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Synthesis and Modification of New Phenolic Resins Bearing Pendant 1,8-Naphthalimides

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Abstract: ***Four new phenol-formaldehyde resins bearing 1,8-naphthalimides in their repeating units were synthesized via condensation of formaldehyde with N-(hydroxy phenyl)-1,8-naphthalimides under conditions similar to these used in novolac preparation. Inthis work structural modifications were performed first via synthesis of new phenolic component represented by phenolic ring linked to thermally stable 1,8-naphthalimide moiety which condensed with formaldehyde and second by introducing of phenolic hydroxyl groups present in the newly synthesized resins in esterification reaction with benzoyl chloride producing the corresponding benzoyloxy substituted resins.Both the synthesized and the cured resins have new properties which may serve different applications.***

Keywords: phenol-formaldehyde resins, 1,8-naphthalimide, novolac,structural modifications

1. Introduction

Phenolic resins are the most important thermosetting resins having excellent mechanical properties,chemical resistance and retention of propertiesafter long term exposure to high temperature[1,2].

These resins are used in awide variety of applications including varnishes,adhesives,laminates and surface coatings[3-5].Since the discovery of phenol-formaldehyde resins in 1907 many attempts have been carried by many researchers to incorporate structural modifications[6-12] either by using other aldehyde instead of formaldehyde or by using different phenols to obtain new resins having new properties .In the present work four new phenol-formaldehyde resins bearing pendant 1,8-naphthalimides in their repeating units were synthesized via poly condensation of N-(hydroxy phenyl)-1,8-naphthalimides with formaldehyde under condition similar to those used in novolac preparation.

The prepared phenolic resins were modified by esterification via treatment with benzoyl chloride in the presence of pyridine.The newly synthesized phenolic resins and the modified ones have new properties in hope to use in new applications.

2. Experimental

Instruments

Melting points were determined on Gallenkamp capillary melting point apparatus and were uncorrected. FTIR spectra were recorded on SHIMADZU FTIR-8400 Fourier Transform Infrared spectrophotometer.^{1}HNMR and ^{13}CNMR spectra were recorded on near magnetic resonance Burker ,ultrashield 300MHz using tetramethylsilane as internal standard and DMSO-d6 as solvent. Softening points were determined on thermal microscope Riechertthermover.

Chemicals

All chemicals employed were of analytical reagent grade and were used with out further purification.

1-Synthesis of N-(hydroxyphenyl)-1,8-naphthalimides (1-4)[13]

A mixture of of (0.01mol,1.98 g) of 1,8-naphthalic anhydride and (0.01 mol) of ortho or meta or para-amino phenol were placed in a wide pyrex tube supplied with a thermometer and immersed in sand bath. The sand bath was heated gradually until the complete fusion of the mixture. Subsequently sand bath temperature was kept at ten degrees above melting point of the mixture for one hour. The resulted fused product was cooled to room temperature and the obtained solid was recrystallized from a suitable solvent.

2-Synthesis of N-(1,8-naphthalimidyl)phenol-formaldehyde Resins(5-8)[9]

A mixture of (0.01 mol, 2.89g) N-(hydroxy phenyl)-1,8-naphthalimide, (0.01 mol) of formaldehyde 37% and (15 mL) of DMF was placed in a three neck round bottomed flask fitted with a reflux condenser, thermometer and dropping funnel. The dropping funnel was charged with (0.2 mL) of conc. sulphuric acid and (1 mL) of distilled water then this solution was added drop wise with stirring and the resulted mixture was refluxed at (110°C) for three hours.

The solvent was distilled off and the polymeric residue was dissolved in DMF then filtered and the filtrate was added to excess water to precipitate the polymer. The resulted polymer was filtered, washed with ether and dried in the oven at (65-70°C) for twenty four hours.

