

Studying the mechanical properties , thermogravimetric analysis and flame resistance of novel IPNs based on some organophosphate resins and epoxy

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Key words : organophosphate resins , epoxy resin , mechanical properties , flame resistance , IPNs , TGA

Abstract

Tow organophosphate compounds namely triallyl phosphate (I) and Triphenyl phosphate (II) were prepared . The compound (I) was polymerized (addition polymerization) by adding ethyl methyl keton peroxide and Cobalt octate as accelerator to obtain triallyl phosphate resin (III) . The compound (II) was polymerized (condensation polymerization) by adding paraformaldehyde to obtain Triphenyl phosphate formaldehyde resin (IV) . These compounds were identified by elemental analysis , calculation of the percentage of phosphorus by gravimetric methods and infrared spectroscopy .

Some new interpenetrating polymer networks (IPNs) based on the prepared organophosphate resins and epoxy resin (5-25 %w/w) were prepared . Mechanical properties such as impact strength and hardness for these IPNs were studied and it was found the impact strength was increased with increasing

the content of organophosphate resins in the epoxy resin network while the hardness was decreased in comparison with epoxy resin alone because of the flexibility properties for organophosphate resins.

Moreover , thermal stability of the IPNs was evaluated by thermogravimetric analysis (TGA) . From some thermal stability parameters measured such as decomposition temperature , rate of decomposition , activation energy and char content , it was observed that the organophosphate resins were improved the thermal stability of the epoxy resin network .

Furthermore , flame resistance of these IPNs was investigated according to ASTM 568 . The results were indicated that the organophosphate resins increase flame resistance for the prepared polymeric networks by decreasing the rate of burning and weight loss .

Introduction

The bonding phosphorus with organic polymers such as epoxy resins occur significant changes in the properties . These properties include reducing flame resistance and increasing the forces of adhesion , solubility in polar solvents and thermal stability as well as improving mechanical properties ^(1,2) . The polymers containing phosphorus in the main chain prepare usually by condensation polymerization of

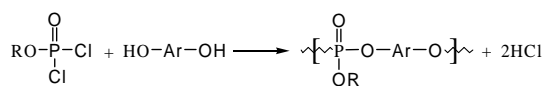
phosphorus compounds contained difunctional groups where the phosphorus is part from the main chain of the polymer through the bonds (P-C) , (P-O-C) or (P-N-C) . Some studies have been shown that the polymers containing bonds (P-C) are more stable against the hydrolysis and most difficult in the preparation ⁽³⁾ . The polymers containing bonds (P-O-C) such as organophosphates and phosphonates can be

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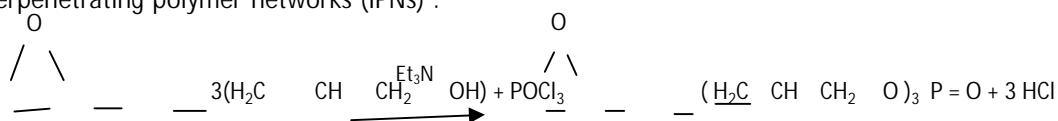
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obtained from the polymerization of phosphoro dichloridates with aromatic diols using alkaline earth halides agents as catalyst (4)



Epoxy resin, important thermosetting polymers, have wide industrial use as structural adhesives and matrix resins for reinforced composites. The cured resins are brittle and have poor resistance to crack propagation (5). However, toughness of epoxy resins has been increased by polymer blends or interpenetrating polymer networks (IPNs).

Inorganic thermoplastics are interesting materials as modifiers for epoxy resin from the viewpoint of maintenance of mechanical as well as thermal properties. One of the study (6) show that the preparation of flame retardant resins from the reaction of glycidol with phosphorus oxychloride as shown below.



These resins have low weight, good resistance to impact and corrosion, good flexibility and ease in the design so that it is used by the airlines as flame retardant materials. Other study (7) was indicated to the development of epoxy resin using interpenetrating polymer networks by mixing bisphenol A and phosphine oxide supported to diepoxide oligomers in the presence of siloxane as crosslinking agent, it was found that the glass

transition temperature was increased with increasing the elastic coefficient and strength of adhesion as well as an increase in the flame resistance for these polymeric networks.

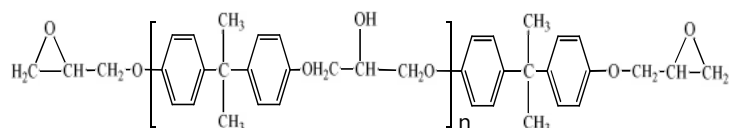
The aim of the present research is to improve the mechanical properties, thermal stability and flame resistance of epoxy resin during the preparation of new IPNs containing some organophosphates resins

Experimental

A- Chemicals

The chemicals used in this study were obtained from several sources as following: Phosphoryl chloride, N,N-dimethyl aniline, allyl alcohol, triethylene tetraamine, petroleum ether (b.p. 40-60 °C) and phenol

from Merck company. Paraformaldehyde, cobalt octate, ethyl methyl keton peroxide and epoxy resin from Arkoma company. Epoxy resin have the following structure:



B- Preparation of triallyl phosphate (I) (8)

The reaction vessel was charged with 102.5 ml (1.5 mole) allyl alcohol, 190.14 ml (1.5 mole) N,N-dimethyl aniline and 100 ml petroleum ether. This solution was mixed and cooled,

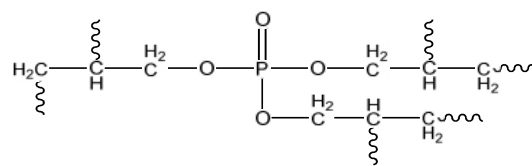
then solution of 46.61 ml (0.5 mole) of phosphoryl chloride in 100 ml petroleum ether was added dropwise over a period 60 min. The mixture was heated under reflux for

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one hour . The product was filtered and distilled under reduced pressure to yield yellow liquid (I) .

