

Modification of Novel phenol-formaldehyde Resins By Esterification

Mustafa Adnan Yasin

Chemistry division, Department of applied science
University of technology

Abstract:

This work involves the preparation of three phenol-formaldehyde resins that have pendant 1-cyclopentene-1,2-dicarboxylimidyl. The target compounds produce by condensation of N-(hydroxyl phenyl)-1-cyclopentene-1,2-dicarboxylimidyl with formaldehyde under conditions similar to those in Novolac preparation. The prepared resins were modified by esterification of phenolic hydroxyl groups in the prepared resins *via* treatment with benzoyl, acryloyl, methacryloyl and cinnamoyl chlorides respectively in the presence of triethylamine. The synthesis compounds were characterized by FTIR and U.V spectral data and determined softening points of crystalline solid resins, intrinsic viscosities of soluble resins.

Introduction:

Phenol-formaldehyde resins are the oldest commercial synthetic polymers, first introduced around (100) years ago^(1,2). Since the discovery of phenol-formaldehyde resin in 1907 many attempts have been carried by several workers to incorporate structural modifications⁽³⁻⁵⁾.

Phenolic resins are the most important thermosetting resins which are used in a wide variety of applications include varnishes, adhesives, laminates, casting, binders and surface coatings industries due to their high performance properties namely; high mechanical and chemical resistance, strong adherence and good absorptivity of fillers⁽⁶⁻⁸⁾.

Modifications were performed through using of aldehydes other than formaldehyde or by using different phenols to obtain new resins having new properties.

Phenolic resins were converted into a hard three dimensional crosslinked network through modification. The primary requirement for high-temperature performance necessitates the selection of polyfunctional phenolic resins and curing agents are capable of creating high crosslink densities^(9,10).

In the work three phenol-formaldehyde resins were prepared by poly condensation of N-(hydroxylphenyl) 1-cyclopentene-1,2-dicarboxylimidyl with formaldehyde under conditions similar to those in Novolac preparation.

Experimental:

Chemicals used in this work are supplied from Sigma Aldrich and Fluka companies and are used without further purification.

Melting points were determined on Gallen Kamp capillary melting point apparatus and were uncorrected. IR spectra were recorded on a Shimadzu FTIR^{٨٠٠٠}, U.V. spectra were recorded on Shimadzu UV-VIS recorder spectrophotometer UV-١٦٠. C.H.N. analyses were determined by Perkin-Elmer ٢٤٠ element analyzer. Softening points were determined on Thermal Microscope Reichert Thermover, SP١, ١٦٠. Intrinsic Viscosities were determined with automatic viscometer at ٢٥°C using acetone as a solvent.

١- Preparation of N-(hydroxyphenyl) ١-cyclopentene-١,٢-dicarboxyl Amic acids

Amic acid were prepared according to literatures^(١,٧) by allowing ١-cyclopentene-١,٢-dicarboxylic anhydride to react with o, m and p-aminophenols using acetone as a solvent. The produced amic acids were purified by recrystallization from ethanol.

Table (١) lists melting points, percent yields and major IR absorptions of the prepared acids.

٢- Preparation of N-(hydroxyl phenyl) ١-cyclopentene-١,٢-dicarboxylimidyl

The titled compounds were prepared according to literature procedures^(١٦,١٧) 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 (٢).

٣- Preparation of N-(hydroxyl phenyl) ١-cyclopentene-١,٢ dicarboxylimidyl Phenol-Formaldehyde Resins Via Poly Condensation

The titled compounds were prepared according to literature procedures^(١١,١٢) with few modifications: (١,٨٩ gm, ٠,٠١ mole) of N-(hydroxyl phenyl) ١-cyclopentene-١,٢-dicarboxylimidyl, (١ ml, ٠,٠٠٨ mole) of formaline (٣٧%) and (١٠ 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 (٠,١ ml) of concentrated sulphuric acid and (٠,٥ ml) of distilled water.

The acid was added dropwise with stirring then the mixture was refluxed for (٣ hrs) at (١١٠°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.

Modification of Novel phenol-formaldehyde Resins By Esterification.....

Mustafa Adnan Yasin

The produced polymer was purified by dissolving in DMF followed by reprecipitation with excess water.

