Synthesis, characterization, thermal and fire retardant properties of new homo- and block copolymers of polyacrylate and epoxy resin with cyclotriphosphazene core

Alaa Shaban[1], **Salah Mahdi Al-Shukri**[1), *)], **Hussein Ismail Kahlaf**[1], **Othman A. Al Hanbali**[2]

DOI: dx.doi.org/10.14314/polimery.2019.9.2

Abstract: New homo- and block copolymers composed of polyacrylate and epoxy resin with hexafunctional cyclotriphosphazene core were synthesized and characterized by FT-IR and ^{1}H-, ^{13}C-, and ^{31}P- NMR. The first homopolymer, PN-polyacry was prepared from the direct condensation of 2-hydroxyethylacrylate with acyl chloride of hexakis(4-carboxyphenoxy)cyclotriphosphazene, PN-acyl. The second homopolymer, PN-Ep, was prepared in a direct reaction of catalyzed carboxyl groups of hexakis(4-carboxyphenoxy)cyclotriphosphazene PN-COOH with epoxy resin *via* an oxirane ring opening reaction. The block copolymer, PN-Ep/polyacry, was prepared from the partial coupling of 2-hydroxyethyl acrylate with the PN-acyl, followed by the reaction of unreacted carboxyl groups with epoxy resin. Differential scanning calorimetry (DSC) analysis of the PN-Ep/polyacry copolymer exhibited good compatibility between polyacrylate and cured epoxy resin. Thermal gravimetric analysis (TGA) revealed that the prepared polymeric systems accumulate 30–38 wt % char at elevated temperatures, compared to neat polyacrylate and cured epoxy resin, which accumulate negligible char at 700 °C. The limiting oxygen index (*LOI*) exhibited significant enhancement of fire retardant properties of the prepared polymeric systems. A scanning electron microscopy (SEM) morphology study revealed that PN-polyacry and PN-Ep/polyacrylate produced intumescent char residues while PN-Ep produced solid dense char with a nonporous surface.

Keywords: synthesis, cyclotriphosphazene, epoxy resin, polyacrylate, thermal stability, flame retardant.

Synteza, charakterystyka, właściwości termiczne i ognioodporne nowych homopolimerów i kopolimerów blokowych poliakrylanu i żywicy epoksydowej z rdzeniem cyklotrifosfazenowym

Streszczenie: Zsyntetyzowano nowe homopolimery i kopolimery blokowe złożone z poliakrylanu i żywicy epoksydowej z sześciofunkcyjnym rdzeniem cyklotrifosfazenu. Struktury scharakteryzowano metodami FT-IR i ^{1}H-, ^{13}C- oraz ^{31}P-NMR. Pierwszy homopolimer, poliakrylan (PN), wytworzono w bezpośredniej kondensacji akrylanu 2-hydroksyetylu z chlorkiem acylu heksakis(4--karboksyfenoksy)cyklotrifosfazenu (PN-acyl). Drugi homopolimer (PN-Ep) wytworzono w katalizowanej bezpośredniej reakcji grup karboksylowych heksakis(4-karboksyfenoksy) cyklotrifosfazenu (PN-COOH) z żywicą epoksydową w wyniku otwarcia pierścienia oksiranowego. Kopolimer blokowy (PN-Ep/poliakry) otrzymano w procesie częściowego sprzęgania akrylanu 2-hydroksyetylu z PN-acylem i następnej reakcji nieprzereagowanych grup karboksylowych z żywicą epoksydową. Analiza kopolimeru PN-Ep/poliakry za pomocą różnicowego kalorymetru skaningowego (DSC) wykazała dobrą kompatybilność między poliakrylanem i utwardzoną żywicą epoksydową, a na podstawie analizy termograwimetrycznej (TGA) stwierdzono, że przygotowane układy polimerowe spalają się w podwyższonej temperaturze do karbonizatu (30—38% mas.), podczas gdy czysty poliakrylan i utwardzona żywica epoksydowa w 700 °C wytwarzają jego pomijalne ilości. Wartość granicznego wskaźnika tlenowego (*LOI*) wskazywała na znaczące zwiększenie ognioodporności przygotowanych układów polimerowych. Badanie morfologii przy użyciu skaningowego mikroskopu elektronowego (SEM) wykazało, że

---

[1] Mustansiriyah University, Department of Chemistry, College of Science, Baghdad 10052, Iraq.

[2] The University of Sydney, School of Pharmacy, Sydney NSW 2006, Australia.

*) Author for correspondence; e-mail: salah_M@uomustansiriyah.edu.iq

w wyniku spalania poliakrylanu PN i PN-Ep/poliakrylanu wytwarza się pozostałość pęczniejących karbonizatów, podczas gdy w procesie spalania PN-Ep wytwarzał się zwarty gęsty osad o nieporowatej powierzchni.