This product (I) was polymerized by efficient mixing with 5%w/w ethyl methyl keton peroxide and 2%w/w cobalt octate as accelerator to form viscous resin (III) ⁽⁹⁾ .The

chemical structure of this resin was shown below :

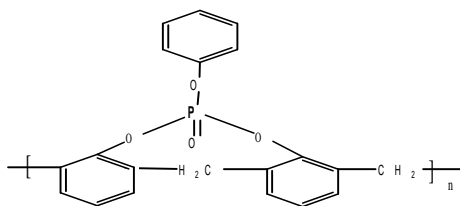


C- Preparation of triphenyl phosphate (II) ⁽⁸⁾

In a tow necked flask fitted with condenser and dropping funnel , it was placed 141.2 gm (1.5 mole) phenol , 190.14 ml (1.5 mole) N,N-dimethyl aniline and 100 ml petroleum ether . The components were mixed and cooled . Solution of 46.61 ml (0.5 mole) of phosphoryl chloride in 100 ml petroleum ether was added dropwise over a period 60

min . The solution was refluxed for 1.5 hour then cooled , filtered and evaporated to yield white solid product (II) .

54.38 gm of the product (II) was polymerized by mixing with 45 gm of Paraformaldehyde at 120 °C for 15 min to yield yellow very viscous-semisolid resin (IV) ⁽⁹⁾ .The chemical structure of this resin was shown below :



D- Preparation of the new interpenetrating polymer networks (IPNs)

Several IPNs consisting of different percent (5-25 %w/w) from the organophosphates compounds (I or II) and epoxy resin were prepared by efficient mixing for 3 min at room temperature . Curing agents were added gently including 5%w/w ethyl methyl keton peroxide and 2%w/w cobalt octate for polymerizing and curing the compound (I) , Paraformaldehyde for polymerizing and curing

the compound (II) and 30 %w/w triethylene tetraamine for curing the epoxy resin . The composites were lifted overnight at room temperature for curing , then the post cured at 120 °C for 3 hours . The composites were used for the mechanical properties , thermogravimetric analysis (TGA) and flame resistance studies .

Results and discussion

Identification of organophosphates and resins

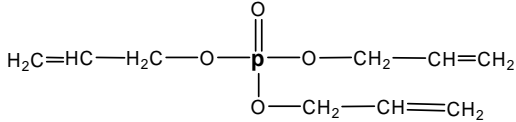
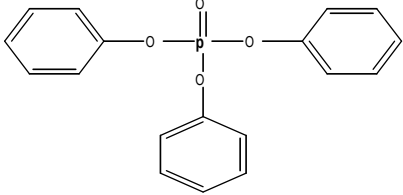
Some of the physical constants of the prepared organophosphates were shown in table (1) . These organophosphates were identified by elemental analysis (Eurovector S.P.A. VIA Torona 5 Melano Mod Euro EA3000) and calculation of the percentage of phosphorus by gravimetric methods ⁽¹⁰⁾ . It was found that the practical percentages of

carbon hydrogen and phosphorus were equivalent to theoretical values as assigned in table (2) . In addition , These organophosphates and their resins were also identified by infrared spectra (FTIR-8400 in the petrochemical company – Basra) as shown in figures (1-4) and table (3) .

Table (1) :Some physical constants of the prepared organophosphates

Name	Symbol	Color	Boiling point (Melting point) (°C)	Refractive index at 20°C (n _D ²⁰)	Yield %	Description of product
Triallyl phosphate	I	Yellow	113	1.447	88	liquid
Triphenyl phosphate	II	White	(48 – 50)	—	82	Solid

Table (2) : Elemental analysis data of the prepared organophosphates

Symbol	Chemical structure	Molecular weight	Elemental analysis Calculated / (Found)		
			C%	H%	P%
I		218.164	49.545 (49.743)	6.923 (6.981)	14.197 (14.342)
II		326.254	66.261 (66.476)	4.629 (4.654)	9.493 (9.285)

Transmittance (%)

Transmittance(%)

Wavenumber (cm⁻¹)

Figure (1) : Infrared spectrum of organophosphate (I)

Transmittance (%)

Wavenumber (cm⁻¹)

Figure (2) : Infrared spectrum of organophosphate (II)

Transmittance (%)

Transmittance (%)

Wavenumber (cm⁻¹)

Figure (4) : Infrared spectrum of organophosphate resin (IV)

Table (3) : The important bands in the infrared spectra for prepared organophosphates and resins

symbol	Stret. Vibr. Of C-H (alkene) (cm ⁻¹)	Stret. Vibr. Of C-H (aromatic) (cm ⁻¹)	Stret. vibr of C-H (aliphatic) (cm ⁻¹)	Stret.vibr. of C=C (cm ⁻¹)	Stret.vibr. of P=O (cm ⁻¹)	Stret. Vibr. Of P-O-C (cm ⁻¹)
I	3050 (M)	-	2950 (M)	1680 (S)	1250 (S)	1040 (S)
II	-	3080 (M)	-	1600 (S)	1350 (M)	1040 (M)
III	-	-	2950 (M)	-	1250 (M)	1040 (M)
IV	-	3100 (S)	2900 (S)	1600 (S)	1360 (M)	1020 (M)

M = Medium

S = Strong

Studying the mechanical properties of the prepared IPNs

Impact strength and hardness of prepared IPNs containing different weight percentages were studied in the petrochemical company – Basra according to the standard conditions .

