

Preparation of a New Acrylonitrile Co-Polymer and Studying the Flammability and Mechanical Properties of Its Composites

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Abstract

Acrylonitrile co-polymer was prepared, by four steps, the first was prepared the hetro-cyclic monomer, the second include prepared linear polymer, the third step includes prepared partially cross-linked polymer and the fourth step includes added four different moles (0.5, 1.0, 1.5 and 2.0 mole) of acrylonitrile monomer. The effect of four types of inorganic phosphors salts in four different weight percentage (0.2, 0.4, 0.6 and 0.8%), on flammability and mechanical properties (Flexural and Tensile) strength of co- polymer, has been studied. Four standard test methods used to measure the flame retardation and mechanical properties, which are: ASTM: D-2863, ASTM: D-635, ASTM: D - 790 and ASTM:D-638. Results obtained from these tests indicated that, the co-polymer which prepared has high value of flame retardant and mechanical properties comparing with any thermosetting polymer, on the other hand, additive IV has high efficiency as a flame retardant and high effect on the values of mechanical properties, but additive I show low effect on retard composition and low effect on the values of mechanical properties. This ability to flame retardency increased with the increasing in the number of monomers of acrylonitrile.

Keywords: *Polymer, Modified co-polymer, Acrylonitrile co-polymer, Condensation Polymerization, Fire retardant, Flammability, Additives.*

Introduction

Modified polymers are widely used in the packaging industry because of their good barrier and mechanical properties, good chemical stability and processability, low costs and low toxicity. Polyethylene, polyethyleneterphthalate, polyamides, epoxy and unsaturated polyester resins, are important classes of polymers with different properties [1].

Very wide applications for polymeric materials were extended to use them as composites that covered most aspects of life. So these materials have to modified in aspect of reducing the hazarded of heat and fire [2]. Different polymers vary in the rate of combustion and thus difference may depend on the degree of exposure to ignition source [3]. The process of combustion of polymeric materials by a heat source and a sufficient amount of oxygen of the

atmosphere contains a series of physical and chemical changes that occur to both the polymer and the environment [4]. Many organic and inorganic phosphorus compounds are used as flame- retardants materials in polymeric compounds [5], Although the mechanism of action is less understood of the halogenated compounds [6], and often used phosphorus compounds synergistic with nitrogen compounds [7].

Synergistic effect means, that using two or more of the flame- retardant materials with polymeric material for the purpose of increasing the efficiency of the disability, and in any case it is not necessary that all phosphorus compounds are flame- retardant with the same degree of efficiency, also the retarded of the flame is not linear function relative to the content of the phosphorus in the used material [8].

Composite is generally defined as any physical combination of two or more dissimilar materials used to produce a result that cannot be obtained by each component individually [9].

Properties of composites are strongly influenced by the properties of their constituent materials, their distribution and the interaction between them. Besides specifying the constituent materials and their properties, a composite material as a system is described by the geometry of reinforcement [10].

The geometry of reinforcement may be described by some important factors [11]: shape, size and size distribution of reinforcing materials ; concentration distribution and orientation of reinforcing material.

Most composite materials developed thus far have been fabricated to improve mechanical properties [12]. The interaction between the matrix and fibers are effective in improving the fracture resistance of the matrix. The fibers have small cross sectional dimensions so that they are embedded in matrix materials to form fibrous composites [13]. Most of reinforced plastics are glass fiber reinforced polyesters.

They are used in many important applications [14, 15], so that, in this work the effect of increasing the ratio of additives as flame-resistance on mechanical properties of reinforced co-polymer composites were studied.

Experimental Part

Materials

- All chemicals were used in this work analytical grade.
- Flame-retardant

Monoammoniumphosphate, with purity 99% (additive I); Diammoniumphosphate, with purity 99.5% (additive II); Triammoniumphosphate, with purity 98% (additive III) & Polyammoniumphosphate with purity 97% (additive IV), in powder form; imported from MERCK Co.

Standard Tests

- **ASTM: D-2863:** The measurement of limiting oxygen index (LOI), is widely used for measuring flammability of polymers [16].
- **b- ASTM: D-635 :** The measurement of rate of burning (R.B), average extent of burning (A.E.B), average time of burning (A.T.B), self - extinguishing (S.E) and non – burning (N.B.) [17].
- **ASTM : D-790 :** The measurement of flexural strength, by three point method [18], with constant rate of displacement (crosshead speed) equal to 1 mm/Min., by using Instron-1122 instrument.
- **d-ASTM: D-638 :** The measurement of tensile strength [19], with constant rate of displacement (crosshead speed) equal to 1 mm/Min., by using Instron - 1122 instrument.

