

## Studies on Modified Poly (Methyl Methacrylate) by Some Phenolic Resins

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**Abstract:** Modified Poly (methyl methacrylate) PMMA was prepared by chain addition of methyl methacrylate MMA in the presence of initiator and different percentages of phenolic resins, such as resol phenol formaldehyde RPF, novolac phenol formaldehyde NPF or epoxy novolac phenol formaldehyde ENPF to obtain modified PMMA polymers having superior properties. The results showed that the introducing of RPF or NPF resins between the chain of PMMA polymer forming modified PMMA polymers. ENPF resin were introduced in the main chain of PMMA polymers forming Copoly MMA. The prepared modified polymers were characterized by mechanical, electrical and thermal properties. The results showed that the introducing of RPF or NPF enhance the electrical resistance and thermal stability of the prepared modified PMMA polymers. The introducing of ENPF resin enhances all of mechanical, electrical resistance and thermal stability of the prepared copolyMMA polymers.

**Key words:** Poly (methyl methacrylate), resol phenol formaldehyde, novolac phenol formaldehyde, epoxy novolac phenol formaldehyde, mechanical, electrical properties, and thermal stability.

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### INTRODUCTION

Block copolymers are defined as a linear arrangement which consist of two unites occurred in long sequences called blocks. Several types of block arrangements are possible<sup>[1]</sup>. Block copolymers consist of two chemically dissimilar polymers covalently bonded end-to-end. Under certain conditions, a net repulsion between the polymer blocks induces their local segregation, or micro-phase separation, into periodically spaced nanoscopic domains<sup>[2,5]</sup>. Most naturally occurring polymers are homopolymer, but both protein and nucleic acids are copolymers, while many synthetic polymers are homopolymer, the most widely used synthetic polymer are copolymer as styrene butadiene rubber which a copolymer of styrene and butadiene<sup>[6]</sup>.

The wide-ranging applications of poly (methyl methacrylate) are well documented<sup>[7,10]</sup>. These polymers unlike ionic and metallic crystals and low molecular weight substances consist of long chain molecules arranged in aggregates, which assume complex shapes and structures. The structural information gives an insight into the physical and mechanical properties of polymers<sup>[11]</sup>. Broad industrial user of polymers modified by copolymerization aims to an improvement of their specific properties, such modification may also result in

some undesirable changes. The resultant magnitude and direction of changes is of utmost important both to understand and predict its recognized, for example, that thermal properties of the polymers are very sensitive to the presence of small quantity of other substances<sup>[12]</sup>, also mechanical and Electrical conductivity of the polymer are affected by the presence of other polymer, properties of unmodified polymers are fairly well established, yet, their modification may have properties quite different from what could have been predicted by simple approximation. Previous studies of polymer modification show that the effect of modifier on polymer properties depends not only on its kind but also on its concentration<sup>[13,14]</sup>.

### MATERIALS AND METHODS

**Materials:** Methyl Methacrylate, MMA monomer (ICI) UK, phenol, formaldehyde 37%, sodium hydroxide, oxalic acid and epichlorohydrin were obtained from ADWIC, Egypt and azo-bis-isobutyronitrile (AIBN) (Amerchem) USA.

**Preparation of Resol Phenol Formaldehyde Resin (RPF):** Into 250 two necked round bottom flask fitted with reflux condenser, thermometer and magnetic stirrer,

phenol (47 g) was mixed with aqueous formaldehyde solution (37%, 63 g) and ammonia solution (18%, 2 ml) were introduced. The mixture was heated on water bath at 70 °C for two hours with continuous stirring the pH value of the reaction mixture was adjusted to 6-7 by addition of sulfuric acid (10%). The aqueous phase was allowed to separate. The resinous contents of the flask were then poured out and allowed to solidify to a soluble, fusible mass RPF resin<sup>[6]</sup>.

**Preparation of Novolac Phenol Formaldehyde Resins (NPF):** Into 250 two necked round bottom flask fitted with reflux condenser, thermometer and magnetic stirrer, phenol (65 g) was mixed with aqueous formaldehyde solution (37%, 46 g) and oxalic acid dehydrate (1 ml) were introduced. The mixture was heated on water bath at 90°C for 1.5 hours with continuous stirring. The aqueous phase was allowed to separate. The resinous layer were then poured out and allowed to solidify to a soluble, fusible mass NPF resin<sup>[6]</sup>.

