

Evaluation of Mechanical and Thermal properties for Polymer blends based on Epoxy and some Organophosphorus Resins containing Silicon.

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Abstract;

In this paper we prepared a number of polymer blends between organophosphorus resins contain silicon (p-si-resins) namely polytris((dimethyl ethoxy silyl)phosphate and polytris(dimethyl phenyloxy silyl)phosphate separately and epoxy resin by weight percentages (5-25)%. Some mechanical properties such as impact strength and hardness of the prepared polymer blend were studied, it was observed that the impact strength increases with increasing the proportion of p-si-resins. The hardness has been decreased in values when compared with the epoxy resin alone. This is due to the flexibility provided by the p-si-resins. Thermal stability of the prepared polymer blends were studied by thermo gravimetric analysis technique TGA with measuring some functions such as decomposition temperature, activation energy, rate of decomposition and char content. The results showed that thermal stability of the polymer blends increase with increasing the proportion of p-si-resins. In addition the flame resistance of prepared polymer blends according to standard specifications (ASTM D 568) was evaluated. The results showed an improvement in flame resistance and that by observing the decrease in the rate of burning and weight loss with the increase in the proportion of p-si- resins.

Keyword : *Mechanical Properties , Thermal stability, Epoxy, Phosphorus Resins.*

Introduction

Phosphorus-containing polymers are a relatively new family compared with many other polymers. They have aroused wide interest mainly due to their excellent fire resistance and good mechanical properties. In addition the phosphonyl link group may disrupt the symmetry of the molecules. Thus many high performance phosphorus-containing polymers are amorphous and soluble in common organic solvent that may otherwise be crystalline (1). Many phosphorus-containing polymers have been synthesized(2,3), these include poly(styrene phosphonate diethylester), poly(v-vinylbenzen phosphoric acid diethyl ester), poly phosphszincs, ploy phosphonites, poly phosphonate, polyurethane, epoxies, etc. In addition, incorporating pendant phosphonate ester groups into poly siloxane chain may important various unique properties lin et al reported a method to synthesize poly(phosphonosiloxane)(4). Hydrcsilylation of vinylbenzyl chloride with a poly(methyl hydrcsiloxane) o its cyclic monomer followed by phosphonylation with triethyl phosphate afforded stable phosphonosiloxanes.

Several commercial polymers were developed such as epoxy by mixing with inorganic polymers. Epoxy resins are one of the most important classes of thermosetting polymers which are widely used as material for fiber-reinforced composite materials and as structural adhesives. These inorganic polymers are considered interesting materials as modifiers for mechanical and thermal properties of epoxy resin (5, 9).

The aim of the present research is to improve the mechanical and thermal properties of epoxy by formation polymers blends with some organo phosphorus resins containing silicon.

Experimental

A-Chemicals

The chemicals used in this study were obtained from several sources as following table 1.

Table 1. Materials used in present study

Compounds	FORMLA	Company
Poly tris(dimethyl ethoxy silyl)phosphate (I)		Ref [10]
poly tris(dimethyl phenyloxy silyl)phosphate (II)		Ref [10]
Epoxy Resins		Degussa Construction Chemicals –Co. Dubai-Emirates
Triethylene Tetraamine TETA	$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$	Degussa Construction Chemicals –Co. Dubai-Emirates

B - Preparation of organophosphorus resins containing silicon:

Poly tris(dimethyl ethoxy silyl)phosphate(I) and poly tris(dimethyl phenyloxy silyl)phosphate(II) were prepared according to recent paper [10] and were identified by elemental analysis. For (I), yield 88%, Anal, Calcd, C -35.891; H-7.477; Found C- 35.441; H-6.97. While for (II), yield 83%, Anal, Calcd, C - 53.782; H-5.474; Found C- 53.651; H- 5.221.

C - Instruments

1 - Thermogravimetric Analyzer (TGA):

TGA curves were measured by using SHIMADZU TGA-50H in Micro Analytical Center-Faculty of Science-Cairo University-Egypt. The heating rate of 10°C /min was employed by dynamic nitrogen atmosphere with the gas flow rate 30 ml/min.