Impact strength is the ability of a material to resist breaking under a shock loading or the ability to resist fracture under stress applied at high speed . Impact properties of the polymeric material are directly related to the overall toughness of the material . Toughness is defined as the ability of the polymer to absorb applied energy ⁽¹¹⁾ . Test specimens were evaluated according to the test specification of ASTM D-256 . Impact strength was calculated by the following equation :

$$\text{Impact strength} = \frac{\text{fracture energy required}}{\text{cross section area of the sample}}$$

Hardness is defined as the resistance of a material to deformation , particularly

permanent deformation , indentation , or scratching ⁽¹²⁾ . Two types of Durometers are most commonly used type A and type D . Due to the slightly harder sample being examined ; the Durometer hardness tester shore instrument Zwick type D-2240 was used in the present study .

It was observed that the impact strength of IPNs containing resin (III) increases with increasing the percentage of this resin in the epoxy network as shown in table (4) and figure (5) . This is belonged to aliphatic structures and side branching in the resin (III) as well as presence of the bonds (P-O-C) which give sufficient movement to distribute the energy on the polymeric chains ⁽¹³⁾ . Furthermore , these reasons also led to decrease the hardness of the epoxy network containing resin (III) as shown in table (4) and figure (6) .

Moreover, it was noted in the table (5) and figure (7) that the low weight percentages (5, 10, 15 %w/w) of the resin (IV) in the epoxy network increase the impact strength of prepared IPNs because the chemical bonds in the resin (IV) introduce the spaces and flexibility properties for the polymeric chains and then they disperse the energy in the form of mechanical reduction. In addition, the impact strength begins to decrease at higher percentages (20, 25 %w/w) but it remains high when compared to the impact strength of epoxy resin alone, this is due to arising the content of aromatic structures and cross-linking in the

prepared IPNs resulted from the presence of the resin (IV) which leads to increase the stiffness and restriction of the polymeric chains⁽¹⁴⁾. On the other hand, the reversible behavior was observed to measure the hardness of the prepared IPNs containing resin (IV) as shown in table (5) and figure (8). The hardness was reduced at the percentages (5, 10, 15 %w/w) and then increased slowly because of the considerable cross-link densities of the epoxy – organophosphate resin interpenetrating networks which take place at high percentages of the resin (IV)⁽¹⁴⁾.

Table (4) : Impact strength and hardness of IPNs based on resin (III)

IPNs based on		Impact strength J/cm ²	Hardness
Epoxy w/w %	Resin (III) w/w %		
100	0	2.65	61
95	5	3.81	58
90	10	5.01	55
85	15	6.79	52
80	20	7.70	47
75	25	8.24	45

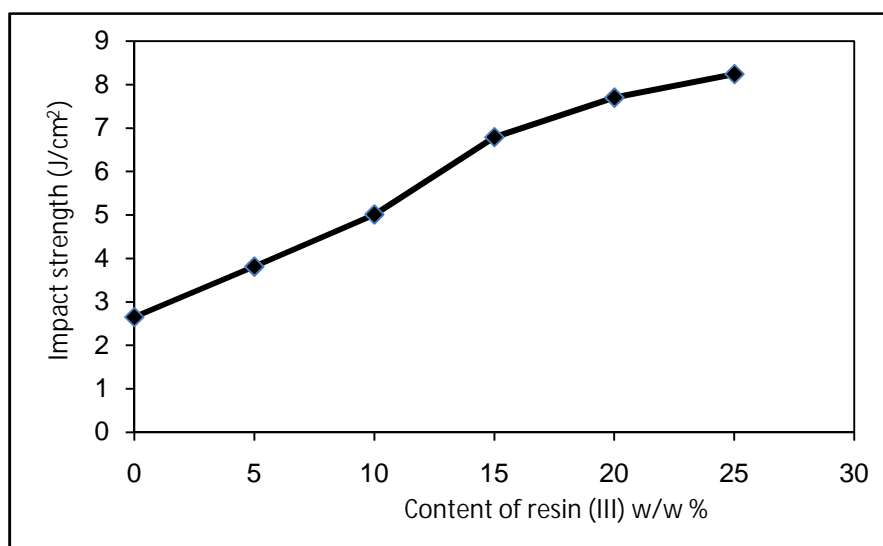


Figure (5) : Impact strength of prepared IPNs as a function of resin (III) content