**Preparation of Epoxy Novolac Phenol Formaldehyde Resin (ENPF):** Into 250 two necked round bottom flask fitted with reflux condenser, separating funnel and magnetic stirrer, the prepared novolac phenol formaldehyde solution (6 g in methanol) and epichlorohydrin (5.1 ml) were added and heated in a water bath for 2.5 hours under continuous stirring at 65-70°C. Drop wise addition of NaOH (0.1 N, 2 mol) was carried out within the reaction time. Distilled water (100 ml) was then added with stirring at room temperature for 30 min then the distilled water was trough out and the resin content was then poured out and allowed to solidify as ENPF resin<sup>[6]</sup>.

**Preparation of Modified and Unmodified MMA Pre-polymer Syrup:** Into a round bottom flask, 250 ml, fitted with reflux condenser, different ratio of dissolved RPF (1, 2.5, 5, 10, 20 and 30 % w/w) in MMA monomer (100g) and azo bis isobutyronitrile (AIBN) (0.1 g) were introduced. The mixture was heated on water bath at 80 °C within 25-30 min with continuous magnetic stirring<sup>[15,16]</sup>. The modified MMA/RPF was obtained.

By the above mentioned preparatory technique and the same ratio, (1, 2.5, 5, 10, 20 and 30 % w/w of NPF or ENPF), modified MMA/NPF and modified MMA/ENPF pre-polymer syrup samples were prepared respectively. Unmodified MMA pre-polymer syrup were prepared by the same technique by using MMA monomer (100g) and azo-bis-isobutyronitrile (AIBN) (0.1g) only.

**Preparation of Poly (Methyl Methacrylate) PMMA Modified by Phenolic Resins:** The prepared modified MMA/RPF and unmodified pre-polymer syrup (100g) was charged between two glass plates as a casting cell provided with a separating poly vinyl acetate PVA gasket round the edges. The cell was hold together by spring loaded clamps so the plates will come closer together. The prepared charged casting cell was immersed in a water bath over night at 60°C, cooled down for room temperature then the sheet of PMMA/RPF was removed from the cell<sup>[17]</sup>. By the above mentioned preparatory technique, the different PMMA/NPF or PMMA/ENPF were prepared from NPF or ENPF pre-polymer respectively.

#### **Measurements:**

**Infrared Spectroscopy:** Infrared spectroscopic analysis of the prepared compounds film samples were recorded using ATI Mattson-Genesis series FTIR<sup>TM</sup> infrared spectroscopy, the prepared compounds were dissolved in spectrograde chloroform and thin film was prepared by evaporation the solvent on KBr disks<sup>[18]</sup>.

**Mechanical Properties:** Tensile, flexural and compressive strengths of the prepared cast samples (with length 210 mm, width 25 mm and thickness 3 mm) was determined using an Instron testing machine (model 1026) at 23 ± 2 °C with crosshead speed 100 mm/min, chart speed 200 mm/min and load cell range 0 – 500 Newton, according to ASTM D638-77A.

**Electrical Properties:** The electrical conductivity (s), Ln conductivity (s), dielectric constant (e) and loss factor (tan δ) were measured on (the AC conductivity of prepared samples were measured at room temperature in the frequency range from 100 Hz to 5 MHz using RCL bridge model Hioki 3532 Hitester) the potential difference between the plates of condenser holding the sample and the current is flowing it were measured using a multimeter type URI/050 from Rohade and Schwar<sup>[13]</sup>. The results are given in Table 2.

**Thermal Stability:** The loss in weight against time at temperature 200 °C was determined, and results are given in Table 3<sup>[12]</sup>.

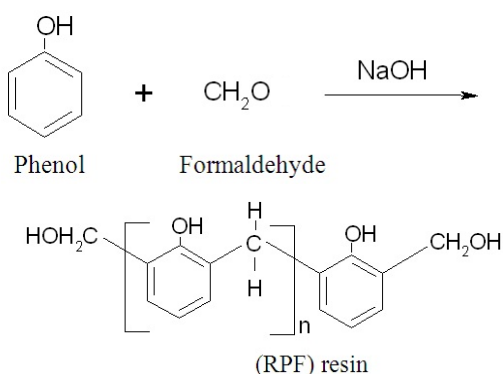
## **RESULT AND DISCUSSION**

Poly methyl methacrylate PMMA was prepared by chain addition of methyl methacrylate MMA in the presence of azo-bis-isobutyronitrile as initiator and different percentages of phenolic resins, such as RPF,

NPF or ENPF to obtain modified PMMA polymers. The prepared samples were tested and evaluated by some investigations. The IR analysis indicates that, each of RPF or NPF resin contains blends with PMMA but ENPF contain copoly with PMMA.