Finally obtained pure polymer was dried in an oven at (٧٠-٧٥)° C for (٢٤ hrs). Table (٣) lists percent conversions, softening points, colors, intrinsic viscosities and table (٤) lists U.V absorptions and major IR absorptions of the prepared polymers.

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

The titled compounds were prepared according to literature procedures (٢٠) with minor modifications: In a suitable round bottomed flask fitted with a dropping funnel was dissolved (٠,٠١ mole) of the prepared resin (١-cyclopentene-١,٢-dicarboxylimidyl phenol-formaldehyde) resin in (٤٠ ml) of DMF. To the resulted solution (٠,٠١ mole) of triethylamine was added followed by dropwise addition of (٠,٠١ mole) of benzoyl chloride with stirring and cooling, then stirring was continued for another (٨ hrs).

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 (٤) and (٥) lists percent yields, softening points, intrinsic viscosities, colors, U.V. absorptions and major IR absorptions of the prepared N-(hydroxyl phenyl)١-cyclopentene-١,٢-dicarboxylimidyl benzoyloxy phenyl-formaldehyde resins.

٥- 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 (٤) and (٥) lists softening points, percent yields, colors, intrinsic viscosities, U.V. absorptions and major IR absorptions of the prepared ١-cyclopentene-١,٢-dicarboxylimidyl methacryloyloxy phenyl-formaldehyde resins.

٦- 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 (٤) and (٥) lists softening points, percent yields, colors, intrinsic viscosities, U.V. absorption and major IR absorptions of the prepared ١-cyclopentene-١,٢-dicarboxylimidyl acryloyloxy phenyl-formaldehyde resins.

٧- 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 (٤) and (٥) lists softening points, percent yields, colors, intrinsic viscosities, U.V. absorptions and major IR absorptions of the prepared γ -cyclopentene- γ , δ -dicarboxylimidyl cinnamoyloxyphenyl-formaldehyde resins.

Discussion and Results:

The core of this work is to introduce prepared γ -cyclopentene- γ , δ -dicarboxylimidyl to produce new resins with new properties. In order to perform this target must be includes preparation of three N-(hydroxyl phenyl)- γ -cyclopentene- γ , δ -dicarboxylic acids by reaction of γ -cyclopentene- γ , δ -dicarboxylic anhydride with o, m and p-amino phenols and prepared N-(hydroxyl phenyl)- γ -cyclopentene- γ , δ -dicarboxylimidyls were dehydrated from the corresponding amic acids by using fusion technique.

Poly condensation of the prepared imides with formaldehyde under conditions similar to those in Novolac preparation was performed to produce three phenol-formaldehyde resins having pendant γ -cyclopentene- γ , δ -dicarboxylimidyls. modified of the prepared phenolic resins by esterification of phenolic hydroxyl groups via treatment of the prepared phenolic resins with different acid chlorides including benzoyl, acryloyl, methacryloyl and cinnamoyl chlorides in the presence of triethyl amine to produce the corresponding benzoate, acrylate, methacrylate and cinnamate esters.

Physical properties, U.V. and major IR absorptions of the prepared resins and cured resins via esterification are listed in Tables (١,٢,٣,٤,٥). IR spectra of the prepared (γ -cyclopentene- γ , δ -dicarboxylimidyl phenol-formaldehyde) resins revealed a clear band in the region $(3410-3380)cm^{-1}$ 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 $(1780-1720)cm^{-1}$ and $(1210-1167)cm^{-1}$ due to ester (C=O) and ester (C-O) respectively.

On the other hand U.V spectra of the modified resins showed absorptions at λ_{max} $(331-344)nm$ due to $(\pi \rightarrow \pi^*)$ transitions in the conjugated system of carbonyl groups with phenyl ring in imide moiety and phenyl ring with attached benzoate, methacrylate and cinnamate groups^(٧).

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

Modification of Novel phenol-formaldehyde Resins By Esterification.....