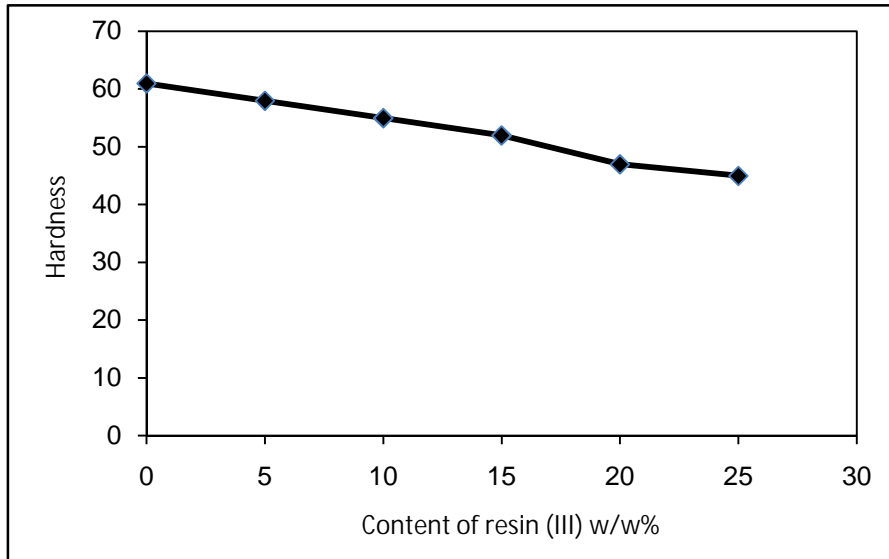


Figure (6) : Hardness of prepared IPNs as a function of resin (III) content

Table (5) : Impact strength and hardness of IPNs based on resin (IV)

IPNs based on		Impact strength J/cm ²	Hardness
Epoxy w/w %	Resin (IV) w/w %		
100	0	2.65	61
95	5	3.64	59
90	10	4.93	55
85	15	5.94	48
80	20	5.56	52
75	25	5.43	54

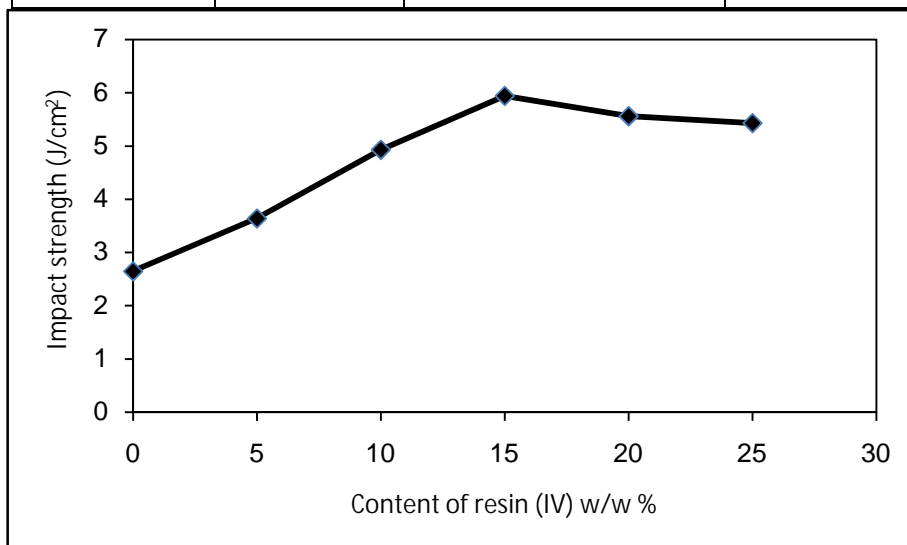


Figure (7) : Impact strength of prepared IPNs as a function of resin (IV) content

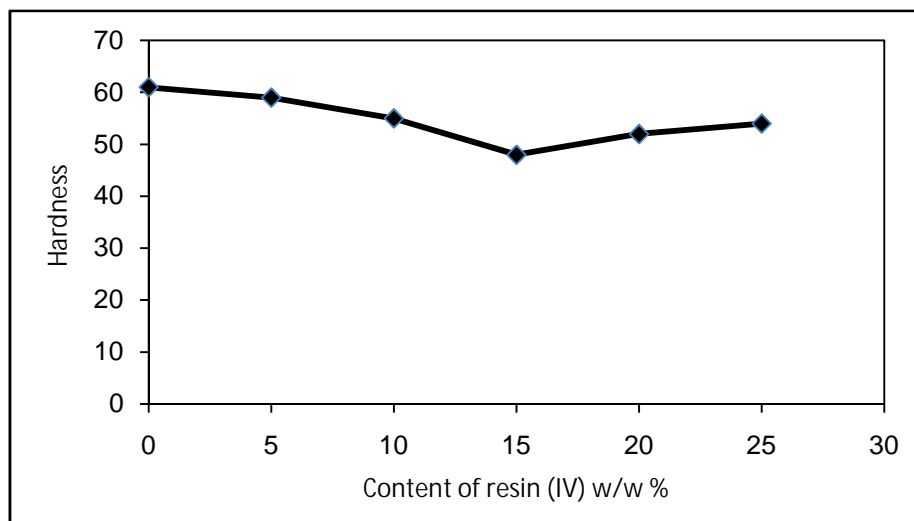


Figure (8) : Hardness of prepared IPNs as a function of resin (IV) content

Studying the thermogravimetric analysis of the prepared IPNs

Curves of the thermogravimetric analysis of the prepared IPNs were measured by TGA 50 H Shimadzu in micro analytical center – Cairo university – Egypt . The heating rate of 10 °C /min was employed under dynamic nitrogen atmosphere with the gas flow rate of 30 ml/min.