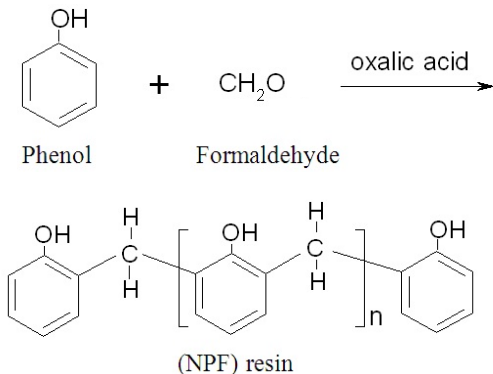
**Infrared Investigation for Prepared Resins and Polymer:** The IR analysis of the prepared resins is matching the structure of the RPF, NPF and ENPF<sup>[19]</sup>. Where the infrared spectra show the following absorption bands:

**For the Prepared RPF Resin:**



IR spectra of RPF is showed in Fig. (1) and showed that, the absorption peak at 2950  $\text{cm}^{-1}$  is characteristic of C–H aromatic, peak at 1600  $\text{cm}^{-1}$  is characteristic of C=C aromatic, broad peak with high intensity at 3300  $\text{cm}^{-1}$  characteristic to H– bonded OH, peak at 1470  $\text{cm}^{-1}$  characteristic to  $\text{CH}_2$  aliphatic and a combination bands appear between 1600 – 2000  $\text{cm}^{-1}$  characteristic to ortho substituted ring, IR spectra of RPF is shown in Fig (1).

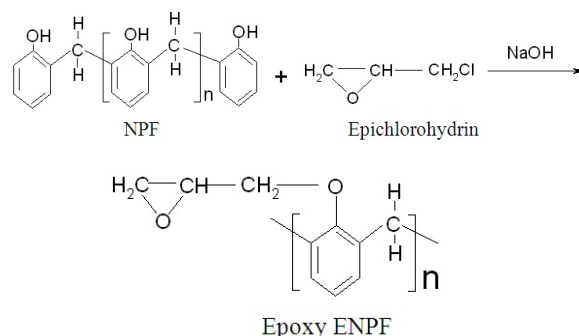
**For the Prepared NPF Resin:**



IR spectra of NPF is given in Fig. (2) and showed that, the absorption peak at 2950  $\text{cm}^{-1}$  is characteristic of C–H aromatic, peak at 1600  $\text{cm}^{-1}$  is characteristic of

C=C aromatic, broad peak with low intensity at 3300  $\text{cm}^{-1}$  characteristic to H– bonded OH, peak at 1470  $\text{cm}^{-1}$  characteristic to  $\text{CH}_2$  aliphatic and a combination bands appear between 1600–2000  $\text{cm}^{-1}$  characteristic to ortho substituted ring.

**For the Prepared ENPF Resin:**



The IR analysis Fig. (3) shows the absorption peak at 2950  $\text{cm}^{-1}$  is characteristic of C–H aromatic, peak at 1600  $\text{cm}^{-1}$  is characteristic of C=C aromatic, broad peak with lower intensity at 3300  $\text{cm}^{-1}$  characteristic to H– bonded OH, peak at 1470  $\text{cm}^{-1}$  characteristic to  $\text{CH}_2$  aliphatic, peak at 2800  $\text{cm}^{-1}$  characteristic to C–H aliphatic, peak at 1100  $\text{cm}^{-1}$  characteristic of epoxy group and a combination bands appear between 1600–2000  $\text{cm}^{-1}$  characteristic of ortho substituted ring.

**For the Unmodified PMMA:** The IR analysis Fig. 4 shows that the peak at 2950  $\text{cm}^{-1}$  is characteristic of C–H aliphatic peak at 1470  $\text{cm}^{-1}$  characteristic to  $\text{CH}_2$  aliphatic, peak at 1060  $\text{cm}^{-1}$  characteristic to ether group, peak at 1730  $\text{cm}^{-1}$  characteristic of normal ester, and peak at 1360  $\text{cm}^{-1}$  characteristic to methyl group.