Mustafa Adnan Yasin

It is noticeable that most of the cured resins by esterification are dark oils or low softening point^(٢٢-٢٥) resins which are soluble in many organic solvents including (Acetone, CHCl₃, DMSO, DMF, Dioxane, THF) but are insoluble in (methanol and benzene) and have low intrinsic viscosities ranged from (٠,١٢-٠,٤٤) 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.^(٢١,٢٢)

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

Comp. No.	Compound Structure	Yield %	Meltin g point C°	IR absorptions, cm ⁻¹			
				v(O-H)	v(N-H)	v(C=O) carboxylic	v(C=O) amide
١		٩٠	١٧٣	٣٣٩٥	٣١٦٤	١٦٩٧	١٦٦٠
٢		٩٢	١٨٥	٣٣٣٦	٣١٦١	١٧٠٠	١٦٦٠
٣		٩٠	١٩٥	٣٣٠٠	٣١٧٠	١٦٩٩	١٦٥٠

Table (٢) Melting points, Percent yields and Major IR absorptions of the prepared Imides

Comp. No.	Compound Structure	Yield %	Meltin g point C°	IR absorptions, cm ⁻¹			
				v(O-H) phenolic	v(C=O) imide	v(C=C) vinylic	v(C-N)
٤		٧٧	١٧٣	٣٣٦٠	١٧٠٠	١٦٤٢	١٤٠٠

Modification of Novel phenol-formaldehyde Resins By Esterification.....

Mustafa Adnan Yasin

٥		٨٠	١٨٥	٣٣٥٠	١٧٠٨	١٦٢٠	١٣٩٠
٦		٧٩	١٩٥	٣٤٠٠	١٧٠٢	١٦١٠	١٤٠٠

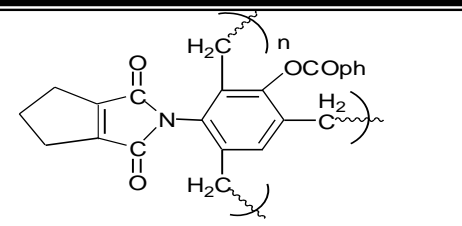
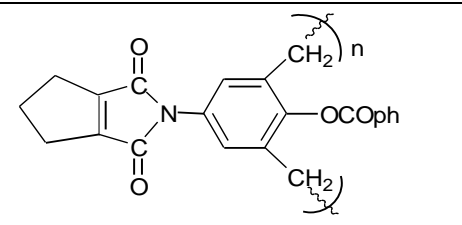
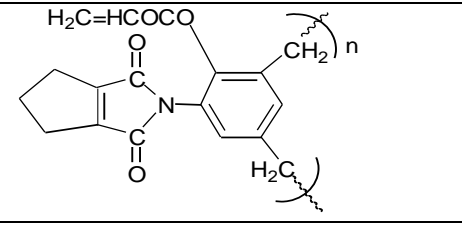
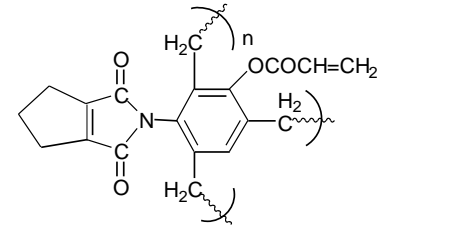
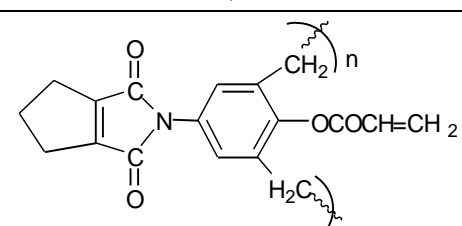
Table (٣) Physical properties of the prepared phenolic resins

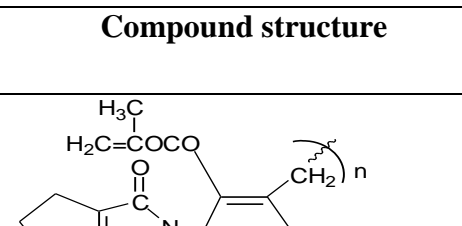
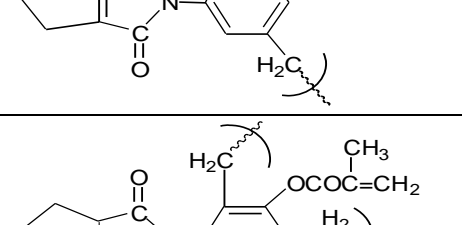
Comp. No.	Compound Structure	Conv. %	Softening point	Color	[η] dL/gm
٧		٧٧	٢٥٠-٢٦٠	Brown	٠,٧٢
٨		٧٥	٢٥٥-٢٦٥	Yellow	٠,٨٩
٩		٧٢	٢٣٠-٢٤٠	Brown	٠,٨٣

Table (٤) Physical properties of (imidyl benzoyloxy phenyl-Formaldehyde) Resins, (imidyl methacryloyloxy phenyl-Formaldehyde) Resins, (imidyl acryloyloxy phenyl-Formaldehyde) Resins and (imidyl cinnamoyloxy phenyl-Formaldehyde) Resins.