Preparation of Co-polymer

- **Preparation of Heterocyclic Monomer [20]**

A mixture of (147 gm, 1.5 mole) of maleic anhydride and (79.5 gm, 1.5 mole) of sodium azide in a 500 ml three-necked flask equipped with a thermometer, a mechanical stirrer and reflux condenser; (80.35 gm, 1.5 mole) of ammonium chloride and (50 ml) THF, were added to the mixture.

The mixture warmed carefully with an electric heating mantle to (60 C°); heating stopped after 3hr.; and then, the mixture was filtered and the solvent was evaporated to give a yellow crystal, (m.p. 144-146 C°). Equation (1) represents that reaction. Figure (1), represents the FT-IR spectrum of this monomer, were showed the following bands: at (3308) cm⁻¹ due to $\nu(\text{NH})$ cyclic, at (2850)cm⁻¹ for $\nu(\text{CH})$ aliphatic, at (1778) cm⁻¹ for $\nu(\text{C}=\text{O})$ anhydride group, and at (1635) cm⁻¹ for $\nu(\text{NH})$ group.

- **Preparation of the Linear Polymer [21]**

About (172.5 gm, 1.5 mole) from the monomer were prepared, dissolved in (216 gm, 3 mole) from Glycerol in a 500 ml three-necked flask equipped with a mechanical

stirrer, with stirred for 1hr. in room temperature until all monomer will be dissolve in Glycerol . (222 gm, 1.5 mole) of phthalic anhydride were add to the mixture and warmed carefully with an electric heating mantle to (160 C°), for 1hr. until a clear liquor is formed.

The mixture was heated to (220 C°), under reflux and about (50 ml) of toluene was then added carefully through the condenser to remove the water which formed as result from the condensation polymerization, and the heating was stopped after 3hr., until no more water came off. The flask was allowed to cool to room temperature. Equation (2), represents that reaction, and Figure (2), represents the FT-IR spectrum of the linear polymer, showed the following bands: at (3444) cm^{-1} due to the overlapping between $\nu(\text{N-H})$ cyclic, $\nu(\text{O-H})$ group and $\nu(\text{CH})$ aromatic, at (2947-2885) cm^{-1} for asymmetric and symmetric stretching vibration of (CH) aliphatic, at (1716) cm^{-1} for $\nu(\text{C=O})$ ester group, at (1643) cm^{-1} for $\nu(\text{NH})$ group, and at (1581) cm^{-1} for $\nu(\text{C=C})$ aromatic. The negative test of NaHCO_3 solution proves that the prepared polymer don't contain any un-reacted anhydride.

• Preparation of Partially Cross-linked Polymer [22]

About (154.5 gm, 0.5 mole) from the linear polymer, were prepared, and mixed with (11.6 gm, 0.1 mole) from fumaric acid in a 500 ml three-necked flask equipped with a mechanical stirrer and a thermometer, with stirred and warmed carefully with an electric heating mantle to (180 C°), under reflux and about (20 ml) of toluene was then added carefully through the condenser, and the heating was stopped after 1hr., until no more water came off. The flask was allowed to cool down to (80 C°), and about (1.36×10^{-3} mole) from hydroquinone as inhibitor, and cobalt octoate (6%) as accelerator, were added with stirred. The flask was allowed to cool approximately (35 C°).

• Preparation Pourable Syrup of Co-polymer

Addition (0.5, 1.0, 1.5 and 2.0 mole) respectively, from acrylonitrile monomer to the partially cross- linked polymer and

stirred for half hours until a pourable syrup was formed. Equation (3), represents that reaction and Figure (3), showed the FT-IR spectrum of the partially cross-linked polymer; this chart appeared, the following bands: at (3437) cm^{-1} due to the overlapping between $\nu(\text{N-H})$ cyclic, $\nu(\text{O-H})$ group and $\nu(\text{CH})$ aromatic, at (2943-2889) cm^{-1} for asymmetric and symmetric stretching vibration of (CH) aliphatic, at (1721) cm^{-1} for $\nu(\text{C=O})$ ester group, at (1630) cm^{-1} for $\nu(\text{NH})$ group, at (1578) cm^{-1} for $\nu(\text{C=C})$ aromatic and at (1121) cm^{-1} for $\nu(\text{C-O})$ ester. Table (3), represents the physical properties measured of the prepared cross-linked polymer after addition of acrylonitrile monomer.