3-Curing Via Esterification of the Synthesized Phenolic Resins to the Corresponding Poly[N-(benzoyloxy phenyl-formaldehyde)-1,8-naphthalimides] (9-12)[9,11]

A mixture of (0.01 mol) of the prepared 1,8-naphthalimidyl phenolic resin, (20 mL) of DMF and (6mL) of pyridine was placed in a suitable round bottomed flask filtted with dropping funnel which was charged with (2mL) of benzoyl chloride.

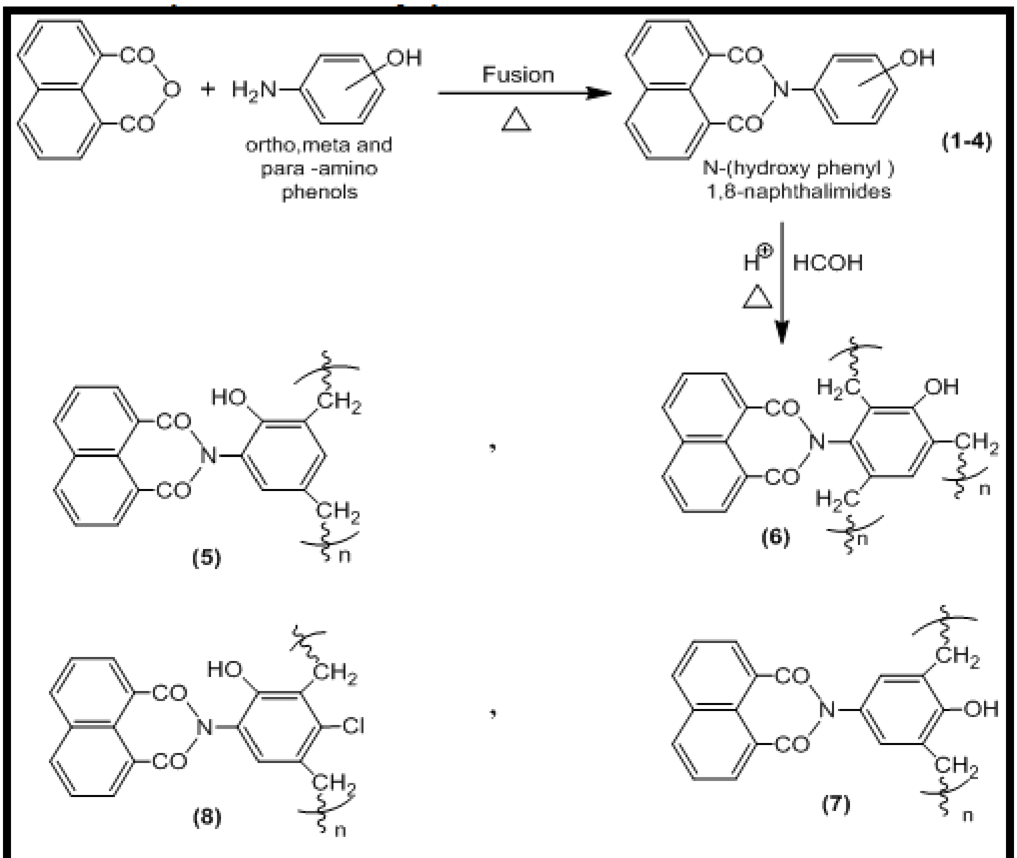
Benzoyl chloride was added dropwise to the mixture with stirring and cooling to (5°C) then stirring was continued for another six hours at room temperature. The resulted mixture was filtered then the filtrate was evaporated and the residue was dissolved in water then extracted with chloroform for three times. The organic layer was dried and the solvent was evaporated to yield a solid product which was purified by dissolving in DMF followed by precipitation by water, then filtration.

Physical properties of naphthalimides(1-4),phenolic resins (5-8)and cured resins (9-12) are shown in Tables 1,2and 3 respectively.

