4), titanium tetrachloride is added to molten phenol, and the hydrogen chloride which is formed to remove by passing nitrogen through and raising the temperature up to the boiling point of phenol.

The esterification (5) of phenol novolak resins with inorganic polybasic such as phosphoric and boric acid or the reaction with phosphorus oxyhalides are a particular importance in increasing the heat or flame resistance of phenolic resins, because of high OH-functionality of novolaks.

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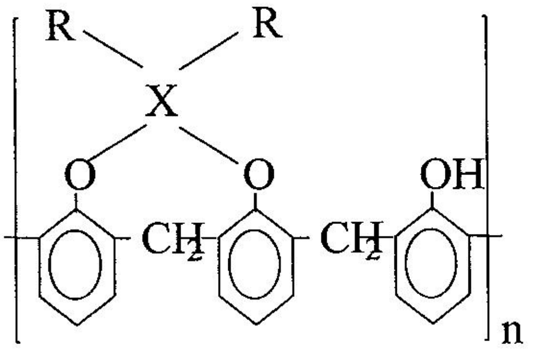
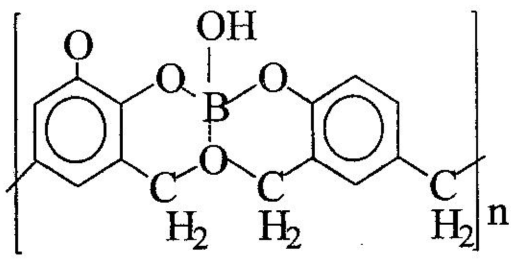


Scheme (1)

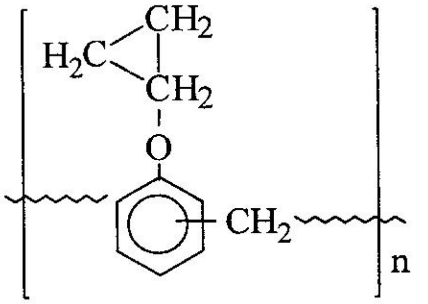
The intermolecular (crosslinking) reaction takes place predominately with ortho-novolaks, the intermolecular esterification [(6)] seems to be the preferred reaction yielding 8-membered rings as in scheme (1).

The increasing thermal resistance of phenolic resins, which modified with boron [(7)] is attributed to a structure as in scheme (2).



Scheme (2)

The addition of silicon compounds [(8)] for the improvement of the thermal resistance of phenol formaldehyde resin was recommended early, since then a series of HMTA to crosslink resins if the release of volatile compounds must be avoided epoxidized novolaks which are generally utilized as solid resins, these materials are readily obtained by the reaction of epichlorohydrine with novolak of sufficiently high M.W. as in scheme (3).

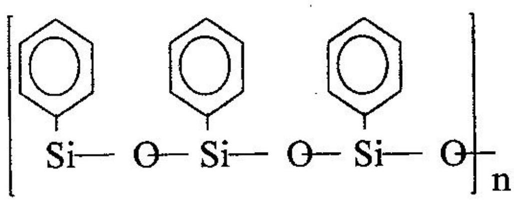


Scheme (3)

Phenolic composite [(9)] is that material which consists essentially of a thermosetting phenol formaldehyde resin as a binder matrix.

Amino phenols were allowed to react with maleic and phthalic anhydride [(10)] then the amic acid were dehydrated to the corresponding maleisomides and noval phenol formaldehyde resins, novolak like were prepared at 50 °C suffered rearrangement to corresponding phenol formaldehyde resins with pendant imide groups [(7)].

The reaction between phenol novolaks and methoxy phenyl poly silicoxanes as in scheme (4).



Scheme (4)

The incorporation of silicon atoms in the polymer chain instead of the methylene linkage is obtained by reaction of p-silyl phenols, which are available by hydrolysis of phenoxy silicones with formaldehyde [(8)].

The addition of silanes as adhesion promoters is widespread, for instance in the manufacturing of mineral wool mats, foundry sands, silicamicrosphere composites [(9)]. The added quantities are, however, very small, mostly far bellow 1%, so that such resins can not be designated as silicon-modified resins. Amino-functional silanes are preferred, for instance, y-amino propyl trimethoxy silane, less frequently epoxy functional type-like glycidoxy propyl triethoxy silane [11].

Experimental:

❖ **Materials:**

Phenol formaldehyde resin material (resole type) supplied by AL-Rayah establishment / Ministry of Industry was used as a binder in preparation of complexed polymers.

Additives:

Powders of $AlCl_3$, $FeCl_3$, $ZnCl_2$ were supplied by BDH-Limited, Pool England.