2 - Elemental Analysis (CHN):

The CHN analyses were measured to compounds in Micro Analytical Center-Faculty of Science-Cairo University-Egypt.

3-Mechanical masurments

The mechanical measurements were accomplished in Petrochemical Company –Basrah –Iraq, according to the standard conditions, and by using the following instruments:

- 1- Molds.
- 2- Impact Strength Instrument, Universal Pendulum, Ceast Co. by using (Izod method)
- 3- Hardness Tester Instrument , Shore instrument type D, MFG Co.
- 4- Notching Instrument, (Notching cutters model (43-15-1)), TMI organization, Co.
- 5- Micrometer, Brown and Sharbe Micrometer

4– Flame resistance apparatus; The flame resistance was measured , according to (ASTM D568).

D-Procedures

1-Preparation of polymer blends.

Several polymer blends containing different weight percentages (5-25) % (Table 2), from the p-si-resins and epoxy resin were prepared by mixing for 10 min at room temperature to homogenize, Triethylene tetraamine (30% w/w) was added as curing agent for epoxy. The components were mixed again and placed in molds then left for 24 hours in an electric furnace at a temperature of 45 C and then raised to 120 c for a period of three hours to complete the process of rigidity. Molded samples were obtained. Mechanical properties and flame resistance measurements for prepared sample were achieved by placing samples in special molds[11-12].

Table 2: The different weight percentages used in the preparation of polymer blends.

I or II (w/w)%	Epoxy (w/w)%
0	100
5	95
10	90
15	85
20	80
25	75

Result and Dissociation

1- Mechanical Properties

In this study, impact strength and hardness of the polymer blends prepared containing different ratios of resins(I,II) were measured and compared it with impact strength and hardness of the epoxy. Figure (1) and Table (3) show impact strength of the polymer blends containing resin (I) where it is noted a gradual increase in impact strength with the increase in the proportion of resin (I) compared with epoxy, these changes can be related directly to that the resin (I) which is an aliphatic resin contains on the branched side chains help to distribute and disperse energy in the form of reduced mechanical as well as flexibility and elastic properties added because of the presence of bonds (P-O-C) and (Si-O-C), which gives freedom of movement of the polymeric chains to exhaust the energy imposed.[13] This in turn leads to decrease gradually in hardness with increase the proportion of resin (I), as observed in Figure (2) and table (3).

As for the resin (II), as shown in Figure (3) and table (4) it is observed that impact strength increases with increasing the proportion of resin (5-15) %, in comparison with the impact strength of the epoxy alone. The low ratios of resin (II) increase impact strength considerably, because the chemical bonds formed in the blend (P-O-C) and (Si-O-C) lead to increasing space between the polymer chains, which provides sufficient freedom to disperse the energy, while at high ratios, impact strength was increased slowly because of the increasing the aromatic structures and crosslinking among polymeric chains, which lead to increased stiffness and restriction of polymeric chains [14-15]. Also it can be seen from Figure (4) and table (3) that there is a reduction to measure the hardness where it was decreased with increasing content of the resins(II) in the polymer blends.

2-Thermogravimetric Analysis

It was observed from thermal analysis curves described in the figures (5,6) and table (5,6) there is an increase in thermal stability of the polymer blends with the increasing proportion of phosphorus-silicon resins (I, II) and that by observing the increase in the values of some thermal functions calculated such as decomposition temperature, activation energy and char content while it was found the decrease in the values of rate of decomposition. This is attributed to the strength of bonds (P-O-C), (Si-O-C) that need additional heat energy to be broken. In addition the good char content in these blends act as insulating layer reduces the decomposition of the lower layers of the polymer blends and thus increase the thermal stability [16]. In addition, the polymer blends containing resin (II) have higher thermal stability than those containing resin (I) due to the resin (II) contain considerable aromatic structures which increase thermal stability [17].