Comp. No.	Compound structure	Yield %	Softening point	Color	[η] dL/gm
١٠		٧٥	oil	Deep brown	٠,١٥

Modification of Novel phenol-formaldehyde Resins By Esterification.....
 Mustafa Adnan Yasin

١١		٧٧	oil	Deep brown	٠,٢٦
١٢		٧٥	oil	Deep yellow	٠,١٩
١٣		٧٠	٥٨-٧٠	Brown	٠,٣٣
١٤		٧٣	٧٧-٩١	Brown	٠,٤٤
١٥		٧٧	٥٩-٦٧	Brown	٠,٣٦

Comp. No.	Compound structure	Yield %	Softening point	Color	[η] dL/gm
١٦		٧٧	Oil	Brown	٠,١٢
١٧		٧٥	Oil	Yellow	٠,١٨

Modification of Novel phenol-formaldehyde Resins By Esterification.....
Mustafa Adnan Yasin

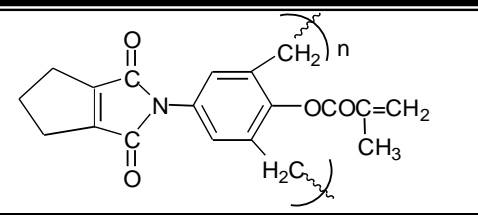
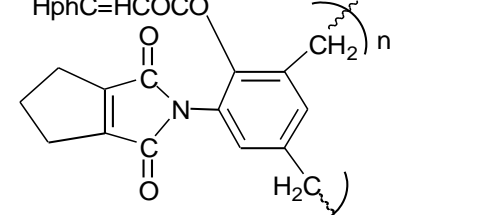
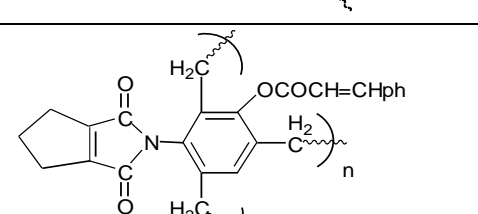
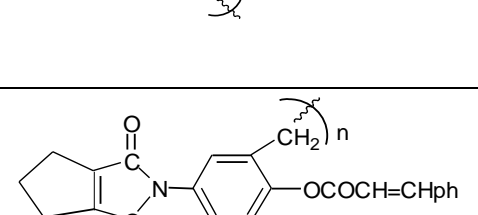
١٨		٨٥	٦٦-٧٩	Deep brown	٠, ١٥
١٩		٦٦	٥٨-٧٣	Deep yellow	٠, ١٣
٢٠		٧٢	Oil	Brown	٠, ١٧
٢١		٦٤	Oil	Brown	٠, ٢٧

Table (٥) Spectral absorption data of phenolic resins, (imidyl benzoyloxy phenyl-Formaldehyde) Resins, (imidyl methacryloyloxy phenyl-Formaldehyde) Resins, (imidyl acryloyloxy phenyl-Formaldehyde) Resins and (imidyl cinnamoyloxy phenyl-Formaldehyde) Resins.

