

## Synthesis, Characterization and Thermal Properties of Styrenated Poly(Ester-Amide) Resin

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### Abstract

New unsaturated maleamic acid (USMA) was synthesized by the reaction of maleic anhydride with 4-aminobenzoic acid in acetone. USMA was crosslinked with styrene monomers in the presence of benzoyl peroxide as an initiator. Subsequently the terminal carboxylic groups of USMA-styrene reacted with epoxy resin in the presence of triethyl amine, affording styrenated poly(ester -amide) resin (SPEM). The structures of the obtained products were characterized by FT:IR, <sup>1</sup>H NMR and C.H.N elemental analysis. The new SPEM resin was reinforced with 10 wt.% of Zeolite, Bentonite and Silica. The thermal properties of the reinforced SPEM resins were investigated by thermal gravimetric analyzer (TGA). SPEM resin (Zeolite bentonite and silica) showed enhanced thermooxidative stability compared to fillers free SPEM resin, and TG curves showed presence of char yield of about 33% up to 700°C.

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**Keywords:** poly(ester-amide); unsaturated amide maleamic acid; epoxy resin; TGA analysis

## **Introduction**

Unsaturated polyesters (UP) are characterized as a high thermally stable polymers with favorable physical and chemical properties, therefore they have a widespread field of applications such as, microelectronic, aerospace, automotive industries, building constructions and furniture (Young 1976), (Anderson and messick, 1980),(O'Hearn 1988). The production technique is quite well known and no sophisticated equipment or controls are needed. The unsaturated polyester, containing double bonds within the polymer chain, is produced by step-growth polycondensation reaction on an unsaturated diacid or anhydride, such as fumaric acid or maleic anhydride, with a diol(Dave and Patel 2011a). Most crosslinking of the structopendant unsaturated polyester is accomplished by co-polymerization with alkene monomers such as styrene or methyl methacrylate, or others using radical initiators(Patel 2009). On the other hand, the reaction of unsaturated anhydride such as maleic anhydride with diamines leads to form bisamic acid. Unsaturated polyesters resins can be compounded with different additives and filling materials to improve and enhance the chemical, mechanical properties and electrical properties (Willett and felker 2005), (Dave and Patel 2011b). Another type of prepolymer is obtained by the interaction of a monofunctional

unsaturated acid with a bisphenoldiepoxy (epoxy resin) having unsaturated sites at the two end of the chain and then it mixed with a vinyl monomer such as styrene. This resin is called vinyl ester, and its appearance, handling properties, and cure is similar to UP resins(Serra et al. 2009a,b).They cost more than UP but have exceptional mechanical and chemical properties(Miskolczi 2010). Besides these conventional reasons, UP resin systems were the first widely used fiber reinforced materials in industry and they gave a high impetus and acceleration to the growth of a new field in industry (Ahmed, etal. 2001). On the other hand polyamides represent a class of high performance usually formed by the reaction of diamines and diacyl chloride. These polymers have found use in a wide variety of applications since they possess many desirable characteristics, such as good process ability, good mechanical properties, good thermal stability, and chemical resistance (Yasumasa 2001), (chernukhina and Gabrielyan 1993).Therefore, it was thought to be of interest to combinepolyester and amide in a polymeric framework to give polymeric material known as poly(ester-amide), which may be used in different applications.

In current study, a newpoly(ester-amide) was synthesized from the reaction of maleic anhydride with 4-aminobenzoic acid in acetone

afforded unsaturated maleamic acid with two terminal carboxylic groups. The unsaturated units were crosslinked with styrene in the presence of benzoyl peroxide and the carboxylic groups were reacted with epoxy resin in the presence of triethylamine as a catalyst afforded new styrenatedpoly(ester-amide) resin. In attempt to improve the thermal properties, different reinforcing agents, such as Bentonite, Zeolite and Silica were blended with the poly(ester-amide). The structural and thermal characteristics are presented and discussed.

## Experimental

### Materials

Maleicanhydride, 4-aminobenzoic acid (BDH), benzoyl peroxide, triethylamine, styrene (Fluka) were used as received. Epoxy resin (diglycidylether bisphenol-A) durcupan with EEW=312(Fluka), Acetone, dimethyl acetamide (DMAC) were supplied by (AJAX Chemicals), Bentonite, Zeolite and Silicawere provided from local market with mesh size of about 150 $\mu$ m.