The thermograms in figures (9 ,10) were analyzed and several thermal stability parameters were determined from TGA curves as following :

1- Decomposition temperature (DT) .

The prepared IPNs of the organophosphates resins (III , IV) with epoxy resin were investigated based on the evaluation of the thermal stability parameters listed in tables (6 ,7) . The obtained data illustrate that the decomposition temperatures and activation energy of the IPNs increase with increasing the percentages of the organophosphates resins while the rate of decomposition decrease in comparison with epoxy resin alone . This is related to the strength of the bonds (P-O-C) which need additional heating energy to be broken ⁽¹⁵⁾ .

2-The rate of decomposition which was measured from the slopes of the TGA curves at DT .

3- The activation energy of the decomposition (E) was calculated from the Arrhenius plots between the rate of decomposition (ln k) and 1/T .

4- Half weight loss temperature ($T_{50\%}$) which represent the temperature in which the sample loses half of its total weight .

5- % char content which was determined from the TGA curves at 500 °C .

Moreover , it can be seen that the prepared IPNs have high char content residue due to the formation of high cross-linked resins . This residue was considered as insulated layer which decreases the decomposition of the lower layers for the polymeric networks ⁽¹⁵⁾ .

On the other hand , it is clearly seen from the tables (6 , 7) that the IPNs based on resin (IV) have higher thermal stability than those containing the resin (III) because of the aromatic structures presented in the resin (IV) which give high char content leading to increase the thermal stability ⁽¹⁶⁾ .

Table (6) : Some thermal stability parameters of IPNs based on resin (III)

IPNs based on		Decomp. temp. (°C)	Temp. of 50% wt. loss (°C)	Rate of decomp. (%/min)	Char content at 500 (°C)	Activation energy (KJ/mole)	Temp. range (°C)
Epoxy w/w %	Resin (III) w/w%						
100	0	213	275	4.8	12	20.25	190-275
95	5	219	288	3.7	16	32.43	200-288
90	10	225	313	3.5	20	35.52	215-313
85	15	232	319	3.2	22	40.35	220-319
80	20	244	325	2.9	25	43.97	230-325

Table (7) : Some thermal stability parameters of IPNs based on resin (IV)

IPNs based on		Decomp. temp. (°C)	Temp. of 50% wt. loss (°C)	Rate of decomp. (%/min)	Char content at 500 (°C)	Activation energy (KJ/mole)	Temp. range (°C)
Epoxy w/w %	Resin (IV) w/w%						
100	0	213	275	4.8	12	20.25	190-275
95	5	224	306	3.6	19	35.13	218-306
90	10	237	325	3.3	23	42.25	228-325
85	15	250	337	3.0	26	46.82	240-337
80	20	254	350	2.7	28	52.16	242-350

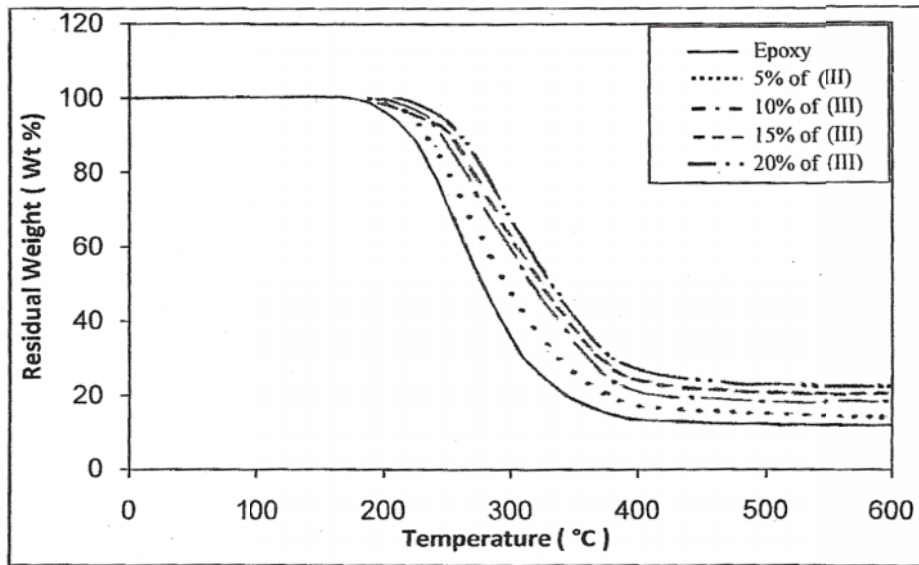


Figure (9) : TGA thermograms of the prepared IPNs based on resin (III)