3. Results and Discussion

Synthesis and modification of phenolic resins by different strategies still the most important subject which play avital role in properties and applications of phenol formaldehyde resins.Thus the core the present work is based on synthesis of new phenolic resins followed by their modification.Our new strategy used in building the target phenolic resins is based on introducing of new phenolic moiety represented by phenolic ring linked to 1,8-naphthalimide in condensation reaction with formaldehyde. Naphthalimide was choosed to incorporate in the newly synthesized phenolic resins since aromatic polyimides possess outstanding thermal and mechanical properties[14]as well as excellent chemical resistance besides insertion of cyclic imides in some polymer chains was greatly improved thermal and chemical stability of these polymers[15].

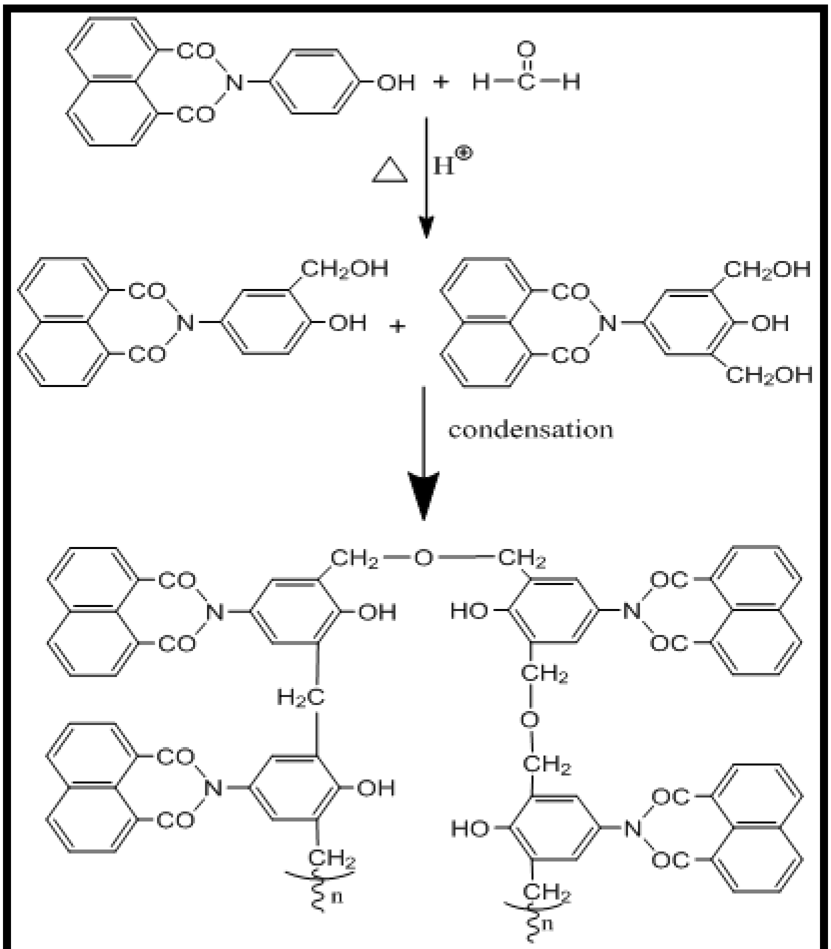
Synthesis sequence of the target phenolic resins which was shown in scheme1involved two steps in the first one four N-(hydroxy phenyl)-1,8-naphthalimides (1-4) were prepared via reaction of ortho ,meta and para-amino phenols[13] with 1,8-naphthalic anhydride.The reaction was performed by fusion of reactants mixture at high temperature producing N-(hydroxy phenyl)-1,8-naphthalamic acid which was not separated but introduced directly in dehydration reaction under the influence of heat leading to ring-closure and producing the corresponding 1,8-naphthalimides[16] (5-8).



Scheme (1)

In the second step the synthesized naphthalimides (1-4) were introduced in condensation reaction with formaldehyde in acidic medium under reflux [9] condition producing the target phenolic resins (5-8).