3- Flame resistance

Flame resistance of prepared polymer blends was studied using the standard specifications (ASTM D568). The rate of burning was calculated by the following law [18].

$$\text{Rate of burning} = \frac{\text{the difference of sample length after combustion}}{\text{time of combustion}}$$

In addition, the weight loss of these polymer blends was calculated which indicate the efficiency of the polymer blends as flame retardants. The rate of burning and weight loss of the prepared polymer blends were compared with epoxy resin alone as shown in figures (7-10) and tables (7,8).

The results indicate that increasing the content of the resins (I,II) in the polymer blend decrease the rate of burning and weight loss and this is attributed to the formation of the char layer of phosphorus and silicon oxides which result of burning. These oxides act as insulating layer which reduces the combustion of down layers of the resin and thus reduce the rate of flame as well as the oxides reduces the arrival of some of the gases generated by combustion to the front of the flame, leading to reduce the rate of burning. As we can be seen that the polymer blends containing resin (II), have higher a flame resistance than these containing the resin (I), because the resin (II) have aromatic structural

which work to increase the percent of char content formed during combustion, and this is increasing the flame resistance[19-20].

Table 3: Values of impact strength and hardness of polymer blends containing resin(I).

Epoxy w/w%	Resin (I) w/w%	Impact Strength J/cm ²	Hardness
100	0	2.65	61
95	5	3.92	57
90	10	5.12	54
85	15	6.80	51
80	20	7.81	48
75	25	8.35	46

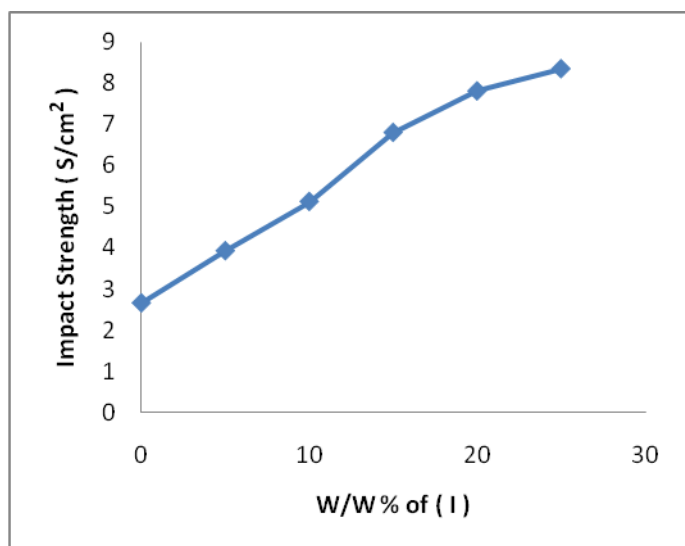


Figure 1. The variation of Impact Strength with content of resin (I) in the polymer blends.

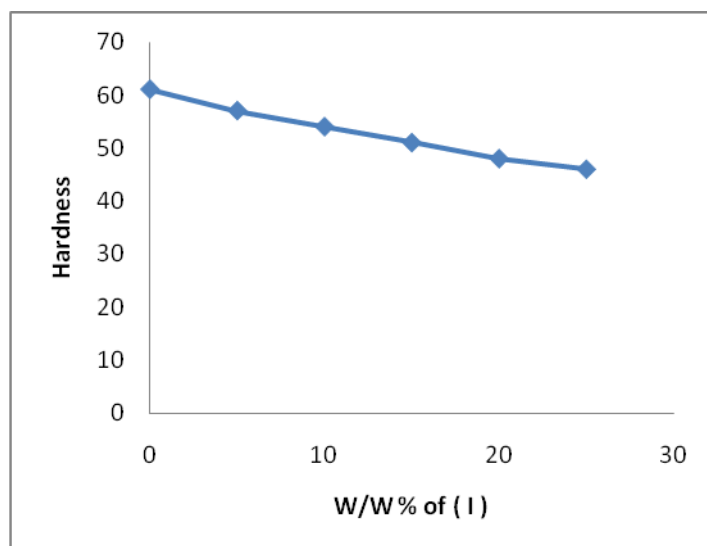


Figure 2. The variation of Hardness with content of resin (I) in the polymer blends.

