Curing of Maleimidyl Phenol-Formaldehyde Resins Via Esterification and Free Radical Polymerization

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Abstract:

Three phenol-formaldehyde resins having pendant maleimides were prepared by poly condensation of N-(hydroxyphenyl) maleimides with formaldehyde under conditions similar to those in Novolac preparation. The prepared resins were modified by two methods, the first one includes esterification of phenolic hydroxyl groups in the prepared resins via their treatment with benzoyl, acryloyl, methacryloyl and cinnamoyl chlorides respectively in the presence of triethylamine, while the second modification includes free radical polymerization of vinylic bonds in the prepared resins to produce cross-linked thermally stable polymers.

Introduction:

Phenol-formaldehyde resins are the oldest commercial synthetic polymers, first introduced around (100) years ago.

In recent decades extensive research efforts have been directed towards modification of phenolic resins via using of new aldehydes or new phenolic moiety in the synthesis of these resins in hope to enhance their properties(1-5).

In the present work three phenol-formaldehyde resins were prepared by poly condensation of N-(hydroxylphenyl) maleimides with formaldehyde under conditions similar to those in Novolac preparation.

The prepared resins were modified by two methods, the first one includes esterification of the prepared resins to the corresponding benzoates, acrylates, methacrylates and cinnnmates via their treatment with suitable acid chloride in the presence of triethylamine while the second method involved free radical polymerization of vinylic bonds in the prepared resins producing thermally stable polymers.

Experimental:

1- Melting points were determined on Gallen Kamp capillary melting point apparatus and were uncorrected.
2- IR spectra were recorded on a Shimadzu FTIR8000.
3- U.V. spectra were recoded on Shimadzu UV-VIS recorder spectrophotometer UV-160.
4- C.H.N. analyses were determined by Perkin-Elmer 240 element analyzer.
5- Softening points were determined on Thermal Microscope Reichert Thermover, SP1, 160.
6- Intrinsic Viscosities were determined with automatic viscometer Tafesa Ubbelohde viscometer at 25°C using acetone as a solvent.

1- Preparation of N-(hydroxyphenyl) Maleamic acids

Amic acids were prepared according to literatures(6,7) by allowing maleic anhydride to react with o, m and p-aminophenols using acetone as a solvent. The produced amic acids were purified by recrystalliaztion from ethanol.

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Table (I) lists melting points, percent yields and major IR absorptions of the prepared acids.

2- Preparation of N-(hydroxyphenyl) Maleimides

The titled compounds were prepared according to literature procedures(8,9) using fusion technique. The prepared imides were purified by recrystallization from cyclohexane.

Melting points, percent yields and major IR absorptions of the prepared imides are listed in Table (II).

3- Preparation of N-Maleimidyl Phenol-Formaldehyde Resins Via Poly Condensation

The titled compounds were prepared according to literature procedures(10,11) with few modifications:

(1.89 gm, 0.01 mole) of N-(hydroxyphenyl) maleimide, (1 ml, 0.008 mole) of formaline (37%) and (10 ml) of DMF were placed in a three neck round bottomed flask fitted with a reflux condenser, thermometer and dropping funnel.

The dropping funnel was charged with (0.1 ml) of concentrated sulphuric acid and (0.5 ml) of distilled water.

The acid was added dropwise with stirring then the mixture was refluxed for (3 hrs) at (110°C) with continuous stirring.

The resulted mixture was added to excess water to precipitate the polymer, then the resulted precipitate was filtered and washed with petroleum ether. The produced polymer was purified by dissolving in DMF followed by reprecipitation with excess water. Finally the obtained pure polymer was dried in an oven at (70-75)°C for (24 hrs).

Table (III) lists percent conversions, softening points, colors, intrinsic viscosities, U.V absorptions and major IR absorptions of the prepared polymers.

Curing of The Prepared Phenolic Resins:

A- Curing of The Prepared Phenolic Resins Via Esterification

Curing by this method includes the following preparations:

4- Esterification of The Prepared Phenol-Formaldehyde Resins to The Corresponding Benzoates

The titled compounds were prepared according to literature procedures(12) with minor modifications:

In a suitable round bottomed flask fitted with a dropping funnel was dissolved (0.01 mole) of the prepared resin (maleimidyl phenol-formaldehyde) resin in (40 ml) of DMF. To the resulted solution (0.01 mole) of triethylamine was added followed by dropwise addition of (0.01 mole) of benzoyl chloride with stirring and cooling, then stirring was continued for another (8 hrs) at room temperature before filtration.