The first stage in acid-catalyzed condensation reaction of phenolic naphthalimides with formaldehyde involved formation of mono methylol, dimethyloland trimethylol phenols while the subsequent stage involved condensation reactions between methylol groups present in different phenolic rings leading to links formation between phenolic rings either through ether($-CH_2-O-CH_2-$)or methylene ($-CH_2-$) bridges producing the phenolic resins as described in scheme2.



Scheme (2)

It seems that the presence of 1,8-naphthalimide moiety in the new phenolic resins exhibit them good thermal stability indicated by their high softening points ,besides resistance against the solubility in many solvents thus the new resins are insoluble in petroleum ether , ethanol, diethyl ether and water.

Phenolic resins (5) and (6) are insoluble in acetone and dioxane while phenolic resins (7) and (8) showed partial solubility in hot acetone and hot dioxane .Besides phenolic resin (5) showed resistance to solubility in chloroform while the remaining resins showed partial solubility in hot chloroform. Finally all the prepared resins showed acceptable solubility in both DMF and DMSO solvents.

Chemical structures of the prepared imides and resins are confirmed in the basis of FTIR,^{1}H-NMR and ^{13}C-NMR spectral data.

FTIR spectra of the prepared naphthalimides (1-4) showed absorption bands at (3259-3413)cm^{-1} and (3070-3076)cm^{-1} due to ν(O-H) phenolic and ν(C-H)aromatic. Absorption bands due to asym. and sym. ν(C=O)imide appeared at (1772-1774) cm^{-1} as sholder,(1703-1706) cm^{-1} and (1649-1660) cm^{-1}.Other absorption bands appeared at(1587-1620) cm^{-1},(1355-1377) cm^{-1} and (1238-1272) cm^{-1}, (1193-1195) cm^{-1} which are due to ν(C=C) aromatic,ν(C-N) imide and ν(C-OH) respectively[17].

^{1}H-NMR spectrum of compound(1) N-(2-hydroxy phenyl)-1,8-naphthalimide showed two multiplet signals at (δ=6.90-7.0) and (δ=7.23-7.31)ppm belong to four aromatic protons and triplet signals at(δ=7.88-7.92)ppm and (δ=8.49-8.51)ppm belong to other six aromatic protons.Singlet singal appeared at (δ=9.62)ppm belong to phenolic OH proton.On the other hand ^{13}C-NMR spectrum of compound (1) showed signals at (δ=116.93-153.89)ppm belong to aromatic carbons and signals at(δ=163.49-163.82)ppm belong to (C=O) imide carbons.

FTIR spectra of the newly synthesized phenolic resins showed absorption bands at (3334-3396) cm^{-1} due to ν(O-H) phenolic and bands at (3060-3072) cm^{-1},(2920-2980) cm^{-1} and (2860-2890) cm^{-1} which are due to ν(C-H) aromatic,asym. and sym. ν(C-H) aliphatic. Absorption bands due to asym. and sym. ν(C=O) imide appeared at (1772-1774) cm^{-1} as sholder,(1701-1706) cm^{-1} and (1652-1665) cm^{-1}.

Absorption bands due to ν(C=C) aromatic and ν(C-N) imide appeared at (1585-1623) cm^{-1} and (1357-1377) cm^{-1} beside new strong absorption bands appeared at (1008-1124) cm^{-1} which are due to ν(C-O) ether proving the presence of ether bridges ($-CH_2-O-CH_2-$).

^{1}H-NMR spectrum of phenolic resin (5) showed singlet signal at (δ=1.99)ppm and signals at (δ=2.70-2.89)ppm belong to ($-CH_2-$)and ($-CH_2O-$) protons.The spectrum showed also four multiplet signals at (δ=6.86-6.88)ppm, (7.13-7.15),(7.88-7.9) and (8.49-8.51)ppm belong to ten aromatic protons. The signal which belong to phenolic (OH) proton appeared at (δ=9.65)ppm.