Table 4: Values of impact strength and hardness of polymer blends containing resin(II).

Epoxy w/w%	Resin (II) w/w%	Impact Strength J/cm ²	Hardness
100	0	2.65	61
95	5	3.25	58
90	10	4.94	56
85	15	5.95	50
80	20	6.45	48
75	25	6.85	46

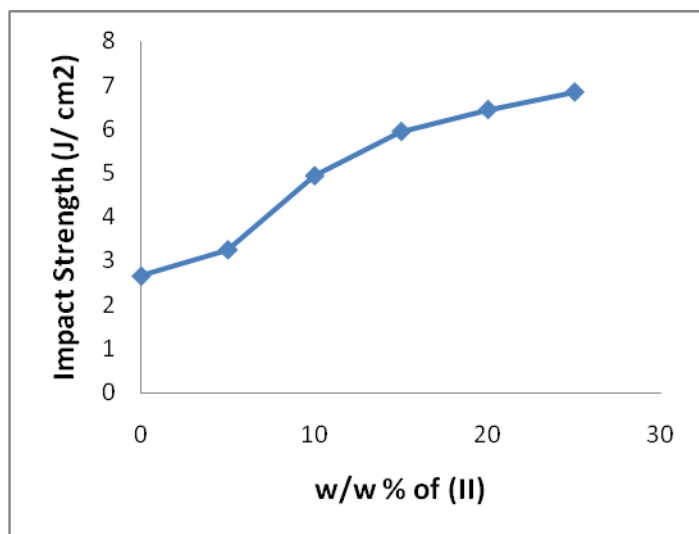


Figure 3. The variation of Impact Strength with content of resin (II) in the polymer blends.

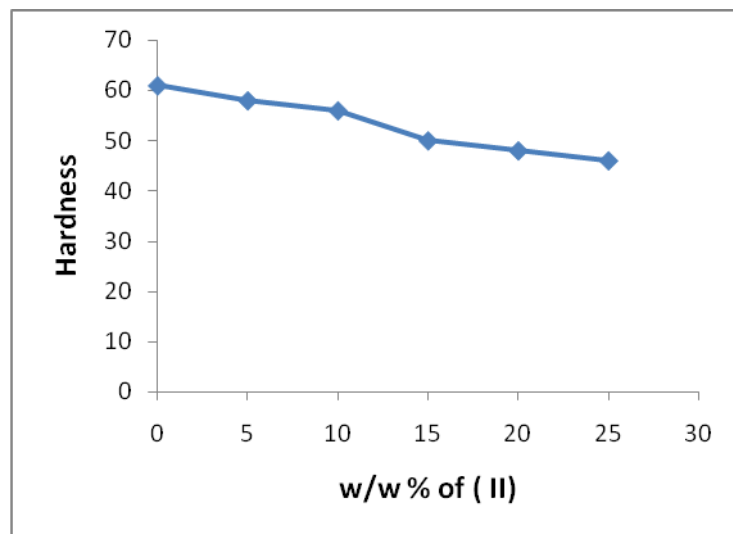


Figure 4. The variation of Hardness with content of resin (II) in the polymer blends.

Table 5: Some thermal stability parameters of polymer blends containing resin(I)

I w/w%	Decom. Temp (°C)	Temp. of 50% wt.loss (°C)	Rate of decom. %/min	Char content at 550 °C	Activation energy KJ/mole	Temp range (°C)
0	230	295	4.5	13	22.13	190-240
5	237	312	3.9	16	35.85	215-320
10	245	320	3.7	17	38.16	208-325
15	250	325	3.4	19	43.53	210-330
20	263	337	3.0	22	49.36	230-332

Table 6: Some thermal stability parameters of polymer blends containing resin(II).