**Infrared Investigation for Prepared Modified PMMA Blend:**

**For the Modified PMMA/RPF Blend:** The infrared spectra Fig. (5) shows the absorption peak at 2950  $\text{cm}^{-1}$  is characteristic of C–H aromatic, peak at 1600  $\text{cm}^{-1}$  is characteristic of C=C aromatic, broad peak with high intensity at 3300  $\text{cm}^{-1}$  characteristic to H– bonded OH, peak at 1470  $\text{cm}^{-1}$  characteristic to  $\text{CH}_2$  aliphatic, peak at 1060  $\text{cm}^{-1}$  characteristic to ether group, peak at 1730  $\text{cm}^{-1}$  characteristic of normal ester, and peak at 1360  $\text{cm}^{-1}$  characteristic to methyl group.

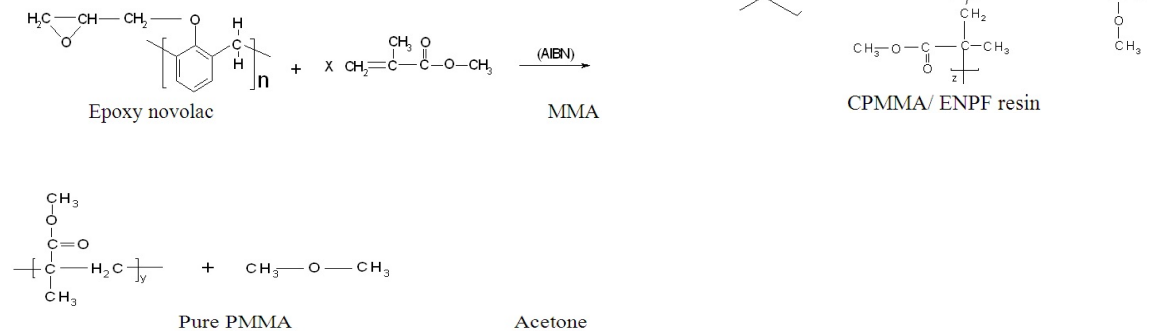
**For the Modified PMMA/NPF Blend:** The IR spectra Fig. (6) shows the following absorption bands:

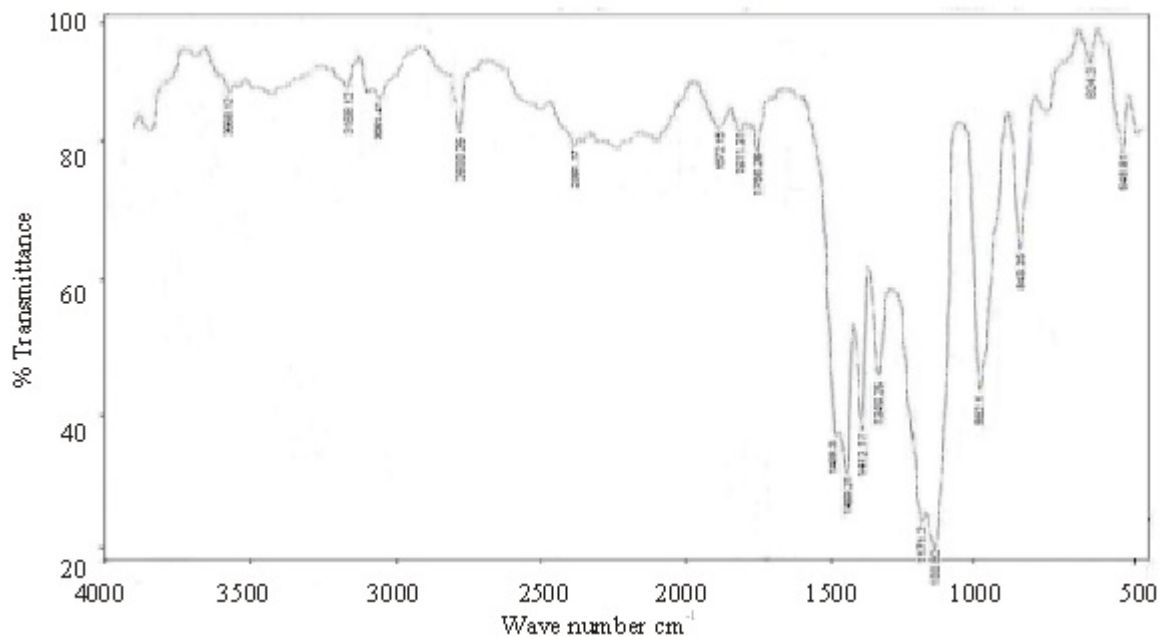


**Table 1:** Mechanical properties of the prepared PMMA and modified PMMA polymers.

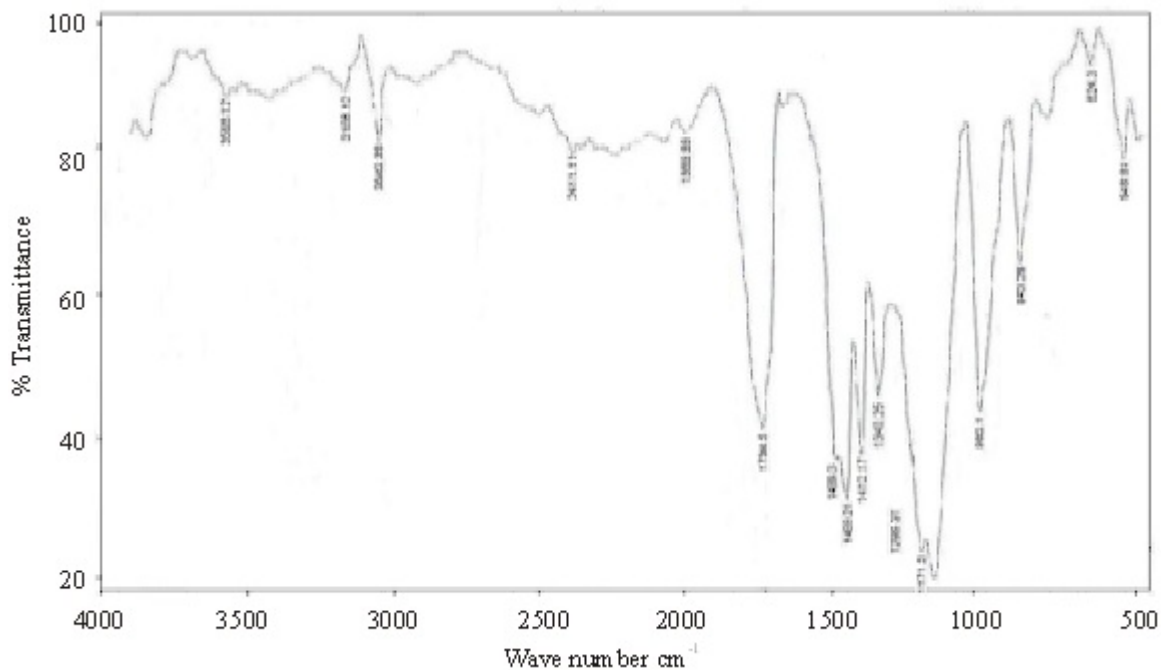
Sample no.	Symbols	Formulation of (100 g, w/w) cast				Mechanical properties		
		PMMA%	RPF%	NPF%	ENPF %	Tensile strength (MPa)	Compressive strength (MPa)	Flexural strength (MPa)
1	MMA/ RPF	100	-	-	-	57.4	60.1	110.8
2		99	1	-	-	56.1	58.2	102.8
3		97.5	2.5	-	-	55	56.5	98.2
4		95	5	-	-	51.1	54.2	90.1
5		90	10	-	-	42.7	50.3	85
6		80	20	-	-	31.2	47.2	72
7		70	30	-	-	19	40.7	66
8	PMMA/ NPF	99	-	1	-	53	59	88.5
9		97.5	-	2.5	-	51.5	41.9	80.2
10		95	-	5	-	41	35	75.3
11		90	-	10	-	32.6	33.2	70.1
12		80	-	20	-	25.7	31	55.1
13		70	-	30	-	18.5	23.1	49.5
14		PMMA/ ENPF	99	-	-	1	68.3	62.4
15	97.5		-	-	2.5	71	65.2	210.6
16	95		-	-	5	72.1	70.3	230.4
17	90		-	-	10	73	71	245
18	80		-	-	20	73.9	73	270
19	70		-	-	30	78	76	276

**Infrared Investigation for Prepared Modified PMMA Copolymer with ENPF:** Copoly of PMMA and epoxy resin ENPF were prepared when MMA polymerized in presence of azo-bis-isobutyronitrile as initiator and ENPF resin. the equation formation of copolymer may be illustrated as:





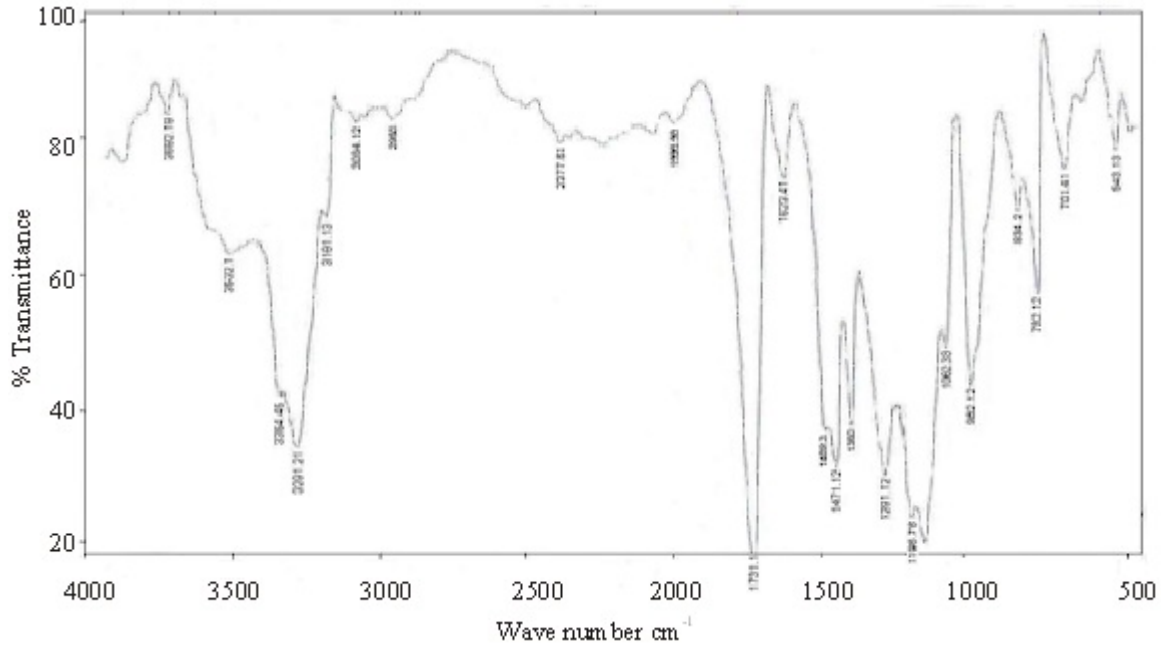
**Fig. 3:** IR spectra for ENPF resin.



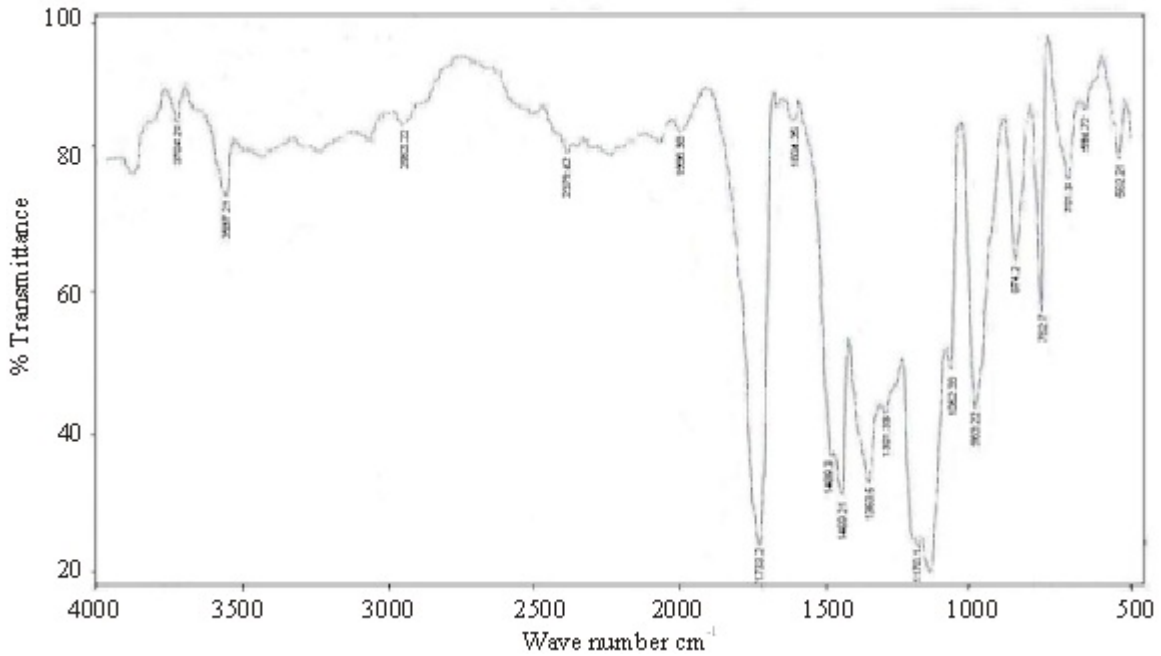
**Fig. 4:** IR spectra for unmodified PMMA.