^{13}C-NMR spectrum of resin(5) showed signals at (δ=14.56) ppm and (δ=21.24)ppm belong to(-CH_2-) carbons .signals belong to (-OCH_2-) carbons appeared at (δ=45.03 and 60.23)ppm, while signals belong to aromatic carbons appeared at (δ=115.85-157.39)ppm and signal belong to(C=O) imide carbons appeared at (δ=164.35)ppm.

^{1}H-NMRspectrum of phenolic resin (7) showed signals at (δ=1.99)ppm and (δ=2.75-2.99)ppm belong to (-CH_2-) and (-CH_2O-) protons. Signals belong to aromatic carbons appeared as multi signals at (δ=6.88-6.99),(7.22-7.29),(7.9) and (8.5-8.53) ppm and finally signal belong to phenolic (OH) proton appeared at (δ=9.6) ppm.

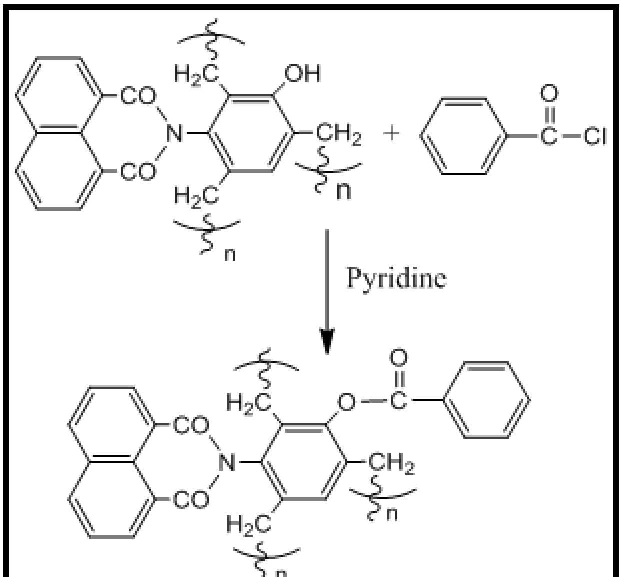
^{13}C-NMR spectrum of phenolic resin (7) showed signals at (δ=15)ppm and (δ=21)ppm belong to (-CH_2-) carbons and signals at (δ=44.8)ppm and (δ=60.23)ppm belong to (-CH_2O-) carbons[17].Signals belong to aromatic carbons abeared at (δ=115.85-153.88)ppm and signal for (C=O) imide carbons abeared at (δ=163.82)ppm.

^{1}H-NMR spectrum of phenolic resin(8) showed signals at (δ=1.99)ppm and (δ=2.51,3.17)ppm belong to (-CH_2-) protons and (-CH_2O-) protons respectively. Multiplet signals appeared at (δ=6.9-6.99) ppm,(δ=7.20-7.28),(7.95)and (8.57)ppm belong to aromatic protons and signal at (δ=9.6)ppm belong to phenolic (OH) proton.

^{13}C-NMR spectrum of phenolic resin (8) showed signals at (δ=14.56)and (δ=21.24)ppm belong to (-CH_2-)carbons and signal at (δ=60.10)ppm belong to (-CH_2O-) carbons. Signals belong to aromatic carbons appeared at (δ=119.0-154)ppm while signal belong to (C=O) imide carbon appeared at (δ=168)ppm.

The second part of this work involved curing of the prepared resins via introducing of the present phenolic hydroxyl groups in esterification reaction with benzoyl chloride in the presence of pyridine[9].

During esterification reaction phenolic hydroxyl groups are converted to benzoyloxygroups as described in scheme3.



Scheme (3)

Physical properties of the modified resins (9-12) indicated that esterification method was quiet convenient to incorporate structural modification in the prepared resins (5-8) since the modified resins have different physical properties from those of the strarting resins thus they have lower softening points and showed good solubility in all organic solvents.