II w/w%	Decom. Temp (°C)	Temp. of 50% wt.loss (°C)	Rate of decom. %/min	Char content at 550 °C	Activation energy KJ/mole	Temp range (°C)
0	230	295	4.5	13	22.13	190-240
5	239	314	3.7	18	37.24	218-323
10	246	322	3.5	20	45.51	210-330
15	253	330	3.1	22	49.73	224-336

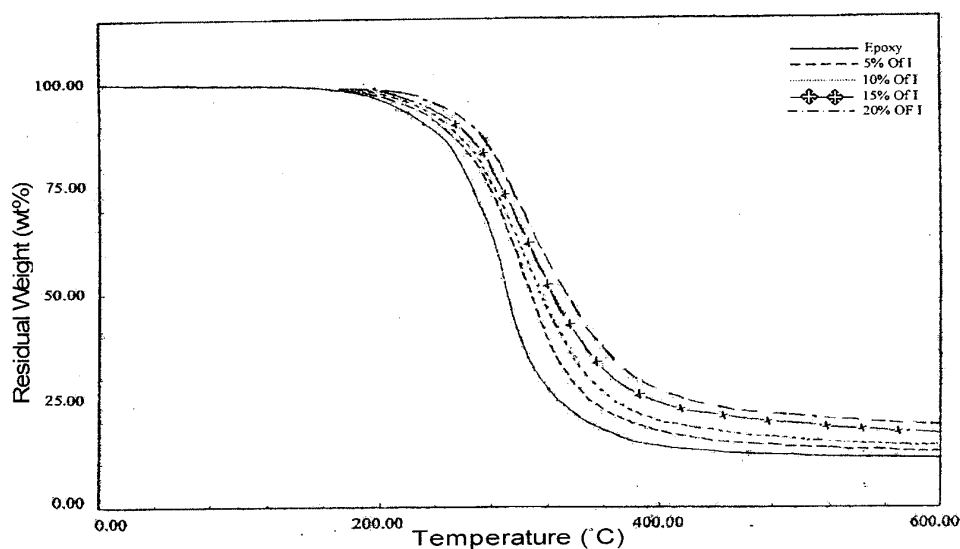


Figure 5. TGA thermograms of polymer blends containing different percent of resin (I).

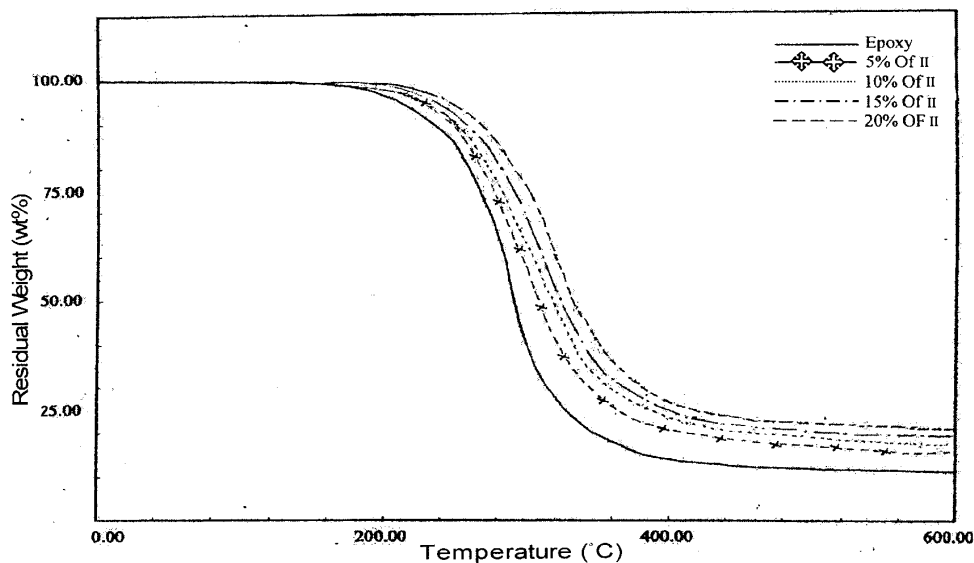


Figure 6. TGA thermograms of polymer blends containing different percent of resin (II).