### Instruments

Infrared spectra (KBr pellets) were recorded on a SHIMADZU 8400s Fourier Transformer Infrared (FTIR) spectrophotometer in the range of 4000-400  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR spectra were obtained with the use of a Bruker Avance-300

NMR spectrometer operating at 300 MHz. Samples were dissolved in DMSO, and the solvent was used as an internal lock. Chemical shifts were recorded in ppm relative to tetramethylsilane (TMS) (0.00ppm) as an internal reference. Elemental analysis was performed using Perkin-Elmer 2400 CHN/O analyzer series-11. Thermogravimetricanalysis (TGA) were obtained on a Perkin Elmer TGA-6 at a heating rate of 20 $^{\circ}\text{C}/\text{min}$  in the range of ambient temperature to 700 $^{\circ}\text{C}$  in atmosphere of  $\text{O}_2$  gas at a flow rate of 30 mL/min.

### Synthesis of unsaturatedmaleamic acid (USMA)

In a 200 mL round bottom flask charged with maleic anhydride (20.0g, 0.2mol) and 50 mL acetone, magnetic bar stirrer, and the flask placed in an ice bath. A solution of 4-aminobenzoic acid (27.9g, 0.2 mol) in 100 mL acetone was added dropwise via dropping funnel over a period of 30 min with continuous stirring. The contents of the flask were further stirred for 3 hrs at 0-5 $^{\circ}\text{C}$  and continued at room temperature for another 24 hrs. A yellow solid product that precipitated was filtered off and the filtrate thoroughly washed with acetone to discharge any unreacted starting materials. The obtained material was subjected to dryness in a vacuum oven at 70 $^{\circ}\text{C}$  for 4 hrs. A pale yellow solid product (USMA, unsaturated maleamic acid) was obtained with a percentage

yield of 95%. Anal. Calcd for  $C_{11}H_9NO_5$ : C, 56.17; H, 3.82; N, 5.95. Found: C, 56.19; H, 3.94; N, 6.11.

#### **Crosslinking of USMA with Styrene, (Styrenatedmaleamic acid USMA Styrene)**

USMA (10.0g, 0.05mol) and 100 mL DMAC were introduced into a 250 mL round bottom flask, equipped with a condenser, a magnetic stirrer, and the flask placed in an oil bath. The content of the flask was stirred until a clear slightly yellowish solution formed, indicating complete dissolution of the USMA. Then, 5gm of styrene monomer (about 50% of the weight of USMA) and 0.01 gm of benzoyl peroxide were added, the reaction temperature was gradually raised up to 80 °C with continuous stirring for 2 hrs. Upon addition of chilled distilled water (250mL), a dark red viscous material precipitated which was collected and thoroughly washed with 200 mL of acetone. A dark red viscous product was obtained, yield 90%.

#### **Reaction of styrenated unsaturated maleamic acid with epoxy resin, preparation of SPEM resin**

USMA-styrene (5.0g) dissolved in a 100 mL DMAC inside a 250 mL round bottom flask, equipped with a condenser, a magnetic stirrer, and the flask placed in an oil bath. The content of the flask was stirred until a clear red solution