The filtrate was evaporated under reduced pressure and the residue was extracted with water and chloroform.

The organic layer was dried and the solvent was evaporated to yield a thick oil which was purified by passing its chloroform solution through a Florisil column or by recrystallization from cyclohexane.

Table (IV) lists percent yields, softening points, intrinsic viscosities, colors, U.V. absorptions and major IR absorptions of the prepared maleimidyl benzoyloxy phenyl-formaldehyde resins.

5- Esterification of The Prepared Phenol-Formaldehyde Resins to The Corresponding Methacrylates

The titled compounds were prepared by the same procedure used in the preparation of benzoates except the using of methacryloyl chloride instead of benzoyl chloride.

Table (V) lists softening points, percent yields, colors, intrinsic viscosities, U.V. absorptions and major IR absorptions of the prepared maleimidyl methacryloyloxy phenyl-formaldehyde resins.

6- Esterification of The Prepared Phenol-Formaldehyde Resins to The Corresponding Acrylates

The titled compounds were prepared by following the same procedure used in the preparation of benzoates except the using of acryloyl chloride instead of benzoyl chloride.

Table (VI) lists softening points, percent yields, colors, intrinsic viscosities, U.V. absorptions and major IR absorptions of the prepared maleimidyl acryloyloxy phenyl-formaldehyde resins.

7- Esterification of The Prepared Phenol-Formaldehyde Resins to The Corresponding Cinnamates

The same procedure used in the preparation of benzoates was followed in the preparation of the titled compounds except using of cinnamoyl chloride instead of benzoyl chloride.

Table (VII) lists softening points, percent yields, colors, intrinsic viscosities, U.V. absorptions and major IR absorptions of the prepared maleimidyl cinnamoyloxy phenyl-formaldehyde resins.

B- Curing of The Prepared Phenol-Formaldehyde Resins Via Polymerization of Vinylic Bonds

Free radical polymerization of vinylic bonds in the prepared phenolic resins was performed by using cubbon method(13).

In a polymerization bottle was dissolved (1 gm) of the monomer (maleimidyl phenol-formaldehyde resin) in (20 ml) of DMF. To this was added (0.03 gm) of (AIBN) then the bottle was purged with nitrogen before heating at (85)°C for 4 hrs. The resulted solution was poured into (30 ml) of dioxane then the precipitated polymer was filtered and dried. Table (VIII) lists percent conversions, colors and major IR absorptions of the cured polymers.

Discussion and Results:

The core of this work is to introduce modifications on the prepared (maleimidyl phenol-formaldehyde) resins to produce new resins with new properties. In order to perform this target there were many steps to be done.

The first step includes preparation of three N-(hydroxyphenyl) maleamic acids by reaction of maleic anhydride with o, m and p-aminophenols.

The prepared amic acids were dehydrated in the second step to the corresponding N-(hydroxylphenyl) maleimides by using fusion technique.

Poly condensation of the prepared imides with formaldehyde under conditions similar to those in Novolac preparation was performed in the third step to produce three phenol-formaldehyde resins having pendant maleimides.

The fourth step in this work includes curing of the prepared phenolic resins. Curing was achieved by two methods, the first one includes esterification of phenolic hyroxyl groups via treatment of the prepared phenolic resins with different acid chlorides including benzoyl, methacryloyl, acryloyl and cinnamoyl chlorides in the presence of triethylamine to produce the corresponding benzoate, methacrylate, acrylate and cinnamate esters.

Physical properties, U.V. and major IR absorptions of the prepared resins and cured resins via esterification are listed in Tables (III, IV, V, VI, VII) while C.H.N. analysis of some of them are listed in Table (XI).

IR spectra of the prepared (maleimidyl phenol-formaldehyde) resins revealed a clear band in the region (3400-3379)cm^{-1} due to stretching vibration of phenolic OH groups but this band disappeared in IR spectra of the cured resins produced by esterification.

Thus success of esterification reaction was confirmed by disappearance of phenolic hydroxyl absorption band in IR spectra of the cured resins and appearance of two characteristic clear absorption bands in the regions (1787-1720) cm^{-1} and (1211-1191) cm^{-1} due to ester (C=O) and ester (C-O) respectively.

Also these cured resins give positive results in characteristic tests for esters.

The second method of curing includes free radical polymerization of vinylic bond in the prepared phenolic resins. Polymerization was performed in DMF using (AIBN) as initiator. The produced resins show no softening even at 320°C and they are insoluble in all organic solvents.