Preparing of Specimens

The specimens of polymeric material containing different moles of acrylonitrile monomer with additives and reinforced with three layers from two types of glass fibers were prepared in dimensions (150 x 150 x 3) mm, three sheets were prepared of each percentage weight (0.2, 0.4, 0.6 and 0.8 %), of flame retardant materials with each number of mole from acrylonitrile monomer and using methylethylketone peroxide (MEKP) as a hardener.. These sheets cut as a samples according to ASTM standard were used in this study.

Results and Discussion

The addition of certain molar percentage of fumaric acid to the linear polymer, this acid is linked by esterification process with two sets of hydroxyl dangling in two series of parallel polymer to formed a bridge between these two chains and the fumaric acid containing double bond, this bonds great benefit in cross linking with acrylonitrile monomer to formed the curing polymer, and this leads to the co-polymer which prepared has high value of mechanical properties comparing with any thermosetting polymer, on the other hand, the presence of a nitrogen atom in the co-polymer which prepared has high value of the flame resistant comparing with any thermosetting polymer.

Mechanical Properties Tests

Mechanical properties of polymers depend on many factors like: molecular structure,

types of branching, space distribution between main chains which contains molecular groups and the percentage of cross linking density between these back-bones chains [23, 24] .

In this work, the mechanical properties of composites depend on twofactors; the structure of additives and number of moles of acrylonitrile monomer. Results obtained of these tests, appeared that the additives caused decrease in mechanical strength and modulus for the samples with increasing of the percentage of additives, as shown in Tables (2 & 3), for both tests (tensile and flexural) respectively. On the other hand, the different moles of acrylonitrile monomer caused inversely proportional with mechanical behavior, where the mechanical behavior increased with increasing the number of moles.

This reduction in the mechanical behaviors is attributed to influence of these additives on matrix, because the hard particles placed in brittle material lead to stress concentration in adjacent matrix and the presence of these additives between polymer chains obstructs local mobility of chains and thus, the polymer will show little strain, and their effect on the interface where they reduce the adhesion (interfacial bonding) between the matrix.

Flammability Tests

The results of the flammability tests of co-polymer were showed in Tables (4-8), for limiting oxygen index and rate of burning respectively.

The limiting oxygen index (LOI), were increased with increasing the weight percentage of additives, also, increasing of the number of acrylonitrile monomer due to increased in the limiting oxygen index

(directly proportional). The efficiency of additives studied was in the following order:

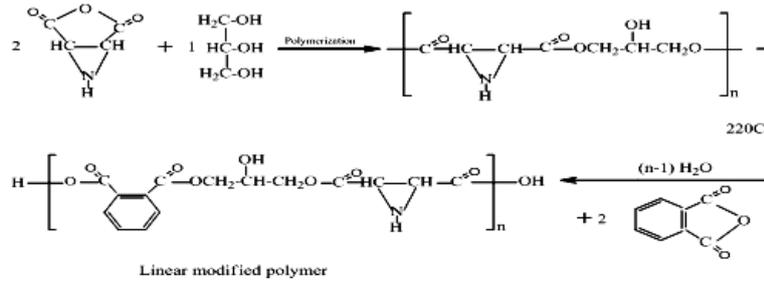


The rate of burning (R.B) of the co-polymer with the additives has a continuous reduction with increasing the percentage weight of additives (inversely proportional), as in Tables (5-8) respectively. This results indicated that, the additives III and IV has high efficiency on self-extinguishing (S.E) of co-polymer, especially in percentage 0.6 % for the co-polymer containing 0.5 mole of acrylonitrile monomer, and non-burning (N.B) occur in percentage 0,8 % for the additive IV the co-polymer containing 0.5 mole of acrylonitrile monomer. This ability to flammability increased with the increasing in the number of monomers of acrylonitrile, so in general, the additive IV will be more effective in flame retardency.