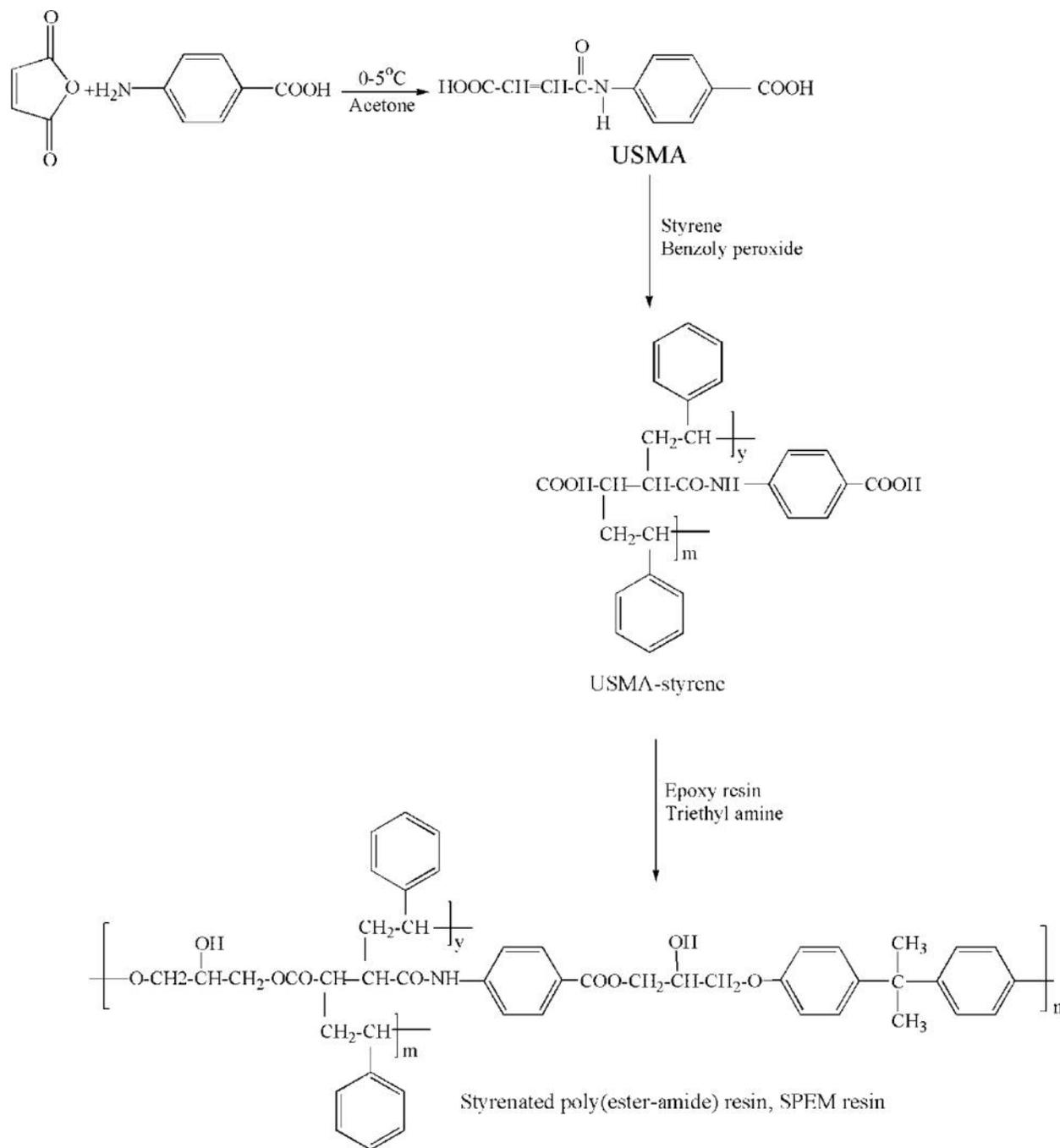
formed. Then, 5.0g of epoxy resin and 2 mL of triethyl amine were mixed, and the reaction temperature was raised to 90 °C with continuous stirring for 2 hrs. Upon addition of chilled distilled water (250 mL), a dark red viscous resinous polymeric material precipitated which was collected and thoroughly washed with 200 mL of acetone. Finally, a dark red product of SPEM resin was obtained, yield 95%.

#### **Reinforcement of SPEM resin**

Three different types of fillers, Bentonite, Zeolite and Silica were used to reinforce the SPEM resin. About 10%wt. of the filler mixed with SPEM, and then dried at 100°C in an oven for 3hrs.

#### **Results and Discussion**

The unsaturated maleamic acid was prepared by the reaction of maleic anhydride and 4-aminobenzoic acid in acetone, and then the product was crosslinked with styrene in the presence of benzoyl peroxide. The styrenated maleamic acid was reacted with epoxy resin in presence of triethyl amine as a catalyst in dimethyl acetamide solvent to prepare styrenated poly(ester-amide) resin. The synthesis reaction is illustrated in Scheme 1:



Scheme (1): Synthesis steps of products

Structural analysis

FTIR analysis of unsaturated maleamic acid,  
USMA

The salient features of the IR spectrum depicted in Figure 1 are as follows:

Absorption at  $3400\text{cm}^{-1}$  due to N-H bond, broad and multiple absorptions appeared within the range of frequencies of  $3300\text{-}3100\text{cm}^{-1}$  are due to O-H of carboxylic acid groups present in USMA. Peaks at  $3018$  and  $2887\text{cm}^{-1}$  are due to C-H stretching of aromatic and aliphatic

groups, respectively. The absorption due to C=O of amide and carboxylic acid group were overlapped at  $1693\text{cm}^{-1}$  and absorption bands at  $1624$  and  $1319\text{cm}^{-1}$  are assigned to CH=CH and C-N bonds, respectively, and those due to C=C of benzene ring were appeared at  $1583$  and  $1541\text{cm}^{-1}$ .