IR spectra of the cured resins (22-24) showed disappearance of absorption band of (C=C) at the region (1600-1570) cm^{-1} indicated saturation due to polymerization.

Also these cured resins give negative results in Br_2/CCl_4 and $KMnO_4$ tests which proved saturation due to polymerization.Conversion ratios, colors and major IR absorption of the cured resins are listed at Table (VIII).

IR spectra of the prepared resins (7, 12, 14, 22) are shown in Figures (1-4) while U.V. spectra are shown in Figures (5-9).

It is noticeable that most of the cured resins by esterification are dark oils or low softening point resins which are soluble in many organic solvents including (Acetone, $CHCl_3$, DMSO, DMF, Dioxane, THF) but are insoluble in (methanol and benzene) and have low intrinsic viscosities ranged from (0.11-0.42) dL/g.

All these physical properties are fitted with the expected results for introducing ester functional groups in the starting phenolic resins and at the same time these properties make the cured resins suitable for certain applications such as plasticization and adhesives.

On the other hand the cured resins by homogenous free radical polymerization are crystalline solids with high softening points and insoluble in all organic solvents. High thermal stability and resistance to solubility of the cured resins (22-24) indicated the effect of curing via polymerization which caused cross-linking between the polymeric chains which inturn lead finally to thermal stable polymers(14).

As a final results it is clear that this work supply us through curing with several new resins having new properties in hope to serve different applications.

Table (I) Melting points, Percent yields and Major IR absorptions of the prepared Amic Acids

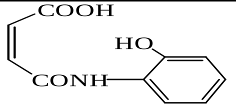
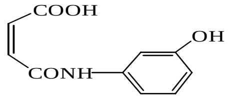
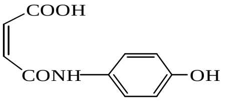
Comp. No.	Compound structure	Yield%	Melting point °C	Major IR absorptions, cm^{-1}			
				νO-H	νN-H	νC=O carboxylic	νC=O amide
1		92	175-176	3395	3164	1697	1616
2		93	178-180	3336	3161	1700	1616
3		90	194-195	3300	3170	1699	1618

Table (II) Melting points, Percent yields and Major IR absorptions of the prepared Imides

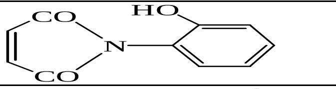
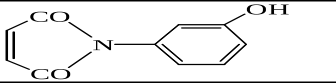
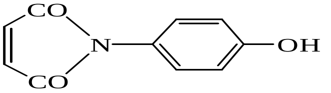
Comp. No.	Compound structure	Yield%	Melting point °C	Major IR absorptions, cm^{-1}			
				νO-H phenolic	νC=O Imide	νC=C Vinylic	νC-N
4		82	120-122	3360	1700	1642	1400
5		77	126-127	3350	1708	1620	1390
6		81	177-178	3400	1702	1610	1400

Table (III) Physical properties and spectral absorption data of the prepared phenolic resins

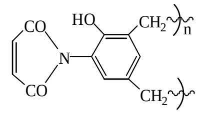
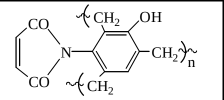
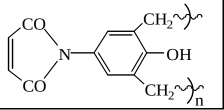
Comp. No.	Compound structure	Conv. %	Softening point °C	Color	[η] dL/gm	U.V. Abs. λ_{max}	Major IR absorptions, cm^{-1}			
							νO-H phenolic	νC=O Imide	νC=C Vinylic	νC-N
7		77	203-210	Yellow	0.67	283	3379	1705	1573	1377
8		72	250-261	Brown	0.93	285	3380	1690	1582	1380
9		75	225-234	Brown	0.81	291	3400	1690	1600	1390

Table (IV) Physical properties and spectral absorption data of (Maleimidyl benzoyloxy phenyl-Formaldehyde) Resins

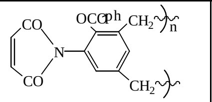
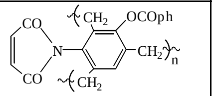
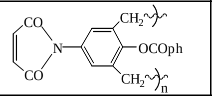
Comp. No.	Compound structure	Yield %	Color	S.P. °C	[η] dL/gm	U.V. Abs. λ_{max}	Major IR absorptions, cm^{-1}			
							νC=O Ester	νC=O Imide	νC-O Ester	νC-N
10		90	Brown	Oil	0.13	264	1780	1692	1205	1410
11		87	Yellow	55-67	0.24	264	1782	1683	1197	1390
12		84	Deep yellow	50-58	0.21	261	1787	1697	1211	1419