Table 7: Some flame resistance parameters of polymer blends containing resin(I).

Epoxy w/w%	I w/w%	Rate of burning (mm/Sec).	Weight loss (gm)
100	0	2.45	0.52
95	5	1.85	0.41
90	10	1.43	0.34
85	15	1.15	0.31
80	20	1.27	0.29

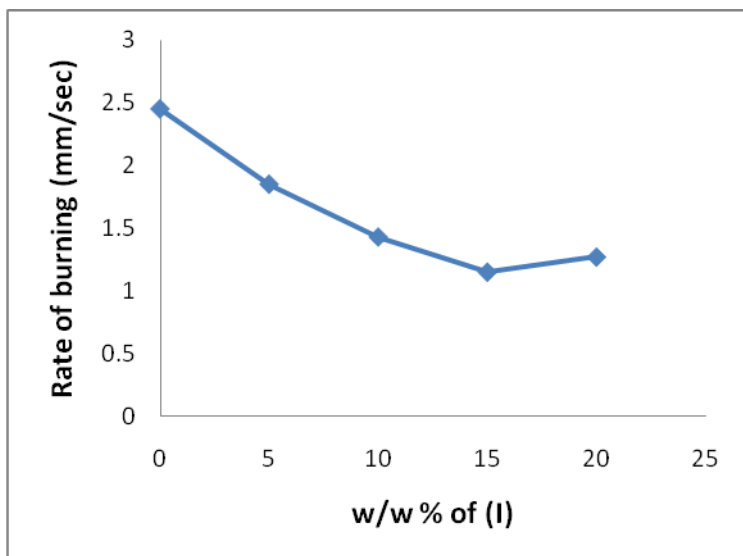


Figure 7. The variation of rate of burning with content of resin (I) in the polymer blends.

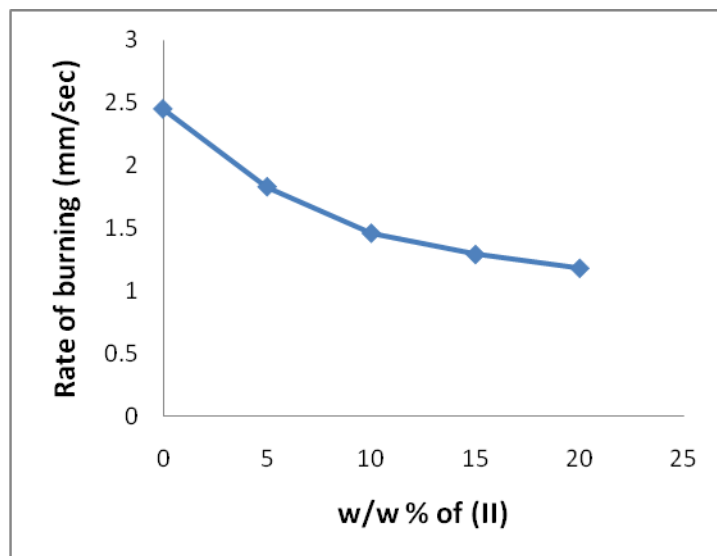


Figure 8. The variation of rate of burning with content of resin (II) in the polymer blends.

Table 8: Some flame resistance parameters of polymer blends containing resin(II).

Epoxy w/w%	II w/w%	Rate of burning (mm/Sec).	Weight loss (gm)
100	0	2.45	0.52
95	5	1.83	0.39
90	10	1.46	0.36
85	15	1.29	0.28
80	20	1.18	0.25