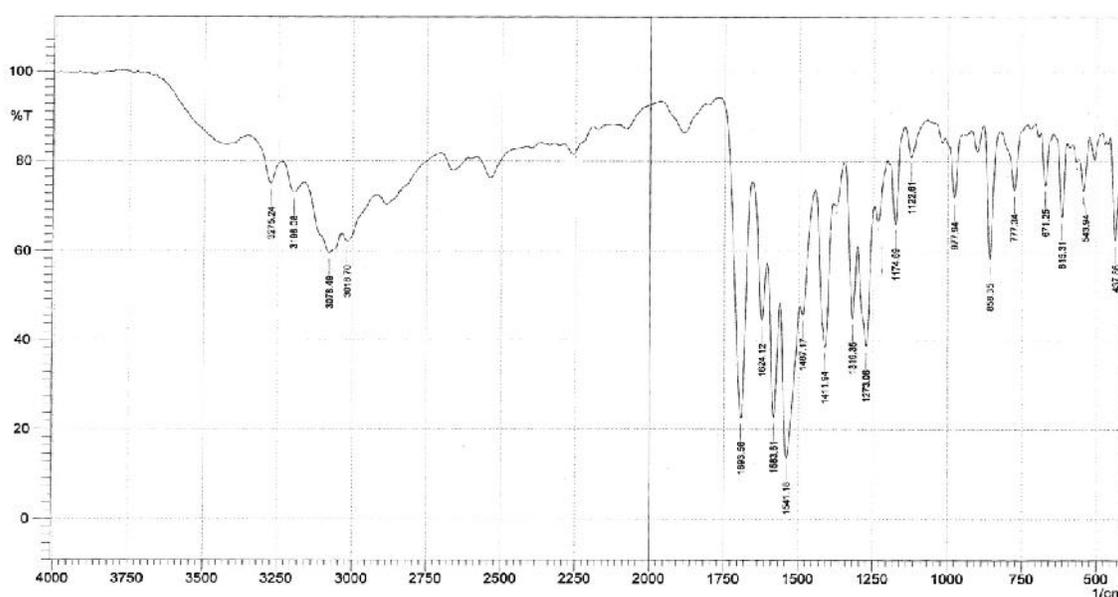
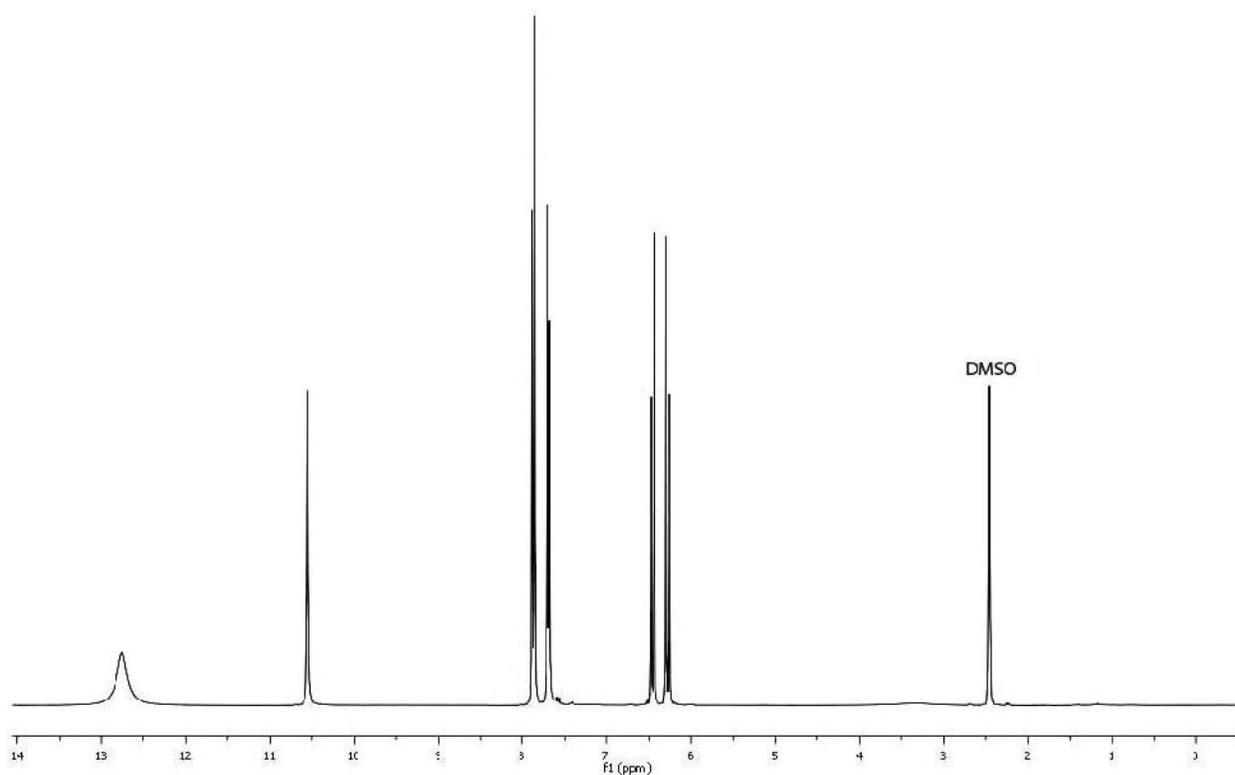


