

CONCLUSIONS

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The following conclusions can be extracted from the previous results:

1. new curable resins such as unsaturated polyester and vinyl ester resins based on rosin adducts were prepared.
2. New vinyl ester resins based on rosin were prepared by preparation of epoxy resins from MPA adducts followed by reaction with acrylic or methacrylic acids.
3. rosin was incorporated in the vinyl ester and UP resins so as to increase the miscibility of the synthesized resins with styrene monomer.
4. UP was obtained from condensation of APA or MPA adducts as dibasic acid with EG and PG as glycols. AdA and PA were used to study the effect of incorporation either aliphatic or aromatic moieties on properties of UP resins.
5. It was observed that upon raising the condensation temperature of reactants from 180 °C to 200 °C, about 70 % of the total quantity of water removed rapidly then reduces smoothly and slowly near to the end of reaction.
6. Molecular weight data of UP indicate that the degree of polymerization was increased with using PA and MPA as dibasic acids and EG as glycol. On the other hand, the degree of polymerization was decreased with using AdA and APA as dibasic acids and PG as glycol.
7. The curing exotherms of UP resins based on APA have greater t_{\max} and lower T_{\max} values than that UP resins based on MPA when cured with styrene hardener at different temperatures. On

the other hand, it can be observed that the structure of UP based on AdA shows high temperature T_{max} and low curing time t_{max} than UP based on PA.

8. Data of curing indicate that incorporation of PG in UP structure decreases curing times although UP resins based on PG have low MA content. This observation was referred to fact that PG increases the miscibility between UP and styrene monomer. The increment of miscibility between UP and styrene increases the probability of curing of UP resins which decreases the curing time.
9. The curing of the vinyl ester resins with unsaturated polyester resins in presence of styrene indicates that the curing times were reduced and the cure exothermic temperatures were increased by the incorporation of VE into the cross-linked networks.
10. Curing data indicate that UP/AVEMPR/styrene resins have lower t_{max} and higher T_{max} values than UP/MAVEMPR styrene resins. This can be attributed to ability of styrene to react with divinyl monomers based on acrylates than that based on methacrylates.
11. DSC measurements indicate that UP resins based on MPA, PG have lower ΔT_g values than UP resins based on APA and EG. On the other hand UP resins based on MPA have higher T_g than that UP resins based on APA. This indicates that the cured UP/styrene resins based on MPA have a tendency to form dangling styrene chains which are not complete cured.

12. DSC measurements indicate that, the cured UP/styrene resins have high crosslink densities when PG, APA and AdA were incorporated in UP resins.
13. It was found that the crosslinking conversion (%) increases as the amount of VE increases and it have much pronounced effect on conversion (%). The increment of conversion (%) with increasing contents of both AVEMPR and MAVEMPR crosslinkers suggests that the obtained networks contain either highly crosslinked copolymer or more of the linear copolymer chains are linked into the gel network.
14. It was also observed that UP/MAVEMPR has a low conversion (%) values than that determined for crosslinked copolymers with AVEMPR.
15. The mechanical properties of cured UP styrene films was increased when APA replaced MPA in structure of UP resins.
16. The cured UP/styrene resins based on PG posse's good mechanical properties than that based on EG.
17. The impact and pull-off resistance values of UP are reduced when AVEMPR replaces MAVEMPR.
16. The data of solvent and hot water resistances for cured UP resins indicate that these networks posses high resistance although they have ester groups.
19. The acid and alkali resistances were increased when APA, PG and AdA were used in preparation of crosslinked networks. The acid and alkali resistances were increased when AVEMPR was used as crosslinker instead of MAVEMPR.

20. Acid and alkali resistances can be referred to formation of UP high crosslink density of networks without formation of dangling chains.
21. The results of salt spray indicate that the strong adhesion of coatings increases coating performance from 75 to 95% for UP after 646h of exposure to the salt spray environment.
22. UP and VE resins based on rosin adducts can be used in linings for petroleum tanks, salt barges and ships, general chemical tankers, as well as exterior coatings for the bottoms, boot-topping, and decks.

SUMMARY

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Using the rosin offers the possibility of a lower source cost for producing useful products. Modification of rosin into useful materials with several applications such as; epoxy resins and reinforced unsaturated polyester, have seen increased research efforts in recent years. It is more economical to convert rosin into curable polymers by conversion rosin to difunctional monomers. These monomers can be reacted with unsaturated anhydride or epichlorohydrine to produce unsaturated polyester or epoxy resin, respectively. Epoxy resins can be reacted with acrylic or methacrylic acids to produce unsaturated vinyl ester resins.