IR spectra of prepared modified copolymer PMMA and ENPF resin given in Fig 7, and show the absorption peak at 2950  $\text{cm}^{-1}$  is characteristic of C–H aromatic, peak at 1600  $\text{cm}^{-1}$  is characteristic of C=C aromatic, broad peak with high intensity at 3300  $\text{cm}^{-1}$

characteristic to H– bonded OH, peak at 1470  $\text{cm}^{-1}$  characteristic to  $\text{CH}_2$  aliphatic, peak at 1060  $\text{cm}^{-1}$  characteristic to ether group, peak at 1730  $\text{cm}^{-1}$  characteristic of normal ester, and peak at 1360  $\text{cm}^{-1}$  characteristic to methyl group.



**Fig. 5:** IR spectra of modified PMMA/RPF blend.

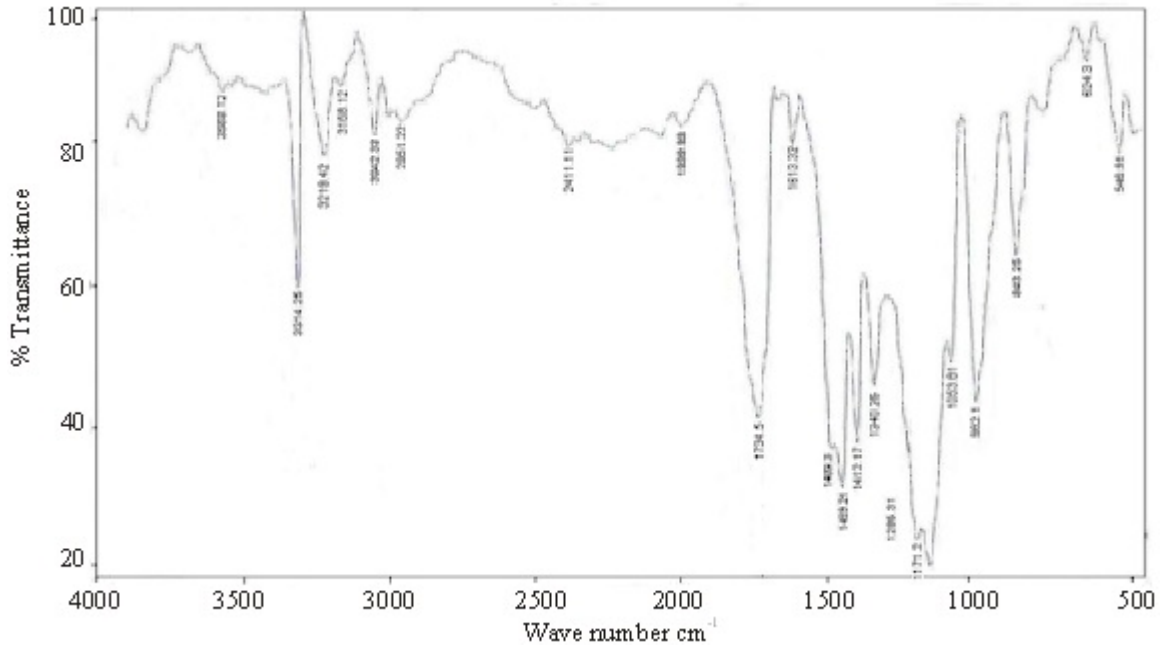


**Fig. 6:** IR spectra of modified PMMA/NPF blend.

**Mechanical Properties Studies:** The tensile, compressive and flexural strengths of the prepared cast samples which contain different ratios of RPF, NPF, or ENPF (0, 1, 2.5, 5, 10, 20 and 30 % w/w) in MMA monomer (100 g) was determined. The results are given in Table (1).