Figure (1): FTIR spectrum of USMA

### <sup>1</sup>H NMR analysis of USMA

The spectrum of USMA depicted in Figure 2 shows all characteristic resonances due to the product, assignments are as follows: broad resonance centered at  $12.70\text{ppm}$  (b, 2H, HO-OC-),  $10.50\text{ppm}$  (s, 1H, -CO-NH-),  $7.87\text{ppm}$  (d, 2H, arom. H) and  $7.75\text{ppm}$  (d, 2H, arom. H),  $6.49\text{ppm}$  (d, 1H,

-CH=CH-CO-NH-),  $6.35\text{ppm}$  (d, 1H, OC-CH=CH-). It is worthwhile to mention here that the appearance of the amide proton (CO-NH) at low field (about  $10.0\text{-}10.5\text{ppm}$ ) is known and had been previously reported (Liou and Hsiao 2002) (Oswal and Pandya 2004).



**Figure (2):  $^1\text{H}$ NMR spectrum of USMA**

### **FTIR of USMA-Styrene**

The important feature of the spectrum given in Figure 3 is the disappearance of the characteristic absorption due to C=C bond at  $1624\text{cm}^{-1}$  indicates that the crosslinking

reaction between USMA and styrene has taken place by effect of benzoyl peroxide. Other important peaks due to C=O amide, C=C of benzene ring and C-N appeared at the same frequencies without any changes or shift.

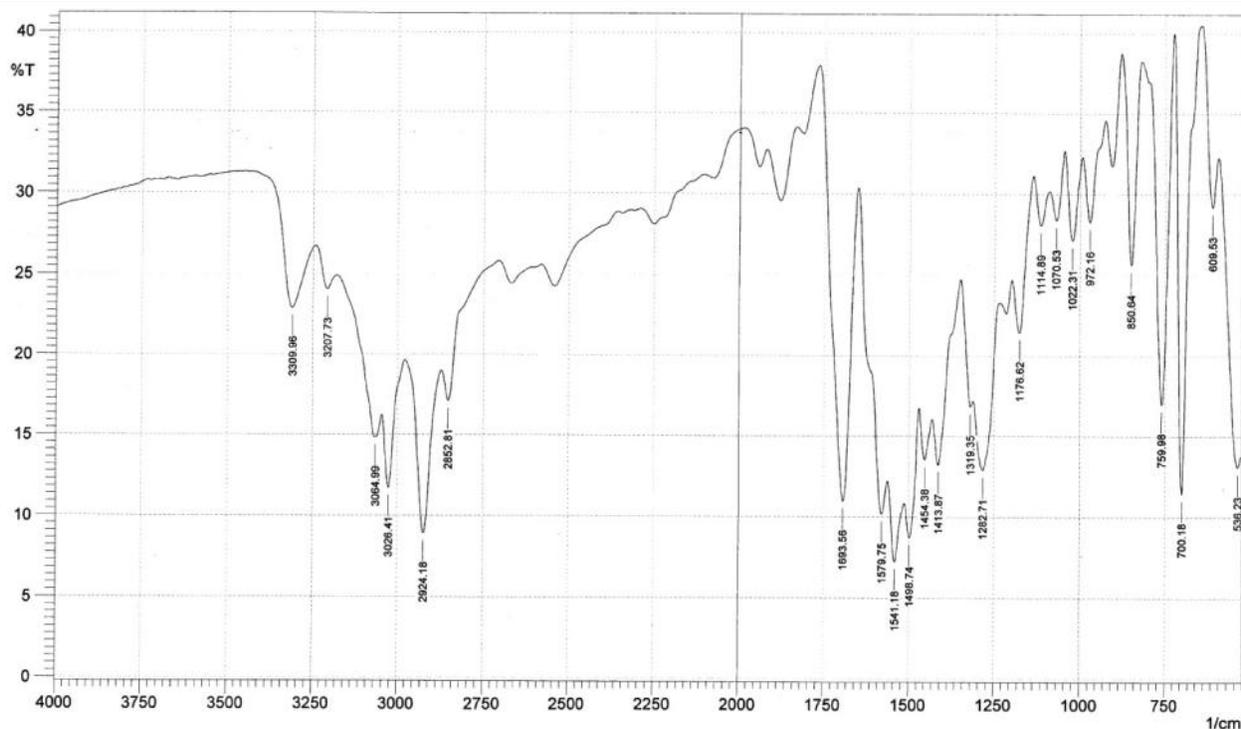


Figure (3): FTIR spectrum of USMA-styrene

### FTIR of SPEM Resin

The spectrum given in Figure 4 shows appearance of new absorption peak at  $1718\text{cm}^{-1}$ , this characteristic peak is due to C=O of ester group. The broad absorption at  $3371\text{cm}^{-1}$  is assigned to O-H bond that resulted from the ring opening reaction of oxirane ring with carboxylic

group of USMA-styrene. Other characteristic absorption discerned from the spectrum are  $1604$  and  $1510\text{cm}^{-1}$  assigned to C=C stretching of benzene ring, absorptions at  $1180\text{cm}^{-1}$  assigned to C-O stretching and at  $831\text{cm}^{-1}$  assigned to *para*-disubstituted benzene ring.