In general, additive IV has the best efficiency on retard combustion. This high efficiency depends in basically on the structure of this material (Polyammonium phosphate), its contain in their structure on phosphor and nitrogenelements, which have high effect on retard combustion. The free radicals were form from decomposition of this materials (P and N-) will reacted rapidly with the free radicals of flame chain, such as (H·, O·, O-OH·, ..., etc.) to form inert compounds like (HPO, NH₄OH,, etc.) and work on inhabitation of thermal decomposition will occur in flame front, because decreases of amount of generation heat and to formed a group from the non-flammable gases, such as (CO, CO₂, H₂O, ..., etc) thus will decreases from volatile materials flammable. The char will form as results from the thermal decomposition of the specimen; it covered the polymer specimen's roof [25].



Equation (1) : Preparation of the hetero-cyclic monomer.



Equation (2): Preparation of the linear modified resin.

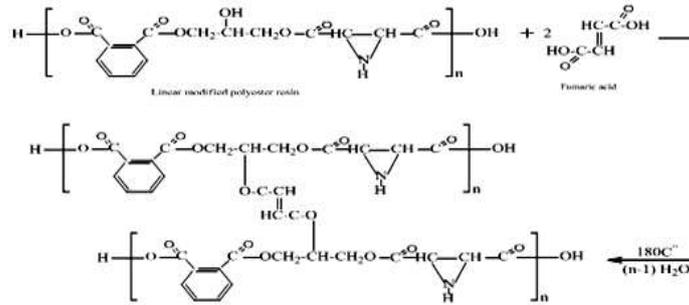


Table 1: Physical properties of the modified resins after the addition of vinyl monomer

Physical properties	Values
Molecular Weight (\overline{Mn})	Around 2400 (gm / mole)
Solid content	33 %
Viscosity	18 poise
Gel time	15 min. at 25C ⁰
Acid Value	24
Density	1.2 (gm /cm ³)

Table 2: The tensile tests of the prepared polymer with additives containing different moles of acrylonitrile monomer

Type of test	Number of moles	Additives %					Additives	
		Non	0.2	0.4	0.6	0.8		
Tensile Strength (σ_T) MPa	0.5	81	77	73	69.3	63.7	I	
		81	75	71	66.5	62	II	
		81	72.6	67	64	59.6	III	
		81	70	65	60.4	56	IV	
	1.0	85	80.2	77	72	68	I	
		85	79	75	70	66	II	
		85	76.3	73	67.8	64	III	
		85	75	71	64.6	61.4	IV	
	1.5	89	84.7	79.7	74.3	69.2	I	
		89	82	77	71	67	II	
		89	78.1	74	68.6	64	III	
		89	76	71.4	65.4	61.7	IV	
	2.0	94	88.5	83.7	78.3	73	I	
		94	86	81	75	69	II	
		94	84	77.8	72	65	III	
		94	82	75	68.8	62	IV	
	Young Modulus (E) GPa	0.5	3.32	2.97	2.53	2.39	1.97	I
			3.32	2.75	2.29	2.10	1.71	II
			3.32	3.52	2.06	1.85	1.53	III
			3.32	2.36	1.81	1.64	1.26	IV
1.0		3.38	3.03	2.59	2.45	2.38	I	
		3.38	2.82	2.38	2.29	2.25	II	
		3.38	2.75	2.31	1.91	1.87	III	
		3.38	2.68	1.87	1.80	1.72	IV	
1.5		3.41	3.06	2.62	2.49	2.40	I	
		3.41	2.89	2.41	2.33	2.27	II	
		3.41	2.62	2.25	2.17	2.14	III	
		3.41	2.41	2.04	2.01	1.91	IV	
2.0		3.44	3.09	2.65	2.56	2.47	I	

		3.44	2.88	2.44	2.41	2.34	II
		3.44	2.67	2.23	2.15	2.21	III
		3.44	2.46	2.02	2.09	2.08	IV

Table 3: The flexural tests of the prepared polymer with additives containing different moles of acrylonitrile monomer