Comp. No.	IR absorptions, cm ⁻¹						U.V. Abs. λ max, nm
	ν(C=O) Ester	ν(C-O) Ester	ν(C=O) Imide	ν(C-N) Imide	ν(C=C) vinylic	ν(O-H) phenolic	
٧	-	-	١٧١٠	١٣٨٠	١٥٨٣	٣٣٨٥	٢٨٠
٨	-	-	١٧٠٥	١٣٧٧	١٥٩٢	٣٣٩٠	٢٨٥
٩	-	-	١٧٠٥	١٣٨٥	١٥٩٠	٣٤١٠	٢٩٣
١٠	١٧٧٠	١٢١٠	١٧١٠	١٤٠٥	١٥٧٠	-	٢٦٥
١١	١٧٨٥	١١٩٩	١٦٩٥	١٣٩٦	١٥٧٧	-	٢٦٢
١٢	١٧٨٢	١٢١٥	١٦٩٩	١٤١٠	١٥٩٠	-	٢٦٠
١٣	١٧٦٠	١٢٠٥	١٧٢٠	١٣٩٥	١٥٧٦	-	٣٣٢
١٤	١٧٦٠	١١٩١	١٧١٠	١٤٠٥	١٦١٠	-	٣٣٤
١٥	١٧٥٥	١١٩٥	١٧٢٠	١٤٠٠	١٥٩٠	-	٣٣٧
١٦	١٧٢٠	١١٩٥	١٦٥٠	١٣٩٠	١٥٨٠	-	٣٣٦
١٧	١٧٤٠	١١٦٧	١٦٧٧	١٣٨٤	١٥٨٣	-	٣٣٤
١٨	١٧٢٥	١١٧٤	١٦٨٤	١٣٩٢	١٦٠٤	-	٣٤٣
١٩	١٧٣٥	١٢٠٥	١٦٦٠	١٣٨٩	١٥٧٩	-	٣٣٦
٢٠	١٧٥٦	١٢٠٢	١٧٣٠	١٣٧٧	١٦١٠	-	٣٣٣
٢١	١٧٦٤	١١٩٧	١٦٩٩	١٣٨٣	١٥٩٣	-	٣٣٨

Modification of Novel phenol-formaldehyde Resins By Esterification..... Mustafa Adnan Yasin

References

- ١- Wang, X.M. and Reidl, B., ١٩٩٥ . The effects of temperature and humidity on phenol-formaldehyde resin bonding. Wood science and Technology., ٢٩:٢٥٣.
- ٢- Pavlos, C.T. and Flanagan, L.W., ١٩٩٧. The mechanism of phenolic polymer dissolution. Macromolecules. , ٣٠:٤٦٥٦.
- ٣- Gao, J.G. and Liu, Y.F., ٢٠٠١. Thermal properties of Boron-Nitrogen containing phenol-formaldehyde resin. European Poly. J., ٣٧:٢٠٧.
- ٤- Liu, Y.G. and Gao, J.G., ٢٠٠٢. Synthesis, characterization and thermal properties of Novel phenolic resins. Polymer Degradation and stability., ٧٧:٩٤٥.
- ٥- Vaughan, J.G., Lackey, E. and Green, D., ٢٠٠٤. New fast cure for phenolic resins. Composites., ٤:٧٢٠.
- ٦- Hussien, A.M., ٢٠٠٠. Synthesis of several new N,N-disubstituted Citraconamic and Itaconamic acid esters and their applications as plasticizers for poly(vinyl chloride). Iraqi Journal of chemistry., ٢٦(٤):٨١٣.
- ٧- Hussien, A.M., ٢٠٠٢. Synthesis of N,N'-substituted bismaleamate esters and their applications as plasticizers for poly(vinyl chloride). Iraqi Journal of chemistry, ٢٨(٢):٣٤٧.
- ٨- Benard, F., J.Y. Buzare, I. Campistron, A. Laguerre, F. Laval, ٢٠٠٧. Influence of silica fillers during the electron irradiation of DGEBA/TETA epoxy resins, part III: Solid-state NMR investigations, Polymer Degradation and Stability, ٩٢: ٧٨٥.
- ٩- Situ, Y., J. Hu, H. Huang, H. Fu, H. Zeng and H. Chen, ٢٠٠٨. Synthesis and application of phenolic resin internally toughened by chain extension polymer of epoxidized soybean oil. Front. Chem. China, ٣(٢): ٢٣٥.
- ١٠- El-Tayeb, N.S.M., ٢٠٠٩. Development and characterization of low-cost polymeric composite materials. Materials and Design, ٣٠: ١١٥١.
- ١١- Xu, S., H. Kudo, T. Nishikubo, S. Nakamura and S. Numata, ٢٠١٠. Model reactions of calixarenes and their esterified derivatives with glycidyl phenyl ether for thermal curing reactions of epoxy resins. Polymer Journal, ٤٢: ٤٥٦-٤٦٣.
- ١٢- Samper, M.D., V. Fombuena, T. Boronat, D. García-Sanoguera and R. Balart ٢٠١٢. Thermal and Mechanical Characterization of Epoxy Resins (ELO and ESO) Cured with Anhydrides. Journal of the American Oil Chemists' Society, Online publication.
- ١٣- Shen, H., A.J. Lavoie, S.R. Nutt, ٢٠٠٣. Enhanced peel resistance of fiber reinforced phenolic foams, Composites: Part A, ٣٤: ٩٤١.
- ١٤- Çolak, A., T. Çoşgun and A.E. Bakırcı, ٢٠٠٩. Effects of environmental factors on the adhesion and durability characteristics of epoxy-bonded concrete prisms. Construction and Building Materials, ٢٣: ٧٥٨.
- ١٥- Custodio, J., J. Broughton and H. Cruz, ٢٠٠٩. A review of factors influencing the durability of structural bonded timber joints. International Journal of Adhesion & Adhesives, ٢٩: ١٧٣.
- ١٦- Mohamed, T., ١٩٩٩. Synthesis, polymerization and curing of N-substituted Citraconimidyl acrylates. J. Poly. Sci., ٣٧: ٤٢٧.
- ١٧- Mohamed, T., ١٩٩٠. Synthesis of several new N-aryl Citraconisoimides from the corresponding amic using different dehydrating agents. Ibn Al-Haitham Journal for pure and applied sciences., ٢: ٦٩.
- ١٨- Abdulameer, I., ٢٠٠٠. Synthesis of phenolic resins with pendant phthalisoimides. J. Poly. Sci., ٣٨: ٣٢٤٤.