❖ **Preparation of Formaldehyde Complexes:**

Resoles were warmed to 110 °C through reflux system to obtain high liquidity, then the powder of $AlCl_3$, $FeCl_3$ or $ZnCl_2$ (20%) was added with continuos stirring to ensure maximum homogeneity through out the resin, until all HCl gas was liberated, about 2 hours.

The mixture was poured in a test tube, and then cured at 80 °C for 24 hours. The resulting cured samples were heated at 30 °C for 30 min. and then soaked for 2 hours in oxygen free atmosphere, and standard control specimens were prepared from resole without any additive to be used as reference.

❖ **IR Spectroscopy:**

1-3 mg of each sample was ground with 100 mg of anhydride potassium bromide (KBr) and a disc was prepared from the mixture. The IR absorptions spectra were recorded by Unicom SP 1100 infra-red spectrophotometer.

❖ **Thermal Analysis:**

A netzch model 916 simultaneous thermal analysis (STA) and TG derivative was monitored through the experiment and TG derivative was monitored through the experiment.

❖ **Mechanical Properties:**

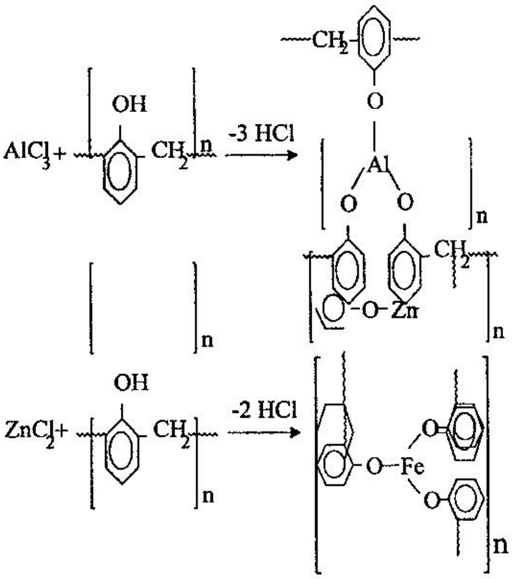
1. Flexural strength and modulus of elasticity were measured by ASTMD 790.
2. Interlaminars shear strength measurement was carried out with standard model of ASTMD 2344-72.
3. Tensile strength was performed by using ASTMD 638 Specification.

Results and Discussion:

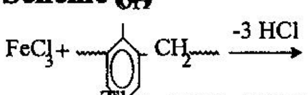
The phenolic resins are the oldest and lowest thermosetting polymer materials. They are derived from the condensation of phenol and aldehydes such as formaldehyde improving the properties of phenolic resins are extensively studied by many authors [11]. They found that the main parameters which affect the details of the effect of additive materials. There are two types of phenolic resins, resole and novolak. Resole is prepared by the interaction of phenol with a molar excess of formaldehyde (1:1.5) under alkaline catalyzed conditions. Novolak is normally prepared by the interactions of a molar excess of phenol with formaldehyde (1.25:1) under acidic catalyzed conditions.

Resole type is converted into network polymer by heating at 80-100 °C for 24 hr. or at 150 °C for 3 hr. conversion of novolak into network polymer can be prepared into addition of a cross-linking agent such as hexamethylene tetramine.

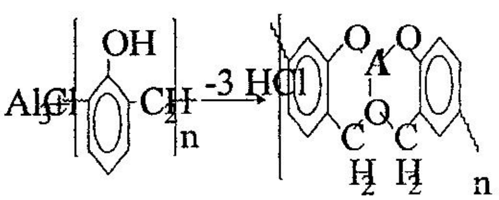
In this work heat and flame resistant resins are obtained by the reaction of phenolic resin with metal halides such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, the reactions occurred between OH phenolic groups with metal halide with liberating HCl during the complex reaction as in scheme (5).



Scheme (5)



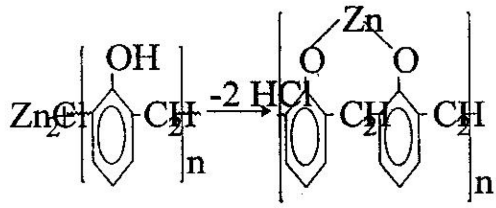
The new prepared resins are deeply coloured, they were illustrated in table (2) the complexing reaction although the thermal resistance is improved by this modification reaction which attributed to the structures as in scheme (5). In general, the reaction is performed at 100-120 °C, the intermolecular (crosslinking) reaction takes place yielding 6-membered ring as in scheme (6).



Scheme (6)

Colored solid complexed polymers were obtained via a moderately strong exothermic reaction between resole and $AlCl_3$ with HMTA.

Although, cyclic structures prevail (8-membered ring) with normal ortho, para isomers may occurs with Zn ion as in scheme (7).



Scheme (7)

The following methods are utilized to improve the thermo-oxidative resistance of phenolic resins:

1. Etherification or esterification of the phenolic hydroxyl group.
2. Complex formation with poly valent elements.
3. Replacement of the methylene groups by heteroatoms.