Type of test	Number of moles	Additives %					Additives
		Non	0.2	0.4	0.6	0.8	
Flexural strength (S_F) MPa	0.5	125	120.6	115.8	110.3	106	I
		125	117	112	107	104	II
		125	114.6	108.9	105	101.8	III
		125	112	106	102.7	98.1	IV
	1.0	129	124.7	118.5	113.5	109	I
		129	121	115	110.2	106.9	II
		129	116.8	112.4	107.4	105	III
		129	113.1	108.2	105.1	103	IV
	1.5	134	129.7	124.6	119	113.7	I
		134	126.4	121.8	116.6	111	II
		134	124	118	113.8	109	III
		134	121.6	116.3	110	106.8	IV
	2.0	138	135	129.6	125	119.3	I
		138	132.6	127	122	117	II
		138	129.4	124.3	120	114	III
		138	126.7	122.8	117.2	111.4	IV
Flexural Modulus (E_F) GPa	0.5	3.19	2.83	2.35	1.94	1.47	I
		3.19	2.61	2.14	1.69	1.22	II
		3.19	2.39	1.86	1.44	1.05	III
		3.19	2.15	1.64	1.26	0.82	IV
	1.0	3.22	2.87	2.39	2.32	1.84	I
		3.22	2.65	2.18	2.15	1.61	II
		3.22	2.43	1.90	1.83	1.48	III
		3.22	2.21	1.73	1.62	1.25	IV
	1.5	3.25	3.00	2.52	2.44	1.97	I
		3.25	2.78	2.26	2.19	1.81	II
		3.25	2.56	2.02	1.90	1.58	III
		3.25	2.34	1.83	1.75	1.40	IV
	2.0	3.28	2.93	2.65	2.57	2.10	I
		3.28	2.81	2.39	2.32	1.94	II
		3.28	2.59	2.16	2.11	1.73	III
		3.28	2.37	1.92	2.02	1.51	IV

Table 4: Limiting oxygen index (LOI) of the polymer with additives containing different moles of acrylonitrile monomer

Additive %	Number of moles					Additives
	Non	0.2	0.4	0.6	0.8	
0.5 mole	20.7	21.3	22.34	23.03	23.58	I
	20.7	21.78	22.63	23.0	23.6	II
	20.7	22.12	22.76	23.56	24.67	III
	20.7	22.6	23.28	24.3	25.56	IV
1.0 mole	21.5	22.05	22.3	22.7	23.2	I
	21.5	23.6	23.92	23.34	23.92	II
	21.5	24.0	24.5	24.9	25.4	III
	21.5	24.5	25.0	25.6	25.93	IV
1.5 mole	21.9	22.42	23.66	23.94	24.52	I
	21.9	23.8	23.97	24.83	25.35	II
	21.9	24.52	24.84	25.5	25.94	III
	21.9	24.91	25.4	25.97	26.47	IV
2.0 mole	22.4	22.96	23.82	24.4	24.93	I
	22.4	24.2	24.93	25.67	26.52	II
	22.4	24.96	25.82	26.54	26.99	III
	22.4	25.64	26.61	27.3	27.87	IV

Table 5: Rate of burning (R.B) of the polymer with additives containing 0.5 mole of acrylonitrile monomer

Additives % Test	Non	0.2	0.4	0.6	0.8	Additives
	AEB (cm)	10	9.3	8.9	7.2	
	10	8.6	8.1	6.6	5.7	II
	10	8.0	7.6	5.8	5.0	III
	10	7.4	6.5	5.3	---	IV
ATB (Min.)	7.24	7.21	7.54	7.13	8.10	I
	7.24	7.17	7.23	7.17	8.26	II
	7.24	7.02	7.38	7.16	8.33	III
	7.24	7.33	8.02	7.36	---	IV
R.B (Cm/Min.)	1.38	1.29	1.18	1.01	0.79	I
	1.38	1.20	1.12	0.92	0.69	II
	1.38	1.14	1.03	0.81	0.60	III
	1.38	1.01	0.81	0.72	---	IV
S.E	---	---	---	---	Yes	I
	---	---	---	---	Yes	II
	---	---	---	Yes	Yes	III
	---	---	---	yes	Yes	IV
N.B	---	---	---	---	---	I
	---	---	---	---	---	II
	---	---	---	---	---	III
	---	---	---	---	Yes	IV

Where:

S.E: Self-extinguishing

N.B: Non-burning

Table 6: Rate of burning (R.B) of the polymer with additives containing 1.0 mole of acrylonitrile monomer