The first part of the work consisted of studying the formation of rosin adducts using rosin acid as diene and maleic anhydride (MA) or acrylic acid (AA) as dienophile. In this respect, rosin acids were converted to levopimaric acid by thermal isomerisation technique. The produced adducts maleopimaric and acrylopimaric adducts MPA and APA were characterized by IR analysis. The produced APA and MPA adducts were used to prepare unsaturated polyester and vinyl ester resins. Unsaturated polyester resins were obtained by reacting the propylene or ethylene glycol, PG or EG, with different dibasic acids i.e., APA or MPA, maleic anhydride as a source of double bond, phthalic anhydride and adipic acid as acid compounds. The molecular weights of UP were determined by end group analysis. The second part of this work deals with preparation of epoxy and vinyl ester resins by reaction of MPA with EG followed by reaction with epichlorohydrine in the presence of NaOH as catalyst to produce epoxy resins. The produced epoxy resins with using MPA

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oligomers were designated as MPE. The chemical structure of the produced resins was determined by IR analysis. Epoxy equivalent weight and epoxy functionality of the produced resins were determined by conventional titration technique. New diacrylate and dimethacrylate vinyl ester resins were then synthesized by reaction of the terminal epoxy groups with acrylic and methacrylic acid in the presence of Triphenyl Phosphite (Ph_3P) as a catalyst. The chemical structures of the resulting vinyl ester resins were confirmed by $^1\text{HNMR}$ analysis.

The third part of the present study is to measure the curing exotherm and curing kinetics of the produced curable resins. The curing behavior of the unsaturated polyester resin, vinyl ester resins and styrene was evaluated at temperatures from 35 to 55 °C. The vinyl ester resins were used as crosslinking agents for unsaturated polyester resin diluted with styrene, using free radical initiator and accelerator. The curing exotherms of UP in presence of different weight percentages ranged from 0-20(wt %) and 40 (wt %) of styrene were measured by two techniques which based on variation of curing viscosity and temperatures with curing times. In this respect, the data showed that UP which having high MA content, have higher curing reaction time and lower heat evolved during curing reaction. It was found that the structure of the UP chains affecting the amount of heat liberated while curing as well as the curing time. The last part of this investigation is based on evaluating of prepared curable resins in the field of steel coating. The cured UP systems were evaluated in coating applications by measuring their mechanical properties and chemical resistance. The mechanical properties of cured films were determined by measuring their adhesion, impact resistance, hardness and bending.

SUMMARY

The chemical resistances of the cured films were estimated by measuring their acid, alkali and solvent resistances. The corrosion testing of cured films was evaluated by salt spray methods. The mechanical properties of the cured UP, vinyl ester and styrene systems were measured and correlated with the chemical structure of both UP and vinyl ester resins. The incorporation of a vinyl ester resin into the unsaturated polyester should improve the flexibility of the cured material. It was observed that the cured films have high UP crosslink densities show better corrosion protection efficiencies than the cured films with low crosslink density.

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ARABIC SUMMARY

جامعة الأزهر

كلية العلوم

قسم الكيمياء

تخليق وتقييم بعض لدائن إسترات الفينيل المعتمدة على مركبات طبيعية كطلاءات عضوية

رسالة مقدمة من

أشرف محمد السعيد عبد المنعم

الى

قسم الكيمياء - كلية العلوم - جامعة الأزهر

للحصول على درجة الدكتوراة

فى العلوم "الكيمياء العضوية"

تحت إشراف

ا.د/أيمن محمدى السيد عطا

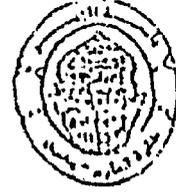
أستاذ كيمياء البوليميرات

بمعهد بحوث البترول

ا.د/ابراهيم عبد السلام صباح

أستاذ الكيمياء العضوية بعلوم الأزهر

كلية العلوم (بنين) جامعة الأزهر



جامعة الأزهر - كلية العلوم (بنين)
الدراسات العليا والبحوث

اسم مقدم الرسالة : أشرف محمد السعيد عبد المنعم

في موضوع :

Synthesis and Evaluation of some Vinyl Ester Resins Based on Natural Products as Organic Coatings

تخليق وتقييم بعض لدائن استرات الفينيل المعتمدة علي مركبات طبيعية كطلاءات عضوية

لجنة إشراف :

أ.د/ إبراهيم عبد السلام صباح الوظيفة : أستاذ الكيمياء العضوية بعلم الأزهر التوقيع
أ.د/ أيمن محمدي السيد عطا الوظيفة : أستاذ كيمياء البوليمرات بمعهد بحوث البترول التوقيع

أعضاء لجنة الحكم :

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أ.د/ إبراهيم عبد السلام صباح الوظيفة : أستاذ الكيمياء العضوية بعلم الأزهر التوقيع
أ.د/ أيمن محمدي السيد عطا الوظيفة : أستاذ كيمياء البوليمرات بمعهد بحوث البترول التوقيع

مدير إدارة الكليه

شؤون: التعليم

المختص

عميد الكلية

الملخص العربي

اهتمت الأبحاث في السنوات الأخيرة بتخليق راتنجات ذات تطبيقات صناعية من منتجات متوفرة ورخيصة الثمن مثل القلفونية، ومن أهم الراتنجات المحضرة من القلفونية راتنجات الإيبوكسي وكذلك راتنجات البولي استر غير المشبعة . وقد إهتمت هذه الدراسة بتحويل القلفونية الى مركبات ثنائية المجموعات الوظيفية حيث تتفاعل هذه المركبات مع أنهيدريد الأحماض غير المشبعة لتحضير مركبات البولي استر غير المشبعة ، كما تم تحضير راتنجات الإيبوكسي والتي يمكن تفاعلها مع حمض الأكريليك أو حمض الميثاكريليك لتحضير راتنجات فينيل الإستر غير المشبعة.