The results in Table (1) show that, the tensile, compressive and flexural strengths values of PMMA/RPF and PMMA/NPF polymers are lower than that of pure PMMA casts. Also, mechanical properties values of PMMA/RPF and PMMA/NPF decrease with increase ratio of RPF and NPF in samples. On the





**Fig. 7:** IR spectra of modified PMMA/ENPF copolymer.

other hand PMMA/RPF are characterized by higher tensile strength values than PMMA/NPF samples. Also the introductions of ring structure in the main chain of the polymer decrease the mechanical properties<sup>[17]</sup>.

The introducing of RPF in the PMMA chain decrease the tensile values of the modified polymers comparing with the pure PMMA due to the introducing of ring structure in the main modified polymer chain and the decrease of the tensile values of the modified PMMA by using NPF than those by using RPF may be attributed to the presence of branches effect on the molecular distribution which decrease the chance of strong bond formation.

The mechanical properties of the prepared modified PMMA samples are effected by the number of -CH<sub>2</sub>-unites, where the increase of the numbers of the -CH<sub>2</sub>-unites improve the mechanical properties of the prepared samples where it increase the interaction force between the chains so the mechanical properties also increase<sup>[20,22]</sup>.

The polymerization of epoxy novolac with another polymer enhance the mechanical properties of the produced modified polymer<sup>[2,3]</sup> and also the epoxy resin acts as a curing agent when it reacts with the ester group<sup>[24]</sup>.

**Electrical Properties Studies** Ln conductivity (s), dielectric constant (ε) and loss factor (tan δ) of the

prepared samples were measured, and the values of the electrical conductivity (s) were given in Table (2). Results given in Table (2) show that, the conductivity values and loss factor of the pure PMMA were higher than that of the modified samples. Ln conductivity and loss factor –on the reverse of dielectric constant (ε)- decrease with increasing the modifier in the sample. In the case of RPF samples were lower than that of pure PMMA, where by the increasing of the RPF ratio the conductivity values decrease. In the case of novolac phenol formaldehyde samples are having conductivity values lower than that of pure PMMA, where by the increasing of the NPF ratio the conductivity values decrease. In case of epoxy novolac resin samples are having conductivity values lower than that of pure PMMA, where by the increasing of the epoxy novolac resin ratio the conductivity values decrease.

The chain composition affects on the electrical conductivity where the presence of the ring structure in the main chain reduces the electrical conductivity of the polymer<sup>[17]</sup> so the introducing of RPF and NPF in the main chain of the modified PMMA reduce its conductivity.

The modified PMMA-RPF polymer has higher conductivity than the modified PMMA-NPF polymer where the modified PMMA-RPF polymer has a polar OH group.

The conductivity of the modified PMMA - ENPF sample is lower than that of the NPF and this is attributed to that the epoxy novolac resin acting as a curing agent so when it undergo to high frequency it get low polarization than NPF lower than RPF.

**Thermal Stability Investigation:** The thermal stability of the prepared samples was studied by determining the main loss percentage after different periods of time at 200 °C. the results are given in Table 3

Results including in Table 3 showed that, the modified PMMA by using RPF, NPF and epoxy novolac having thermal stability higher than that of pure PMMA.

Resol phenol formaldehyde has good thermal properties where at temperature higher than 150 °C RPF make a self curing which decrease the ratio of thermal degradation. So by the increasing of RPF ratio the degree of degradation decrease.

PMMA/NPF samples have higher thermal degradation ratio than that of PMMA / RPF and that due to that RPF making a self-curing at temperature higher than 150 °C<sup>[17]</sup>.

Epoxy resin acts as a curing agent when it reacts with the ester group<sup>[24]</sup>, so when the epoxy novolac reacts with PMMA it decreases the polymer degradation ratio.

**Conclusion:** The introducing of RPF or NPF resins in the main chain of PMMA polymer did not enhance the mechanical properties of the polymer, but gives a reasonable value till 5% of RPF and NPF resin added. In other hand the introducing of RPF or NPF resins in the main chain of PMMA enhance its thermal and isolation, while the introducing of ENPF resin in the main chain of PMMA enhance all of mechanical, thermal and isolation properties.

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