Additives % Test	Non	0.2	0.4	0.6	0.8	Additives
	AEB (cm)	10	9.4	8.7	8.5	
	10	9.1	8.4	7.1	6.4	II
	10	8.3	7.5	6.2	----	III
	10	7.1	----	----	----	IV
ATB (Min.)	7.57	7.76	7.91	9.24	9.24	I
	7.57	8.83	8.23	9.22	9.85	II
	7.57	8.74	8.34	9.84	----	III
	7.57	8.88	----	----	----	IV
R.B (Cm/Min.)	1.32	1.21	1.10	0.92	0.79	I
	1.32	1.13	1.02	0.77	0.65	II
	1.32	0.95	0.90	0.63	----	III
	1.32	0.80	----	----	----	IV
S.E	----	----	----	----	yes	I
	----	yes	yes	yes	yes	II
	----	yes	yes	yes	yes	III
	----	yes	yes	yes	yes	IV
N.B	----	----	----	----	----	I
	----	----	----	----	----	II
	----	----	----	----	yes	III
	----	----	yes	yes	yes	IV

Table 7: Rate of burning (R.B) of the polymer with additives containing 1.5 mole of acrylonitrile monomer

Additives % Test	Non	0.2	0.4	0.6	0.8	Additives
	AEB (cm)	10	9.2	8.4	6.8	
	10	8.1	7.3	5.4	----	II
	10	7.5	5.9	----	----	III
	10	6.8	4.8	----	----	IV
ATB (Min.)	7.73	9.11	9.33	8.09	7.91	I
	7.73	9.87	9.36	7.61	----	II
	7.73	10.7	9.37	----	----	III
	7.73	11.15	9.23	----	----	IV
R.B (Cm/Min.)	1.29	1.01	0.90	0.84	0.67	I
	1.29	0.82	0.78	0.71	----	II

	1.29	0.70	0.63	----	----	III
	1.29	0.61	0.52	----	----	IV
S.E	----	----	----	yes	yes	I
	----	yes	yes	yes	yes	II
	----	yes	yes	yes	yes	III
	----	yes	yes	yes	yes	IV
N.B	----	----	----	----	----	I
	----	----	----	----	yes	II
	----	----	----	yes	yes	III
	----	----	yes	yes	yes	IV

Table 8: Rate of burning (R.B) of the polymer with additives containing 2.0 mole of acrylonitrile monomer

Test	Additives %					Additives
	Non	0.2	0.4	0.6	0.8	
AEB (cm)	10	9.1	7.8	5.4	----	I
	10	8.4	5.9	----	----	II
	10	6.9	----	----	----	III
	10	----	----	----	----	IV
ATB (Min.)	8.26	10.46	9.75	7.94	----	I
	8.26	11.51	9.08	----	----	II
	8.26	11.31	----	----	----	III
	8.26	----	----	----	----	IV
R.B (Cm/Min.)	1.21	0.87	0.80	0.68	----	I
	1.21	0.73	0.65	----	----	II
	1.21	0.61	----	----	----	III
	1.21	----	----	----	----	IV
S.E	----	----	yes	yes	yes	I
	----	yes	yes	yes	yes	II
	----	yes	yes	yes	yes	III
	----	yes	yes	yes	yes	IV
N.B	----	----	----	----	yes	I
	----	----	----	yes	yes	II
	----	----	yes	yes	yes	III
	----	yes	yes	yes	yes	IV

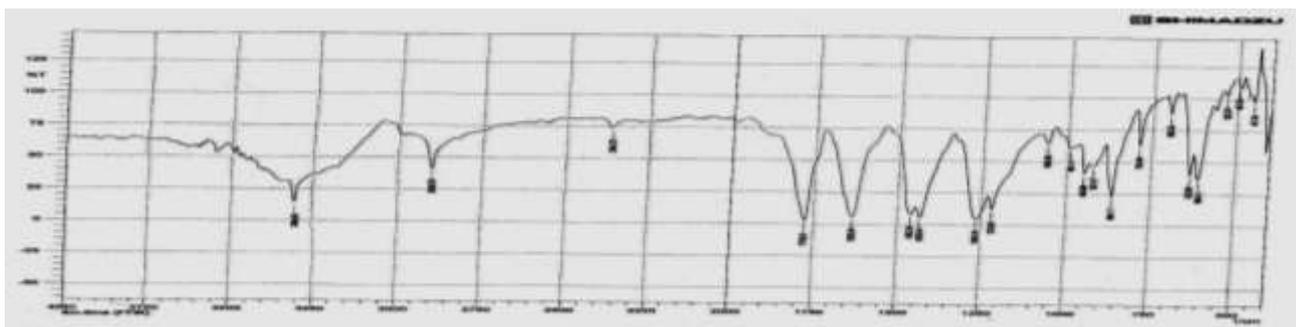


Figure 1: The FT-IR spectrum of the prepared hetero-cyclic monomer.