The presence of (C-O-C) ester bonds in the incorporated ester moiety exhibit the modified resins softness and flexibility leading to decrease their softening points and resistance to solubility and this made the cured resins suitable for certain applications like adhesives and coating[2,18].

FTIR spectra of the cured resins (9-12) showed atrophy in ν(O-H) phenolic absorption band indicating success of esterification process and the weak bands appeared at (3301-3410)cm^{-1} are due to ν(O-H) in methylol groups.The spectra showed also new absorption bands at(1733-1739) cm^{-1} which are due to ν(C=O) ester and bands at (1178-1244)cm^{-1} due to ν(C-O) ester.

Other absorption bands appeared at (1583-1602) cm^{-1},(1352-1371) cm^{-1},(1008-1124) cm^{-1},(3068-3074) cm^{-1} and (2940-2966) cm^{-1},(2831-2887) cm^{-1} which are due toν(C=C) aromatic,ν(C-N) imide,ν(C-O) ether,ν(C-H) aromatic and asym.,sym.ν(C-H) aliphatic respectively[19]. Besides absorption bands due to ν(C=O) imide appeared at (1772-1782) cm^{-1},(1703-1710) cm^{-1}and (1629-1683) cm^{-1}. FTIR spectral data of the prepared imides (1-4),resins (5-8) and the cured resins (9-12) are listed in Tables 4,5 and 6 respectively.

^{1}H-NMRspectrum of the cured resin (9) showed disappearance of the signal belong to phenolic(OH) proton indicating success of curing by esterification.The spectrum showed signals at (δ=1.99)ppm belong to(-CH_2-) protons, and signals at(δ=2.75,2.9,3.17)ppm belong to (-CH_2O-) protons and signals at(δ=7.26-8.57)ppm belong to aromatic protons.

Finally ^{13}C-NMR spectrum of the cured resin(9) showed signals at (δ=14.55 and 21.23)ppm belong to(-CH_2-) carbons and signals at(δ=55.38 and 60.22) ppm belong to (-CH_2O-) carbons. Signals belong to aromatic carbons appeared at(δ=119.55-147.16) ppm,signals belong to(C=O) imide carbons appeared at(δ=163.42-163.48)ppm and signals for (C=O) ester carbons appeared at(δ=167.78 and 170.81)ppm.

Table 1: Physical properties of naphthalimides(1-4)

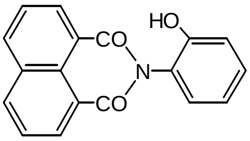
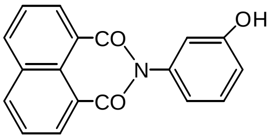
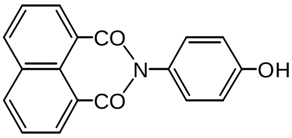
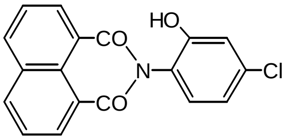
Comp. No.	Compound structure	Yield%	Melting point°C	Colour	Recrystallization Solvent
1		72	204-206	Black	Cyclohexane
2		68	201-203	Black	Acetone
3		66	190-191	Brown	Cyclohexane
4		60	199-200	Gray	Acetone

Table 2: Physical properties of resins (5-8)

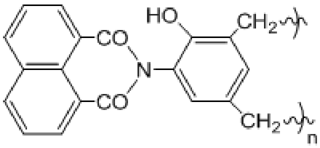
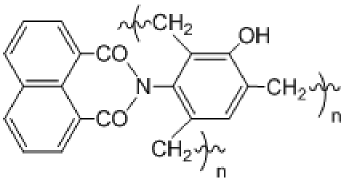
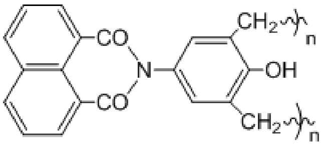
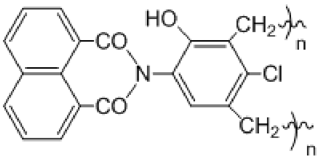
Polym. No.	Polymer structure	Conv. Ratio%	Softening Points °C	Colour	purification
5		75	225-230	Dark gray	Dissolving in DMF then precipitation by water
6		81	236-246	Dark gray	Dissolving in DMF then precipitation by water
7		70	230-240	Dark brown	Dissolving in DMF then precipitation by water
8		85	284-292	Dark gray	Dissolving in DMF then precipitation by water