Table (V) Physical properties and spectral absorption data of (Maleimidyl methacryloyloxy phenyl-Formaldehyde) Resins

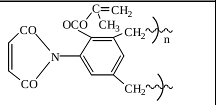
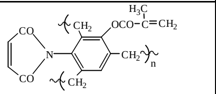
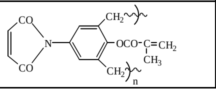
Comp. No.	Compound structure	Yield%	Color	S.P. °C	[η] dL/gm	U.V. Abs. λ_{max}	Major IR absorptions, cm^{-1}			
							νC=O Ester	νC=O Imide	νC-O Ester	νC-N
13		80	Deep Brown	Oil	0.12	336	1725	1650	1199	1386
14		83	Deep Brown	Oil	0.18	334	1718	1604	1151	1380
15		88	Deep Brown	Oil	0.15	342 358	1720	1641	1166	1384

Table (VI) Physical properties and spectral absorption data of (Maleimidyl acryloyloxy phenyl-Formaldehyde) Resins

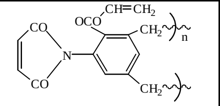
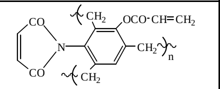
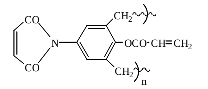
Comp. No.	Compound structure	Yield %	Color	S.P. °C	[η] dL/gm	U.V. Abs. λ_{max}	Major IR absorptions, cm^{-1}			
							νC=O Ester	νC=O Imide	νC-O Ester	νC-N
16		69	Brown	58-70	0.33	337	1760	1720	1200	1390
17		73	Brown	80-97	0.42	332	1760	1722	1191	1393
18		81	Brown	63-77	0.36	334	1740	1710	1205	1400

Table (VII) Physical properties and spectral absorption data of (Maleimidyl cinnamoyloxy phenyl-Formaldehyde) Resins

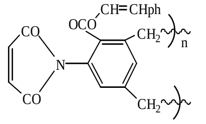
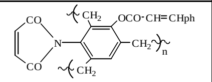
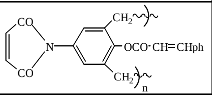
Comp. No.	Compound structure	Yield%	Color	S.P. °C	[η] dL/gm	U.V. Abs. λ_{max}	Major IR absorptions, cm^{-1}			
							νC=O Ester	νC=O Imide	νC-O Ester	νC-N
19		77	Deep Brown	Oil	0.11	336	1730	1635	1195	1381
20		75	Brown	Oil	0.19	333	1757	1640	1202	1371
21		85	Brown	61-75	0.32	338	1766	1702	1135	1380

Table (VIII) Physical properties and major IR absorptions of the cured resins bypolymerization

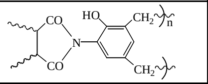
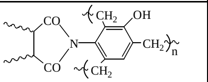
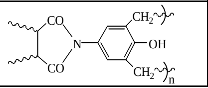
Comp. No.	Compound structure	Conv. %	Softening point °C	Color	Major IR absorptions, cm^{-1}		
					νO-H phenolic	νC=O Imide	νC-N
22		66	> 320	Deep Brown	3409	1705	1400
23		72	> 320	Deep Brown	3402	1695	1402
24		64	> 320	Deep Brown	3413	1703	1411

Table (XI) C.H.N. Analysis of some of the prepared and cured resins

Comp. No.	Calculated			Found		
	%C	%H	%N	%C	%H	%N
7	66.97	4.18	6.51	66.72	4.41	6.38
9	66.97	4.18	6.51	66.75	4.44	6.31
11	72.28	4.21	4.21	72.09	4.38	4.00
12	71.47	4.07	4.38	71.55	4.18	4.20
16	66.91	4.09	5.20	66.64	3.94	5.27
18	66.91	4.09	5.20	66.7	4.29	5.34
21	73.04	4.34	4.05	72.8	4.39	4.15

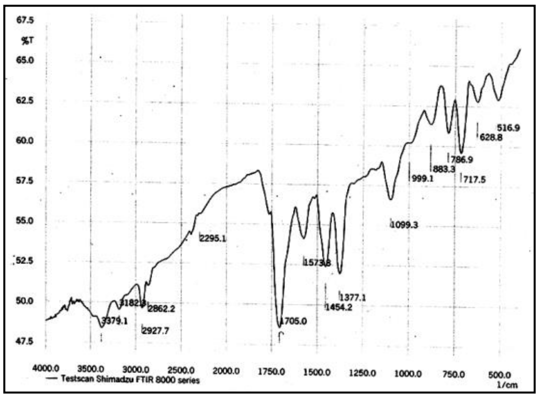


Fig. (1) IR spectrum of compound (7)