❖ **Mechanism of Complexation:**

$AlCl_3$, $FeCl_3$, $ZnCl_2$ behave as complexes agent at high temperature with phenolic resin through OH groups. Increasing of percent of agent exhibited more complexation in structure as shown in IR spectra, Fig. (1).

Three phenolic resin complexes are finding increased application both as structural components and phenolic resin complexes possesses excellent properties and may be used for thermal protection in many applications.

❖ **Mechanical Properties:**

A number of specimens of phenolic resin complexes were prepared as in table (1). The tensile strength measurements are shown in

Fig. (2), which indicates a complexation with increasing $AlCl_3$ content, the tensile strength leveled off 21% complex ratio to characterize various complexes by flexural strength.

All the observed data are listed in table (1). The flexural as drastically enhanced by complexation. The effect of comlexation on the mechanical properties may be attributed to the increasing of crosslinked through polymer molecules and the orientations in the complexes. The little difference may be attributed to the many factors such as the type of metal ion and the method of preparation of samples. The phenolic resin complex (1) was analyzed thermogravimetrically as in Fig. (3b), TG-curve decreases in step-wise manner indicating a steeper slope and complex losses about 20% throughout the temperature range about 600-700 °C. This loss is due to thermal degradation of phenolic resin material producing gases such as water vapor, hydrogen, carbon dioxide, monoxide. At 900-110 °C the pyrolysis of the material continued at slower rate, then converted into polymeric carbon. The TG-curve of resol is shown in Fig. (3a).

Table (3), Fig. (4) shows the weight loss % for three complexes. The different effect of the complexed samples, the presence of additives has a high effect on the decreasing of degradation process and a little effect on the thermal conductivity for complexed polymers in comparison with non complexed phenolic resin. Thermal conductivities of non complexed phenolic resin and thermal conductivities of three complexes are illustrated in table (2).

It was concluded that the complex phenolic resins could be used as insulation material in different aims such as in defence systems and for military applications and many other applications.

Fig. (2) shows the tensile strength of sample (1) indicated a continuos rise with increasing $AlCl_3$ beyond 21 wt% $AlCl_3$ content, the tensile strength leveled off, suggesting that the 21 wt% is the optimum ratio.

Fig. (5) shows the IR spectra as a function of heat treatment temperature, which indicated the intensity of OH phenolic groups were decreasing with increasing temperature reaction during complexation reaction after 2 hrs.

Fig. (3), TG-curves of a resole sample (a) relative to a phenolic resin sample (b), which gave higher thermal resistance, this due to the complexed structure with metal ion. Also, table (3), Fig. (4) indicated the thermosetting, crosslinking, complexing phenolic resins with three different metals.

Heat and flame resistant resins were obtained by the reaction of phenolic resins with metal halides were gave new modification resins.

Table (1): Mechanical Properties of Complexes Phenolic Resin

Sample No.	[illegible]	[illegible]	[illegible]
1	80	1.8	40
2	30	1.5	6.5
3	15	0.9	4.2

Table (2): Thermal Conductivities of Phenolic Resin Complexes

Resin No.	Phenolic Resin With	Colour	Thermal Conductivity [illegible]
1	$AlCl_3$	Black	0.91
2	$FeCl_3$	Red	0.85
3	$ZnCl_2$	White	0.69

Table (3): Thermal Analysis of Phenolic Resin Complexes 1, 2 , 3

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	600-700	20	700-900	30	1000-1100	45
2	600-650	22	850-900	35	1000-1100	50
3	500-600	20	800-850	38	1000-1100	60