Table 3: Physical properties of cured resins (9-12)

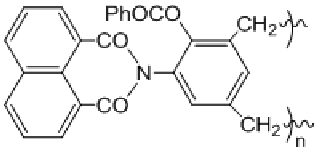
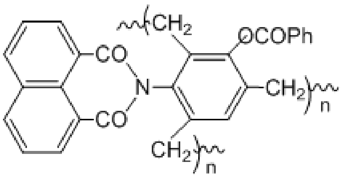
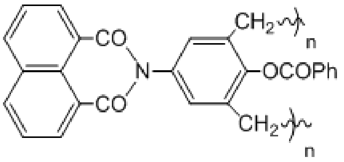
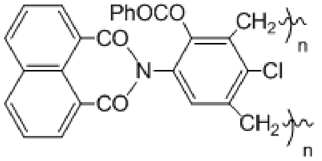
Polym. No.	Polymer structure	Conv. Ratio%	Softening Points °C	Colour	purification
9		74	164-170	Dark brown	Dissolving in DMF then precipitation by water
10		71	145-150	Dark gray	Dissolving in DMF then precipitation by water
11		77	66-72	Dark gray	Dissolving in DMF then precipitation by water
12		69	40-58	Green	Dissolving in DMF then precipitation by water

Table 4: FTIR spectral data (cm^{-1}) of naphthalimides (1-4)

Comp. No.	ν(O-H) Phenolic	ν(C-H) Aromatic	ν(C=O) Imide	ν(C=C) Aromatic	ν(C-N) Imide	ν(C-OH)
1	3413 3326	3074	1772 (sh.) 1706 1658	1587	1355	1238 1193
2	3259	3076	1774(sh.) 1706 1649	1616 1589	1377	1242 1195
3	3344 3307	3070	1774(sh.) 1703 1654	1620 1589	1375	1272 1193
4	3380 3361	3076	1774(sh.) 1706 1660	1587	1355	1240 1193

(Sh=sholder)

Table 5: FTIR spectral data (cm^{-1}) of phenolic resins (5-8)

Polym. No.	ν(O-H)	ν(C-H) aromatic	ν(C-H) aliphatic	ν(C=O) Imide	ν(C=C) aromatic	ν(C-N) Imide	ν(C-O-C) Ether
5	3396 3365	3060	2960 2947	1701 1654	1593	1365	1124
6	3334	3072	2920 2860	1774(sh.) 1706 1660	1587	1377	1008
7	3390 3359	3066	2954 2880	1772(sh.) 1701 1652	1620 1591	1373	1118
8	3369	3068	2980 2890	1774(sh.) 1704 1665	1623 1585	1357	1014

(Sh=sholder)

Table 6: FTIR spectral data (cm^{-1}) of cured resins (9-12)

Polym. No.	ν(C-H) Aromatic	ν(C-H) Aliphatic	ν(C=O) Imide	ν(C=O) Ester	ν(C=C) Aromatic	ν(C-N) Imide	ν(C-O) Ether,ester	ν(O-H) Phenolic
9	3068	2940 2831	1782 1710 1679	1733	1589	1355	1211 1178 1008	3410(w)
10	3053	2947 2860	1704 1629	1704	1602	1371	1244 1054	3407
11	3074	2966 2875	1772 1703 1654	1737	1587	1367	1124 1012	3301
12	3070	2940 2887	1772 1706 1683	1739	1583	1352	1211 1120	3361

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