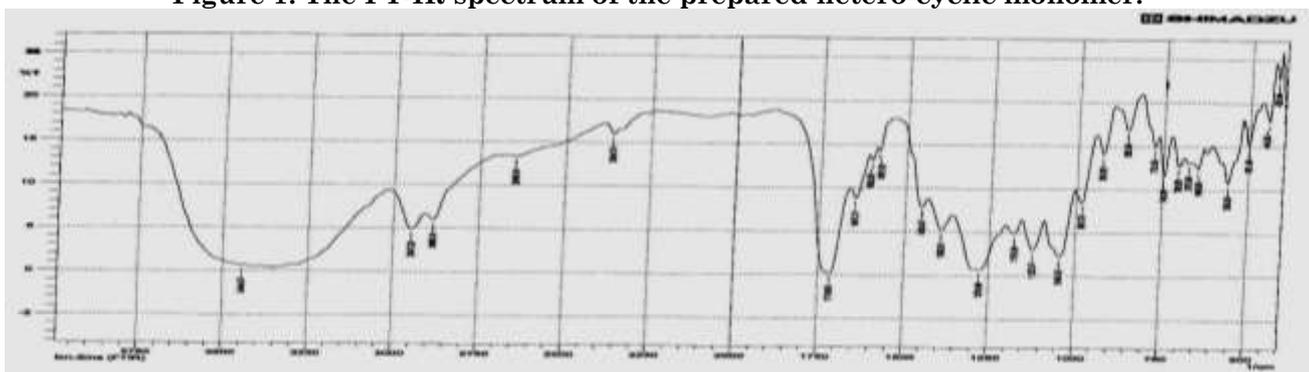


Figure 2: The FT-IR spectrum of the linear polymer.

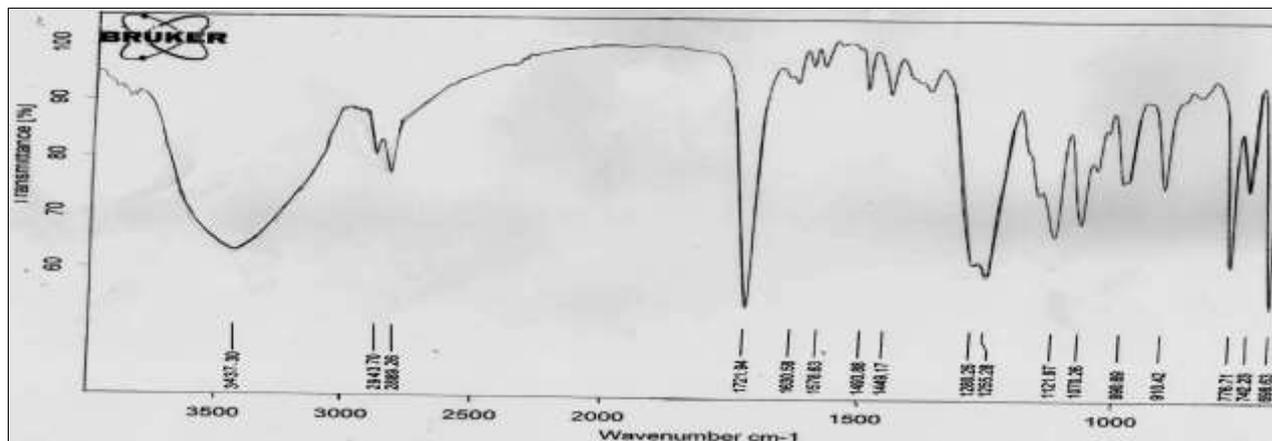


Figure 3: The FT-IR spectrum of the partially cross-linked polymer

Conclusions

The main conclusions of this work can be summarized as follows:

The difference in the number of moles of monomers will result in a difference in flame resistance, where the flame resistant increased with increasing the number of moles, and result in a difference in mechanical behavior

The efficiency of the flame retardation for additives was in the following order:

IV > III > II > I

Limiting oxygen index (LOI) was increased with increasing of weight percentage of additives, but the rate of burning (R.B) was decreased with increasing of weight percentage of additives and additive IV has high effect on retard combustion, but it reduces the mechanical properties, on the other hand, additive I showed low effect on retard combustion, and it showed little effect on the values of mechanical properties comparing with additive IV.

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