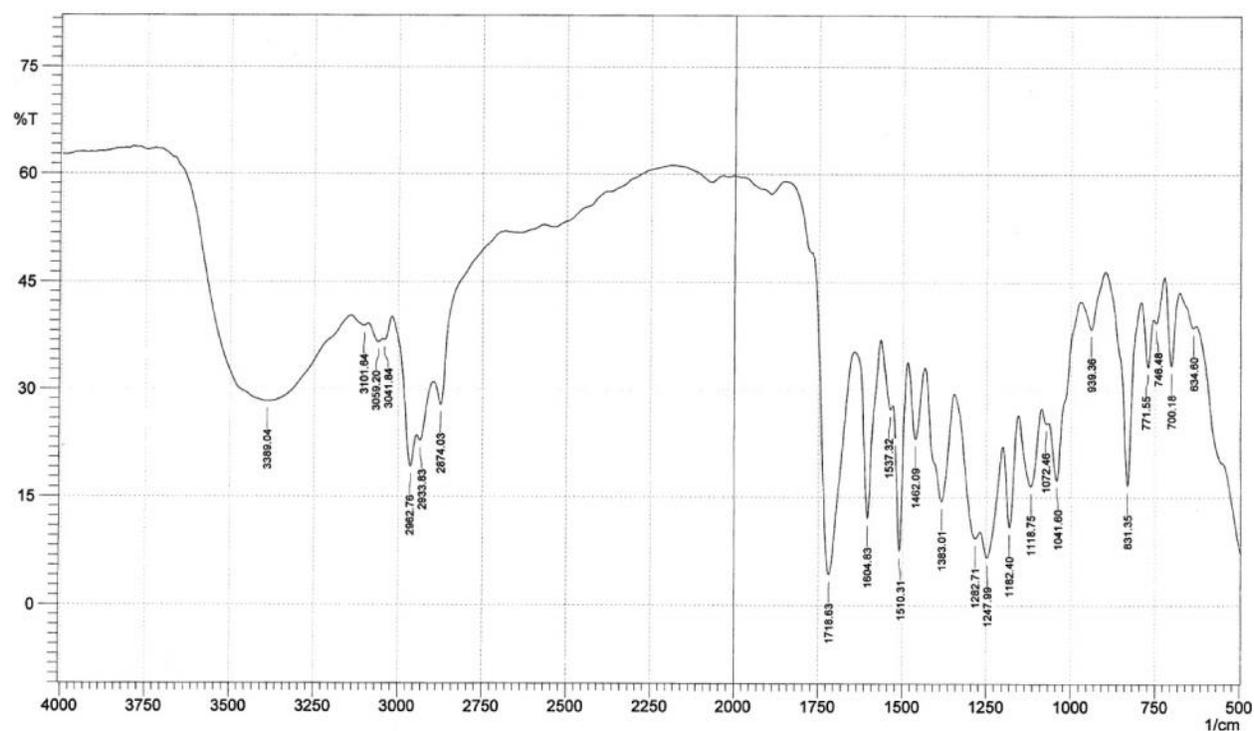


Figure (4): FTIR spectrum of SPEM resin

### <sup>1</sup>HNMR of SPEM Resin

The spectrum depicted in Figure 5 shows appearance of the characteristics resonances at 10.50ppm is assign to the presence of trace amount of  $\text{-HN-}$ , it is important to note here that some of the primary amine  $\text{-HN-CO-}$  moiety might also initiates the ring opening of epoxy ring, therefore the appearance of traces amount might due to this reason. The spectrum also shows broad and multiple resonances at 8.5-6.3ppm due to the aromatic protons in the polymer chain, two doublets at 7.09 and

6.75ppm due to ethane protons and multiple resonances within the range of 5.00-0.50ppm due to aliphatic protons of styrene and epoxy groups. However, the most important features in this spectrum are the complete disappearance of the resonances of hydroxyl of carboxylic groups at 12.70ppm and ethylene resonances at 6.49 and 6.35ppm. This implies that incorporation of epoxy resin and styrene to the backbone of USMA was preceded to completion under the given experimental conditions affording SPEM resin.