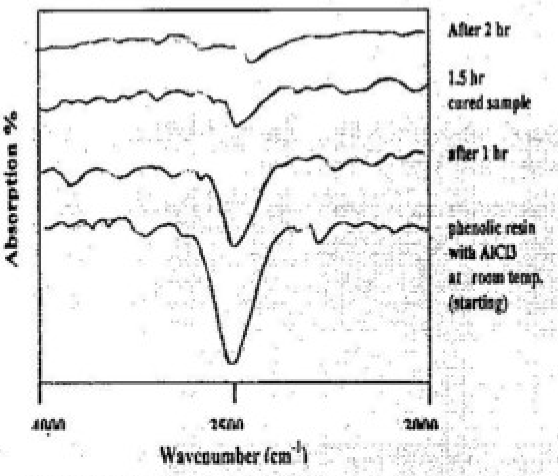


Fig. (1): IR spectra of resole with $AlCl_3$ heated to various temperatures

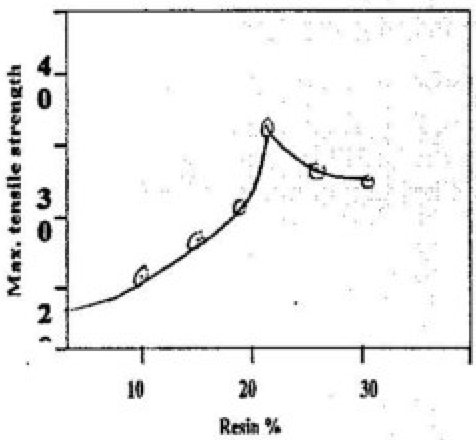


Fig. (2): Tensile strength of phenolic resin 1

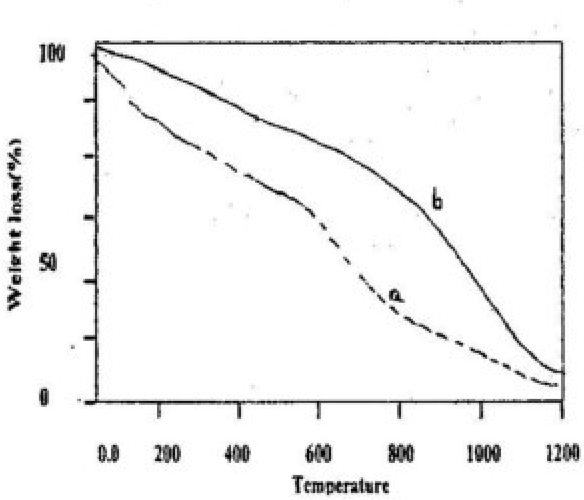


Fig. (3): TG-Curve of (a) resole (b) phenolic resin complex wt% of $AlCl_3$

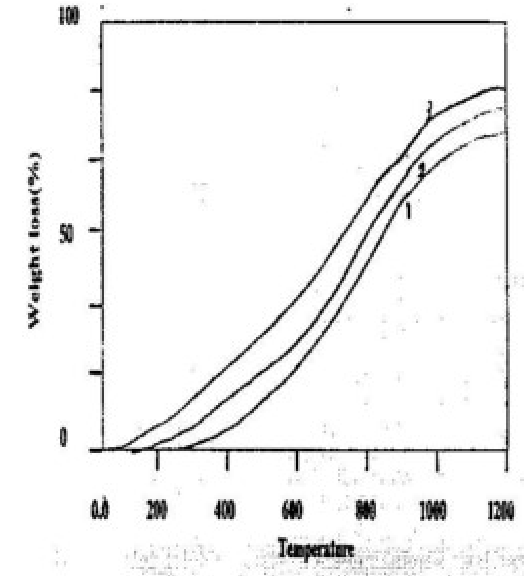


Fig. (4): Weight loss-temperature curves for phenolic resins 1, 2, 3

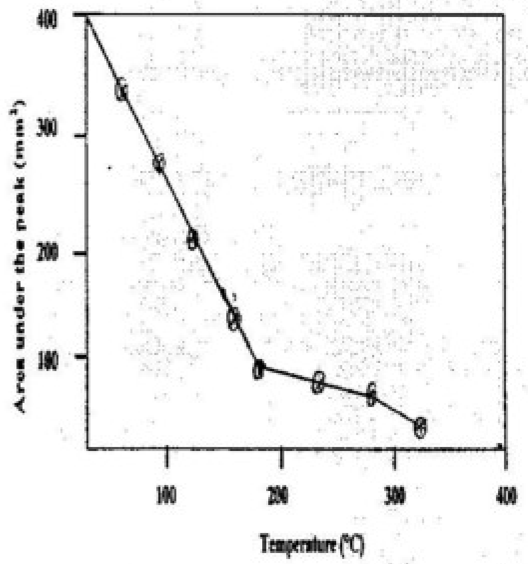


Fig. (5): Intensity of OH phenolic group of IR absorption spectra as a function of heat treatment temperature

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تحضير معقدات الراتنجات الفينولية

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الخلاصة:

تم تحضير ثلاثة أنواع من معقدات الراتنجات الفينولية باستخدام كلوريد الألمنيوم، كلوريد الحديديك وكلوريد الخارصين وذلك بتحوير الراتنجات الفينولية إلى راتنجات أكثر مقاومة حرارية وميكانيكية وبأعلى وزن جزيئي، وذلك نتيجة التشابك بين السلاسل البوليمرية لراتنجات الفينول فورمالديهايد عن طريق تكوين المعقدات البوليمرية التي تكسبها صفات حرارية وميكانيكية تجعلها ممكنة الاستخدام كعوازل حرارية تتحمل أكثر من 1000°م.

لقد تم فحص النماذج الجديدة التحضير بالأشعة تحت الحمراء، التحليل الحراري الوزني والصفات الميكانيكية مثل قوة الشد والطي ووجد أنها بالإمكان استخدامها كعوازل حرارية ولأغراض تطبيقية واسعة.