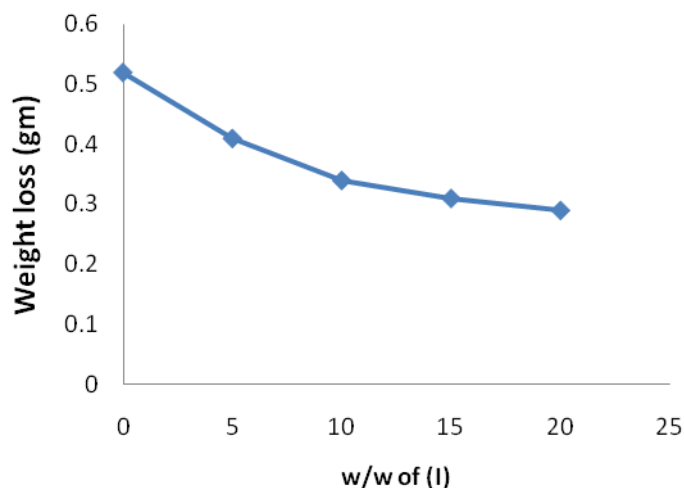


Figure 9. The variation of weight loss with content of resin (I) in the polymer blends.

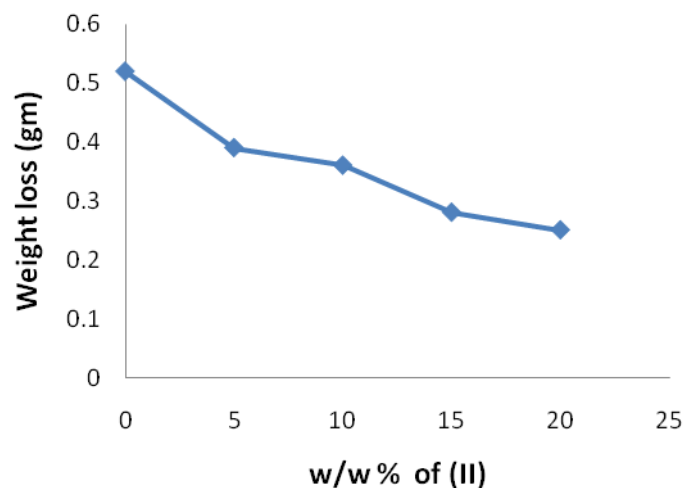


Figure 10. The variation of weight loss with content of resin (II) in the polymer blends.

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تقييم بعض الخواص الميكانيكية والحرارية لمخاليط بوليميرية معتمدة على الايبوكسي و بعض راتنجات السليكون العضوية

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الملخص:

تم تحضير عدد من الامزجة البوليميرية بين راتنجات الفسفور العضوية المحتوية على السليكون وهي polytris(dimethyl ethoxy silyl)phosphate, polytris(dimethyl phenyloxy silyl)phosphate والايبوكسي (epoxy) ونسب وزنية % (5-25). تم دراسة بعض الخواص الميكانيكية مثل مقاومة الصدم والصلادة للامزجة البوليميرية المحضرة وقد وجد ان مقاومة الصدم تزداد مع زيادة محتوى راتنجات (p-si-resin) بينما لوحظ ان قيم الصلادة تقل عند مقارنتها مع راتنج الايبوكسي لوحدة ويعود ذلك الى خواص المرونة التي توفرها راتنجات العضوية المحتوية على سليكون. بالاضافة الى ذلك تم دراسة الثبات الحراري للامزجة البوليميرية المحضرة بواسطة التحليل الحراري الوزني TGA وقد حسبت بعض الدوال الحرارية مثل درجات التفكك وطاقة التنشيط ومعدل سرعة التفكك ومحتوى التفحم وقد بينت النتائج بأن الثبات الحراري للامزجة البوليميرية يزداد مع زيادة محتوى راتنجات الفسفور العضوية المحتوية على السليكون.

كما تم ايضا دراسة مقاومة الاحتراق للامزجة البوليميرية المحضرة بموجب المواصفات القياسية ASTM D568 وقد اشارت النتائج الى تحسن مقاومة الاحتراق للامزجة وذلك من خلال النقصان الملاحظ في معدل سرعة الاحتراق والفقدان بالوزن عند زيادة محتوى راتنجات الفسفور العضوية المحتوية على السليكون في شبكة الايبوكسي.