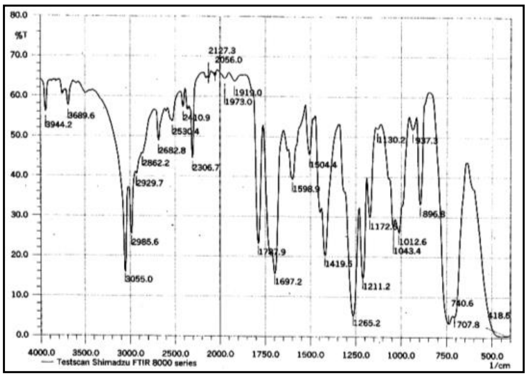


Fig. (2) IR spectrum of compound (12)

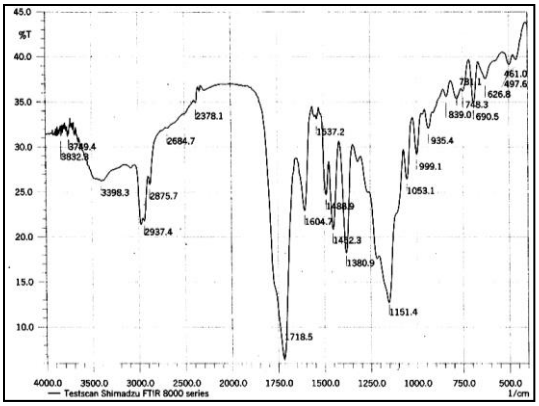


Fig. (3) IR spectrum of compound (14)

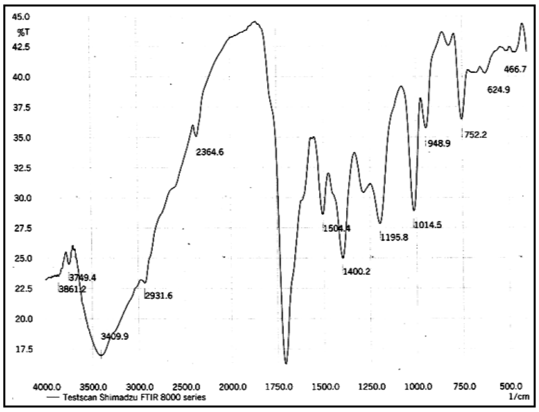


Fig. (4) IR spectrum of

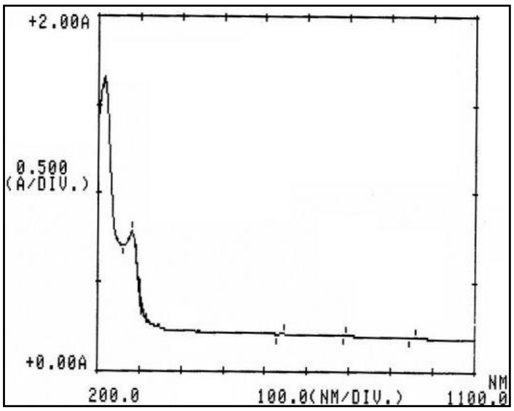


Fig. (5) U.V. spectrum of compound

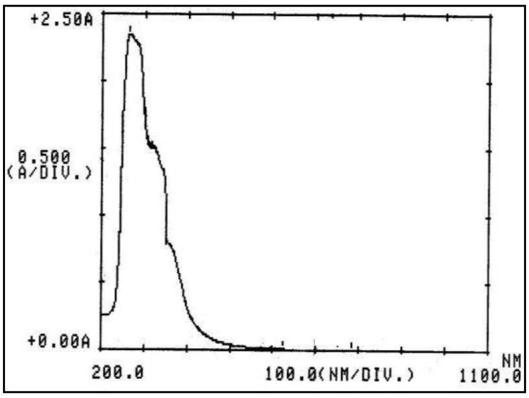


Fig. (6) U.V. spectrum of

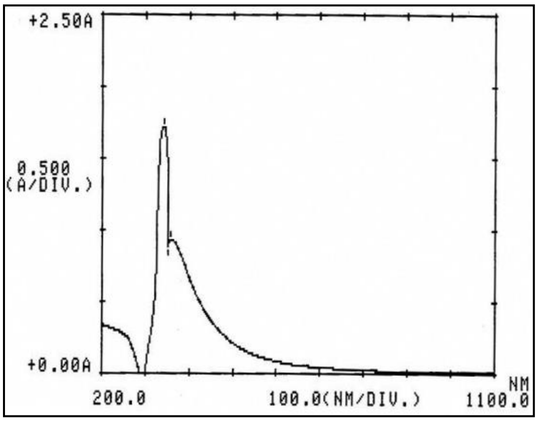


Fig. (7) U.V. spectrum of compound (15)