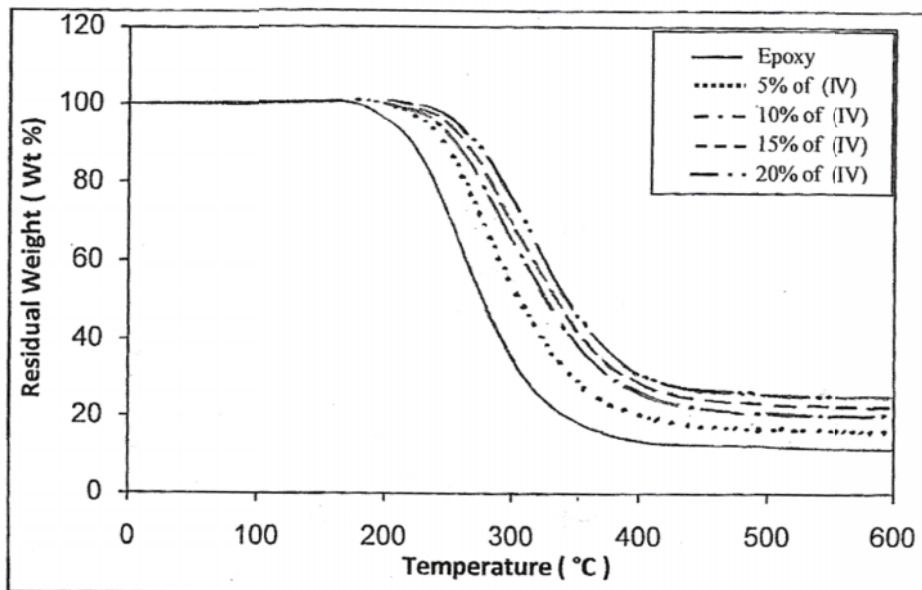


Figure (10) : TGA thermograms of the prepared IPNs based on resin (IV)

Studying the flame resistance of the prepared IPNs

The flame resistance of the prepared IPNs was measured according to standard specification (ASTM D568) . Rate of burning

was calculated depending on the following equation ⁽¹¹⁾ :

$$\text{Rate of burning} = \frac{\text{length of sample before burning} - \text{length of sample after burning}}{\text{time of burning}}$$

The weight loss of these IPNs was also calculated which gives evidence to behavior the sample as flame retardant material .

Rate of burning and weight loss of the prepared IPNs containing the resins (III , IV) were compared with the epoxy resin alone as shown in tables (8 , 9) and figures (11 -14) . It was found that rate of burning and weight loss were reduced with increasing the content of the resins (III , IV) in the epoxy network . This is attributed to the formation of char layer from phosphorus oxides which limits the amount of volatile fuel that can be produced

Conclusion

The new IPNs based on the organophosphate resins (III , IV) improved the mechanical properties of the epoxy resin according to increasing the impact strength and decreasing the hardness . Moreover , thermogravimetric analysis of these IPNs showed that the organophosphate resins especially the resin (IV) containing aromatic structures increase the thermal stability of the epoxy resin

by thermal degradation and insulates the underlying polymer from the heat of the flame , so that these oxides can inhibit the combustion reaction in the flame , reducing the efficiency of combustion and lowering the amount of heat that is produced during burning ^(17,18) . Furthermore , the IPNs containing the resin (IV) were exhibited high flame resistance in comparison with these depending on the resin (III) because the first resin have aromatic structures which increase the char content and flame resistance .

through the observation of different thermal stability parameters calculated . Also the flame resistance study of the prepared IPNs indicated that the rate of burning and weight loss were decreased as a result of the increasing content of prepared organophosphate resins in the polymeric networks .

Table (8) : Some flame resistance parameters of IPNs based on resin (III)

IPNs based on		Rate of burning (mm/sec)	Weight loss (gm)
Epoxy w/w %	Resin (III) w/w %		
100	0	2.45	0.52
95	5	1.85	0.41
90	10	1.43	0.34
85	15	1.35	0.31
80	20	1.28	0.29
75	25	1.25	0.25

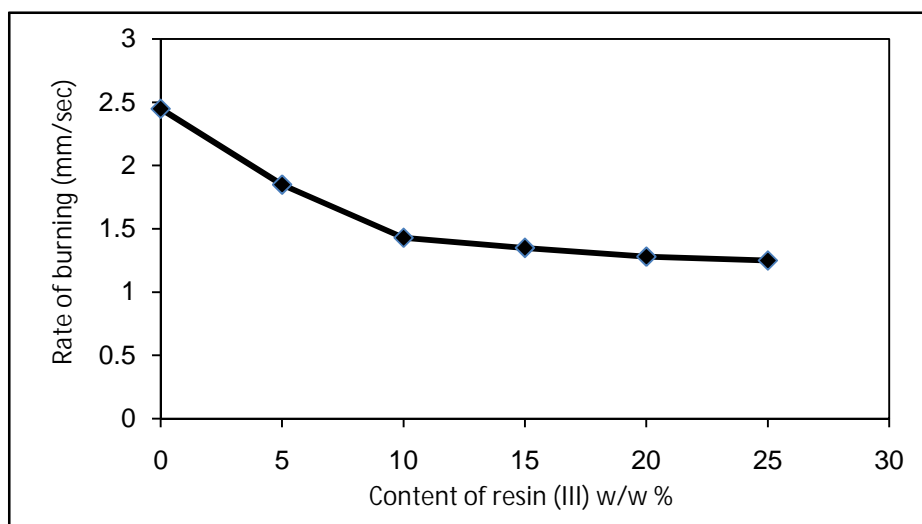


Figure (11) : Rate of burning of prepared IPNs as a function of resin (III) content