Modification of Novel phenol-formaldehyde Resins By Esterification.....

Mustafa Adnan Yasin

- ١٩- Berzinij, A.S., ٢٠٠٢. Synthesis of Phenol-Formaldehyde containing pendant Itaconamic, Itaconimide and poly(N-substituted Itaconimides). Designed monomers and polymers., ٦(١):١١٥.
- ٢٠- Hussien, A.M., and Al-Obydi, K.K., ٢٠٠٣. Synthesis and polymerization of N-substituted phthalimidyl acrylates. National journal of chemistry., ١٢:٥٧٦.
- ٢١- Al-Azzawi , A.M., and Ali , M.S., ٢٠٠٧. Synthesis, Characterization and Evaluation of Antibacterial Activity of Several New ١,٨-naphthalimides Containing Benzothiazole Moiety. NJC., ٢٥,١٥٨-١٧٠.
- ٢٢- Al-Azzawi , A.M., and Ali , M.S., ٢٠٠٧ Modification phthalimidyl phenol-formaldehyde resins Via Esterification. Journal of Al-Nahrain University., ١٠:٣٨-٤٥.
- ٢٣- Al-Azzawi , A.M., and Ali , M.S., ٢٠٠٨ synthesis and curing of novel phenol-formaldehyde containing pendant citraconimides. Journal of Al-Nahrain University ١١(٣), ١٥-٣٠.
- ٢٤- M. A. Yasin, MSc Thesis Chem..Dept. college of sci. Univ. of Baghdad (٢٠٠٧).
- ٢٥- M. S. Ali, MSc Thesis Chem..Dept. college of sci. Univ. of Baghdad (٢٠٠٦).

الخلاصة :

هذا البحث تضمن تحضير ثلاث راتنجات فينول-فورمالديهايد حاوية على مجاميع متدللية من مركب ١-سايكلوبنتين -٢,١-ثنائي كاربوكسيل ايميديل تم انتاج تلك المركبات بواسطة التكتيف للمركب N- (هيدروكسي فينيل)-١-سايكلوبنتين-٢,١-ثنائي كاربوكسيل ايميدات مع الفورمالديهايد تحت ظروف مماثلة لتلك التي في تحضير النوفولاك . تم تحويل الراتنجات المحضرة بواسطة الاسترة لمجاميع الفينول المعوضة في الراتنجات الفينولية من خلال معاملتها مع كل من كلوريد البنزويل, الاكريلويل, الميث اكريلويل والسينامويل على التوالي بوجود ثلاثي اثيل امين . الراتنجات الناتجة من هذا التفاعل ذات مواصفات جديدة مما يتيح استخدامها في مجالات مختلفة تتفق مع مواصفاتها. تم تشخيص هذه الراتنجات المحضرة وذلك من خلال مطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية بالاضافة الى ذلك تم تعيين درجات التلين علاوة على تعيين قيم اللزوجة الجوهرية للراتنجات الذائبة .