يركز الجزء الأول في هذا البحث على اجراء عملية تعديل لمركب القلفونية وتحويلها حراريا الى حمض الليفوبيمارك حيث يحتوى على روابط ثنائية متبادله يمكن تفاعلها مع أنهيدريد حمض الماليك أو مع حمض الأكريليك عن طريق تفاعل ديلز-الدر. وتم اثبات التركيب الكيميائي للمركبات الناتجة من هذا التفاعل عن طريق جهاز الأشعة تحت الحمراء.

تم تحضير مركبات البولي استر غير المشبعة من تفاعل متراكبات القلفونية المحضرة من تفاعل ديلز-ألد مع الاثيلين جليكول و مع البروبيلين جليكول في وجود أنهيدريد حمض الماليك كمصدر للروابط الثنائية غير المشبعة وكذلك وجود أنهيدريد حمض الفيثاليك وحمض الأديبك كمواد محسنة للخواص الكيميائية والفيزيائية للبولي استر الناتج . تم تعيين الوزن الجزيئي للمركبات الناتجة عن طريق تعيين المجموعات الوظيفية في نهاية سلسلة لبوليمرات . وقد تم التعرف على التركيب الكيميائي للراتنجات عن طريق تحاليل الأشعة تحت الحمراء والرنين النووي المغناطيسي لذرة الهيدروجين.

يركز الجزء الثاني في هذه الدراسة على تحضير مركبات الإيبوكسي ومركبات الفينيل استر وذلك بتفاعل حمض الليفوبيمارك مع الاثيلين جليكول ثم مع

إيبوكلووريد الهيدرين فى وجود هيدروكسيد الصوديوم كعامل حفاز ، وذلك لتحضير مركب الإيبوكسى . تم اثبات التركيب الكيمايى لمركبات الإيبوكسى المحضرة عن طريق تحاليل الأشعة تحت الحمراء ، وتم تعيين الوزن الإيبوكسى المكافئ وذلك لتعيين عدد مجموعات الإيبوكسى فى المواد الإيبوكسيه المحضرة . تم تحضير مركبات الفينيل استر لثنائى الأكريلك والميثاكريلك وذلك بتفاعل الإيبوكسى المحضر سابقا مع أحماض الأكريلك والميثاكريلك فى وجود ثلاثى فينيل الفوسفيت كعامل حفاز وأمكن توصيف مركبات الفينيل إستر المحضرة بواسطة جهاز الرنين النووى المغناطيسى لذرة الهيدروجين .

إهتم الجزء الثالث بدراسة وتعيين حرارة التشابك لمركبات البولى استرغير المشبعة والفينيل استر فى وجود الاستايرين عند درجات حرارة متفاوتة من ٣٥ الى ٥٥ درجة مئوية . تم اضافة الفينيل استر الى البولى استر بنسب تتراوح من ٥-٢٠% من وزن البولى استر حيث يعتمد تعيين حرارة التشابك على العلاقة بين درجة الحرارة الناتجة من التصلد والزمن ولوحظ أنه كلما زادت نسبه المالك أنهدريد فى البولى استر كلما زاد من زمن التصلد وقلت حرارة التفاعل ووجد أن شكل سلاسل البوليمر المتصلدة تعتمد على كمية الحرارة المنبعثة أثناء عملية التصلد . تم تعيين كفاءة التصلد لراتنجات البول استر المحضرة فى وجود الاستيرين وذلك عن طريق التحاليل الحرارية DSC.

فى الجزء الرابع من الدراسة تم تطبيق راتنجات البولى استرغير المشبعة كطلاءات لسطح الحديد وتم تقييم كفاءة تلك الطلاءات عن طريق قياس الخواص الميكانيكية وكذلك تقييم المقاومة الكيمايية للطلاءات . تم تقييم الخواص الميكانيكية للطلاءات الناتجة عن طريق قياس قوة الإلتصاق وتحمل التصادم ودرجة الصلادة وتحمل الإ نثناء. تم تقييم المقاومة الكيمايية للطلاءات الناتجة عن طريق قياس مقاومتها الأحماض والقلويات والمذيبات ،

وتم كذلك تقييم مقاومة التآكل للطلاءات الناتجة عن طريق اختبار مقاومة الأملاح. وقد لوحظ أن الخواص الميكانيكية للبولي استر الناتج تعتمد على التركيب الكيميائي له, حيث لوحظ أنه كلما زادت نسبة الفينيل استر المضافة إلى البولي استر كلما زادت درجة مرونة الطلاءات الناتجة ولوحظ أيضا كلما زادت درجة التشابك والتصلد كلما زادت من مقاومة البولي استر للأملاح والمحافظة على الحديد من العوامل المسببة للتآكل.