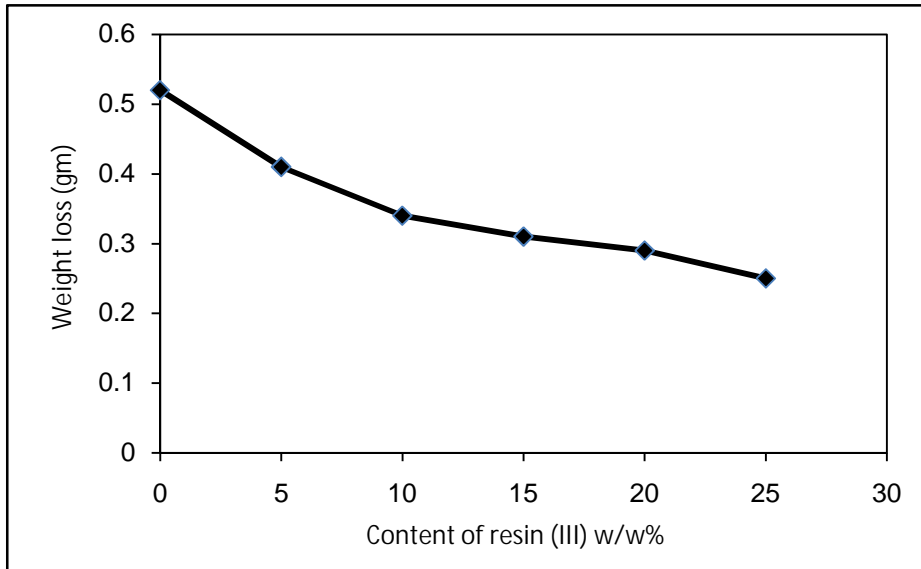


Figure (12) : weight loss of prepared IPNs as a function of resin (III) content

Table (9) : Some flame resistance parameters of IPNs based on resin (IV)

IPNs based on		Rate of burning (mm/sec)	Weight loss (gm)
Epoxy w/w %	Resin (IV) w/w %		
100	0	2.45	0.52
95	5	1.83	0.39
90	10	1.40	0.36
85	15	1.29	0.28
80	20	1.18	0.24
75	25	1.15	0.20

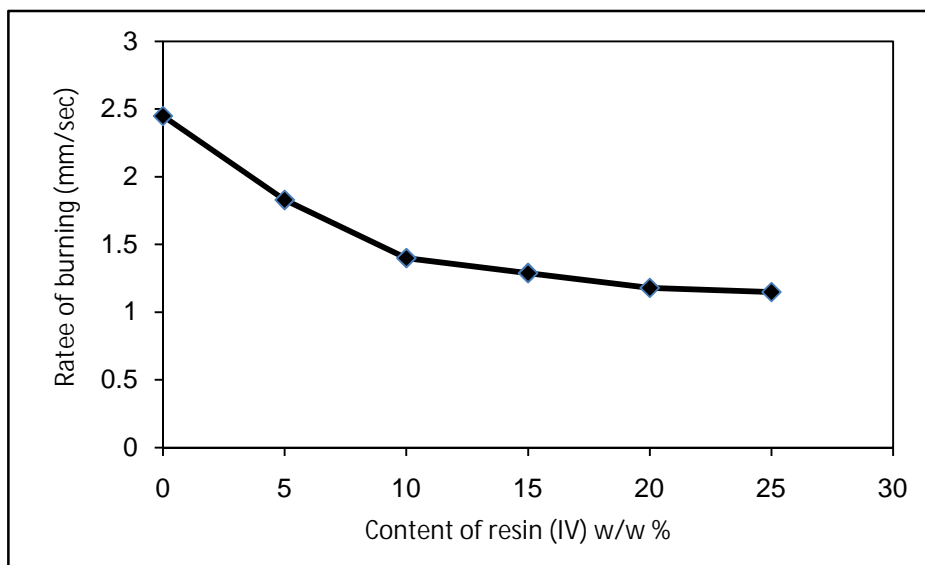


Figure (13) : Rate of burning of prepared IPNs as a function of resin (IV) content