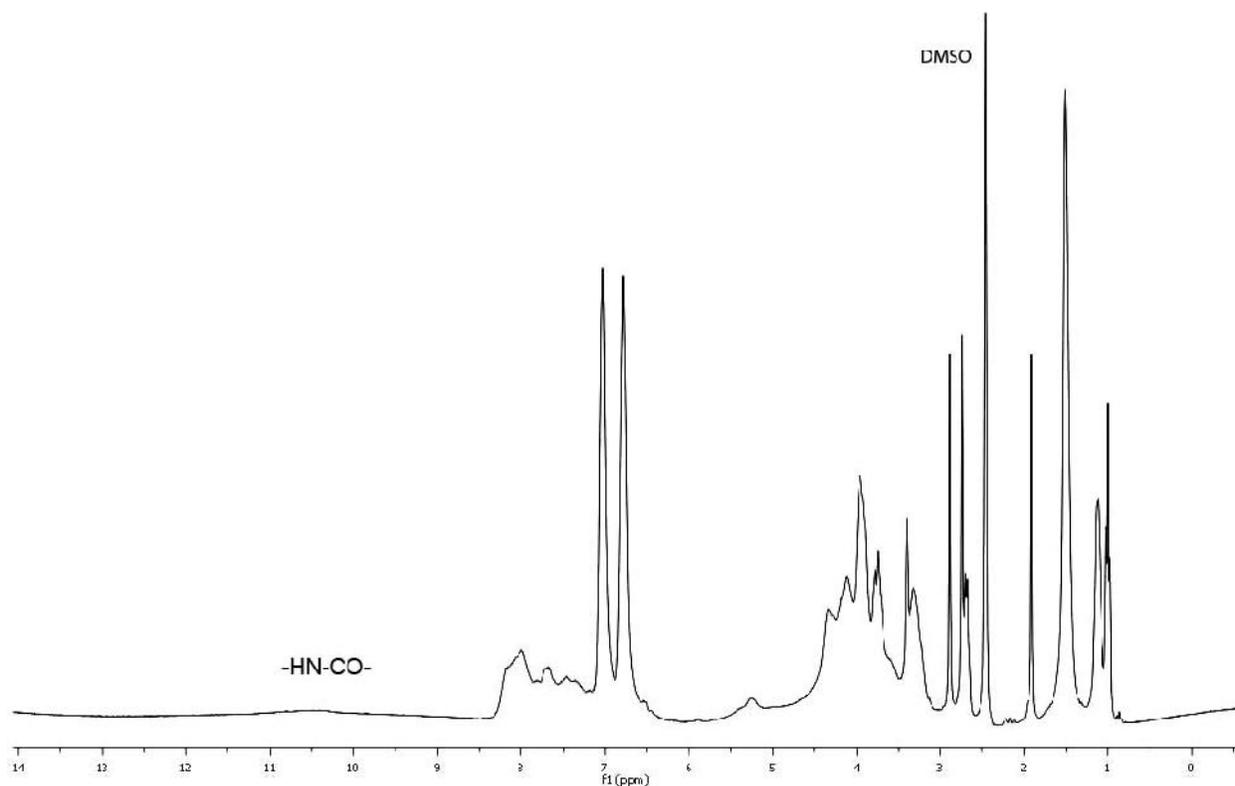


Figure (5): <sup>1</sup>H NMR spectrum of SPEM resin

### Thermal analysis

The stack plot of the TGA curves of polyesters products in Figure 6 exhibited good thermooxidative stability as there is no main weight loss occurred up to 200°C and the decomposition of the products is a two-step degradation process. The first decomposition step of SPEM resin (fillers free) occurred at 260°C with weight loss of about 20% within the temperature range of 220-380°C and the second step occurred at 455°C with weight loss of 44% within the temperature range of 380-530°C. The char residue at 700°C is about 20%.

The thermograms of SPEM resin/bentonite and SPEM resin/silica showed improved thermal stability compare toneat SPEM resin within both decomposition steps whereas SPEM resin/Zeolite showed lower thermal stability and decomposed slightly faster than SPEM resin within only the first decomposition step. However, during the second decomposition step the SPEM resin/Zeolite exhibited better thermal stability, lower weight loss and higher char yield up to 700°C. A summary of the thermal properties of products is given in Table 1.