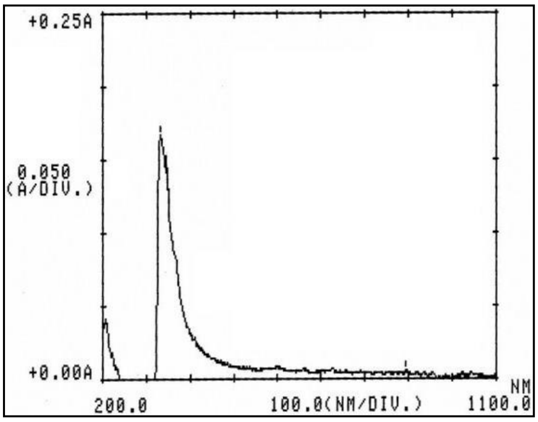


Fig. (8) U.V. spectrum of compound (17)

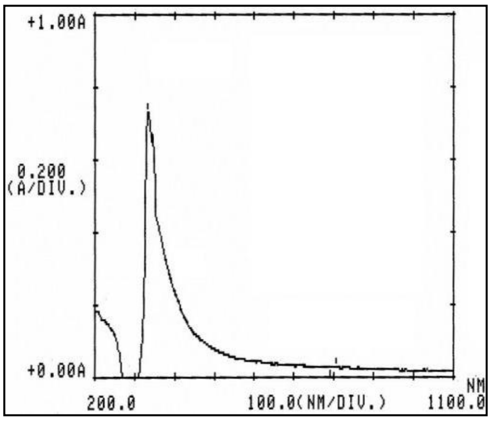


Fig. (9) U.V. spectrum of compound (20)

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معالجة راتنجات مالي ايميديل

فينول –فورمالديهايد بواسطة الاسترة والبلمرة بالجذور الحرة

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الخلاصة:

تضمن البحث اجراء معالجات على راتنجات الفينول-فورمالديهايد الحاوية على المالي ايمايدات كمجاميع متدلية ثم تشخيص ومتابعة صفات نواتج المعالجة.

وعليه فقد تضمنت المرحلة الاولى من البحث تحضير ثلاث راتنجات فينولية حاوية على المالي ايمايدات كمجاميع متدلية من خلال البلمرة التكثيفية لمركبات N-(هيدروكسي فنيل) مالي ايمايدات مع الفورمالديهايد تحت ظروف مطابقة لظروف تحضير النوفولاك.

اما المرحلة الثانية من البحث فقد تضمنت اجراء نوعين من المعالجات على الراتنجات الفينولية المحضرة.

تضمنت المعالجة بالطريقة الاولى اجراء تفاعل استرة لمجاميع الهيدروكسيل المعوضة في الراتنجات الفينولية المحضرة حيث تمت الاسترة بمفاعلة الراتنجات الفينولية مع كلوريدات حامضية مختلفة شملت كلوريد البنزويل، الميث اكريلويل، الاكريلويل والسيناموييل على التوالي بوجود ثلاثي اثيل امين.

اعطت المعالجة وفق هذه الطريقة اثنى عشر راتنج جديد بمواصفات جديدة مما يتيح استخدامها في مجالات عديدة تتفق مع مواصفاتها.

اما المعالجة بالطريقة الثانية فقد تضمنت اجراء بلمرة متجانسة بالجذور الحرة للاصرة الفاينيلية الموجودة في الراتنجات الفينولية المحضرة حيث تم الحصول على ثلاث راتنجات جديدة امتازت بمقاومتها للذوبان في جميع المذيبات العضوية وبثباتها الحراري العالي.

تم تشخيص جميع المركبات المحضرة من خلال مطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية بالاضافة الى تحليل العناصر لبعض منها كما تم تعيين درجات التلين علاوة على تعيين قيم اللزوجة الجوهرية للراتنجات الذائبة.