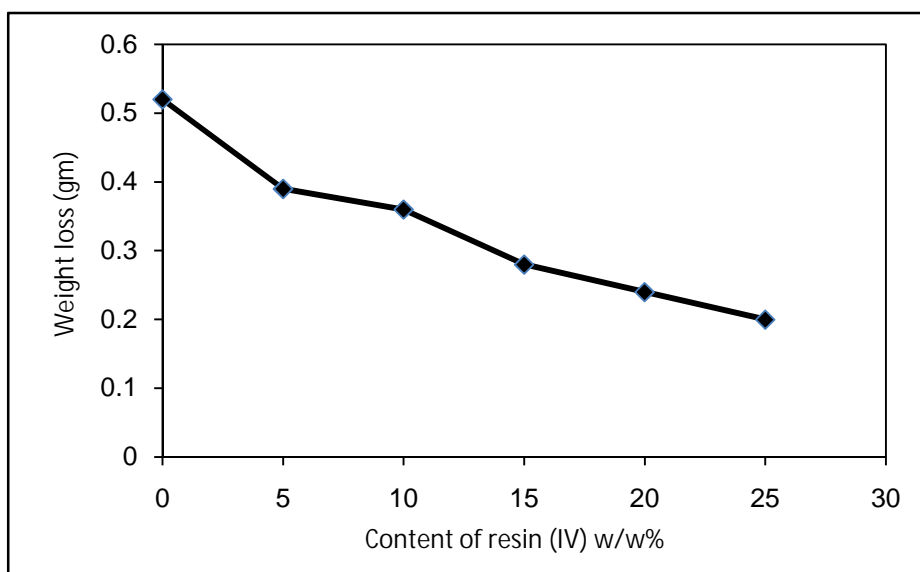


Figure (14) : weight loss of prepared IPNs as a function of resin (IV) content

References

- 1- F.R.Hartley , "The Chemistry of Organophosphorus Compound" , John Wiley and Sons , New York , vol.2 , p.33, (1992) .
- 2- S.Matiti , S.Banerjee and S.K.Palit , Prog. Poly. Sci. , 18 , 227 (1993) .
- 3- H.F.Mark and N.G.Gaylord , "Encyclopedia of Polymer Science and Technology" , Vol.10 , p.123-135 , U.S.A. (1969) .
- 4- H.Zenftman and A.M.Lean , Brit. Patent 644,468 (1950) .
- 5- A.A.Athawale and M.H.Alhousami , J. Reinforced Plastic and Composites , 27 , 605 (2008)
- 6- P.M.Hergenrother and G.M.Thompson , " Flammability of Epoxy Resins Containing Phosphorus " , Office of Aviation Research and Development Washington , DC 20591 (2005) .
- 7- M.B.Maggie , Ph.D. thesis , Virginia Polytechnic Institute and State University (2001) .
- 8- A.H.Ford and B.J.Berry , "Organic Synthesis" , Vol.5 (1976) .
- 9- A.Knop and L.A.Pilato , " Phenolic Resins" , Springer – Verlag , New York (1985)
- 10- L.L.Van Slyke and A.W.Bosworth , J. Biol. Chem. , 14 , 203 (1983)
- 11- V.Shah,"Handbook of Plastics Testing Technology", John Wily and Sons , New York , p.49,199 (1984).
- 12- N.A.Mohammed , Eng. and Tech. J. , 27 , 1197 (2009) .
- 13- S.Panwar , D.D.Goel and O.P.Pandey , J. E. polymer Prepr., 30 , 73 (2007)
- 14- N.N.Ghosh , B.Kiskan and Y.Yagci , Prog. Polymer Sci. 32 , 1344 (2007)
- 15- A.J.Conix , Ger. Patent 1,199,500 , (1965)
- 16- E.L.Gefter and A.Yuldashev , Plastichesskie Massy , 2 , 49 (1962) .
- 17- S.M.Aaliwi, J.R.Ugal and A.F.Ahmad, Iraqi J. Polymers , 6 , 35 (2002) .
- 18- K.Srikulkit , C.lamsamai and S.T.Dubas , J. of Metals , 16 , 41 (2006)

ص الميكانيكية والتحليل الحراري الوزني ومقاومة الاحتراق لبعض IPNS الجديدة المعتمدة على بعض راتنجات الفوسفات العضوية والايوكسي

مؤيد يوسف كاظم

– كلية التربية – قسم الكيمياء

كما تم ايضا د (IPNs)
المواصفة القياسية ASTM 568
ان راتنجات الفوسفات العضوية حسنت مقاومة
الاحتراق للشبكات البوليمرية المحضرة وذلك من خلال
التقليل من معدل سرعة الاحتراق والفقدان بالوزن .

تم تحضير اثنين من مركبات الفوسفات العضوية وهي
ثلاثي الليل فوسفات (I) وثلاثي فنيل فوسفات (II) .

(I)

اضافة اثيل مثيل كيتون بيروكسيد واوكتات الكوبلت
كمعجل للبلمره حيث تم الحصول على راتنج ثلاثي
الليل فوسفات (III) فقد تم بلمرته
بواسطة البلمره التكثيفيه وذلك باضافة
البارافورمالديهايد ليتم الحصول على راتنج ثلاثي فنيل
فوسفات فورمالديهايد (IV) . شخصلت المركبات
المحضرة بواسطة تحليل العناصر وحساب النسبة
المئوية للفسفور بالطرق الوزنية ومطيافية الاشعة

تم تحضير بعض بوليمرات شبكية التداخل الجديدة
(IPNs) المعتمدة على راتنجات الفوسفات العضوية
المحضرة والايوكسي بنسب وزنية مختلفة (25-5)
(w/w) وقد درست بعض الخواص الميكانيكية لهذه
الشبكات مثل مقاومة الصدم والصلادة حيث بينت
النتائج بأن مقاومة الصدم تزداد مع زيادة محتوى
راتنجات الفوسفات العضوية في شبكة راتنج الايوكسي
بينما لوحظ نقصان في قيم الصلادة بالمقارنة مع
راتنج الايوكسي لوحده بسبب خواص المرونة التي
تمتلكها راتنجات الفوسفات العضوية المحضرة .
بالاضافة الى ذلك تم دراسة الثبات الحراري لل
(IPNs) بواسطة التحليل الحراري الوزني فمن ملاحظة
دوال الثبات الحراري المحسوبة مثل درجات حرارة
التفكك ومعدل سرعة التفكك وطاقة التنشيط ومحتوى
التفحم فقد وجد ايضا ان راتنجات الفوسفات العضوية
المحضرة تزيد من الثبات الحراري لشبكة راتنج
الايوكسي .

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