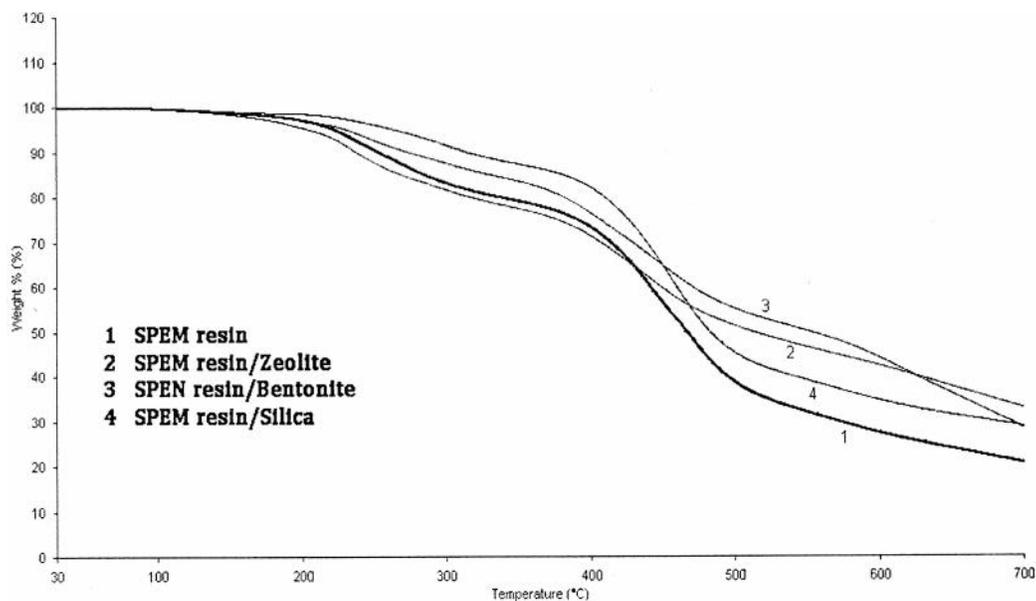


Figure (6): TG curves of products under oxygen gas

Table (1): A summary of the thermal properties of products

Product	1 <sup>st</sup> decomposition step			2 <sup>nd</sup> decomposition step			Char yield at 700°C Wt. %
	Temp. (°C)	Range <sup>a</sup> (°C)	Wt. loss (%) <sup>b</sup>	Temp. (°C)	Range <sup>a</sup> (°C)	Wt. loss (%) <sup>b</sup>	
SPEM	260	220-380	20	452	380-530	44	20
SPEM/Zeolite	240	190-350	22	450	330-560	35	33
SPEM/Bentonite	280	220-380	15	450	330-580	35	30
SPEM/Silica	295	220-350	10	455	360-540	50	30

<sup>a</sup> Temperature range of the decomposition step

<sup>b</sup> Weight loss % at indicated temperature

## Conclusions

Unsaturated amide maleamic acid (USMA) was synthesized from reaction of maleic anhydride with 4-aminobenzoic acid and then crosslinked with styrene monomers in the presence of benzoyl peroxide as an initiator.

The polyester was formed by reaction the later compound with epoxy resin in the presence of triethyl amine as a catalyst. The molecular structure of the new polyester was confirmed by C.H.N elemental analysis, FTIR and <sup>1</sup>HNMR spectroscopy. The SPEN resin was

reinforced with 10% of three types of fillers (Bentonite, Zeolite and Silica). The reinforced SPEM exhibited enhanced thermo-oxidative stability compare to the neat SPEM.

### **Acknowledgements**

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## تحضير وتشخيص راتنج بولي استر أمايد المحتوي على الستايرين ودراسة خواصه الحرارية

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### الخلاصة

في هذا البحث تم تحضير حامض مليناميك الغير مشبع وذلك بتفاعل المالك انهيديرايد مع حامض 4-امينو بنزويك بمذيب الاليتون ثم تشابك المركب الناتج مع مونومير الستايرين باستخدام بادئ بنزويل بيروكسايد في مذيب الدايميثيل اسيتايد وفي الخطوة اللاحقة تم مفاعل مجموعتي الكاربوكسيل الطرفية للمركب الناتج والمتشابك بالستايرين مع الايبوكسي بوجود عامل مساعد قاعدي هو التراي اثيل امين ليتم تحضير راتنج البولي استر امايد. تم دراسة التركيب البنائي للمركبات الناتجة بتقنية مطياف الاشعة تحت الحمراء والرنين النووي المغناطيسي كذلك التحليل الكمي للعناصر. ان البولي استر امايد الجديد المحضر تم تحميله بنسبة 10% من حشوات الزيولايت، البنثونايت والسليكا وفحصت الاستقرار الحرارية للمركبات الناتجة بجهاز التحليل الحراري الوزني في جو من غاز الاوكسجين وظهرت النتائج تحسين في الاكسدة الحرارية قياسا بالنموذج الخالي من الحشوات وكذلك اظهرت مخلفات بنسبة 33% عند درجة حرارة 700 درجة مئوية.