Słowa kluczowe: synteza, cyklotrifosfazen, żywica epoksydowa, poliakrylan, stabilność termiczna, środek zmniejszający palność.

In the last decades, considerable attention has been directed toward improving the thermal and fire retardant properties of organic curable polymers such as epoxy resin and acrylate derivatives by using halogen free compounds, and to gradually replace halogenated flame retardants to reduce the generation of smoke and corrosive, toxic gases during thermal decomposition by using phosphorus-nitrogen containing compounds [1–5]. Hexachlorocyclotriphosphazene is a versatile starting oligomer containing three N=PCl_2 units; all the chlorines on phosphorus atoms are active and can be readily substituted with a wide range of functional organic groups *via* nucleophilic reactions, affording different types of organocyclotriphosphazenes.

Because of their outstanding properties, different structures of organocyclotriphosphazenes: cyclolinear [6], cyclomatrix [7], and a cyclotriphosphazene core [8] were used to enhance the thermal and fire retardant properties of polymers such as polyurethane [9], poly(ethylene terephthalate) [10], poly(methyl methacrylate) [11], Nylon 6 [12], and epoxy resins [13].

Flame retardation is an interruption of the burning process during heating, decomposition, ignition, or flame spread stages. Depending on its nature, a flame retardants can act physically by reducing the temperature of the substrate below that required for sustained combustion, by diluting the concentration of the burning fuel gas to below the minimum required for burning, and/or by forming a protective layer chemically in a solid or liquid (molten) state.

The usual approaches for conferring unique thermal and fire retardant properties of organocyclotriphosphazenes are by physical blending [14–16] or by chemical incorporation [17, 18] into the polymer system. The latter technique is preferred because cyclotriphosphazenes are more effective when they are an integral part of the polymer system than when they are present in a physical blend.

Phosphazene (P=N) units in a condensed phased form a char that provides a protective layer to the underlying polymeric materials, limiting the generation of combustible gases, and decreasing the exothermicity of the pyrolysis reaction. In the vapor phase, (P=N) units are flame quenching materials cause a heat sink effect in the flame zone: lowering the temperature of the flame, disrupting the decomposition process and thereby inhibits combustion. Therefore, phosphazene containing compounds significantly enhance fire retardant characteristics of polymers.

One of the interesting field of the phosphazene chemistry might be the synthesis of cyclotriphosphazene core with multifunctional groups. These groups having the ability to initiate polymerization with a broad range of monomers, and thereby impart useful properties of the phosphazene to the polymers. Synthesized cores can contain one to six functional groups, depending on the ratio of substituents, the functionality, and the synthetic approaches [19, 20]. Functional groups such carboxylic acid [13, 21], aldehyde [22, 23], amine [20, 24], alcohol [25], and phenol [26] have been used to initiate polymerization with different polymerizable monomers to form block copolymers [27] and homopolymers [28] with cyclotriphosphazene cores.

As part of our ongoing program directed towards the development of halogen free flame retardant polymers, we have focused our efforts on designing of hexafunctional cyclotriphosphazene as a multifunctional core for synthesis of new halogen free, thermally stable and fire resistant homo- and block copolymers containing polyacrylate and epoxy resin.

EXPERIMENTAL PART

Materials

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ (HCP, Sigma-Aldrich) was purified by recrystallization from *n*-hexane. Ethyl 4-hydroxybenzoate (Sigma-Aldrich) was purified by recrystallization from hot toluene. Reagent-grade triethylamine (Merck) was predried over ground potassium hydroxide, distilled, and filtered over molecular sieves. 1,4-dioxane (Merck) was freshly distilled from sodium metal in an atmosphere of argon gas.

2-hydroxyethylacrylate (HEA) (Sigma-Aldrich) was distilled under vacuum to remove the inhibitor (mono-ethyl ether hydroquinone) prior to use, and stored under nitrogen. Conventional epoxy resin (diglycidyl ether of bisphenol A, DGEBA) with an epoxy equivalent weight (EEW) of 184–194 g was kindly supplied by Sika concert restoration system co. Other chemicals were used as commercially supplied without further purification.

Synthesis of PN-Et

A solution of HCP (5 mg, 14.38 mmol) in 10 cm^3 of freshly distilled 1,4-dioxane was added drop wise into sodium 4-ethoxycarbonylphenoxide formed from the reaction of sodium metal (2.249 mg, 97.8 mmol) and ethyl 4-hydroxybenzoate (14.77 mg, 88.9 mmol) in 50 cm^3 of 1,4-dioxane and refluxed for 3 h. After being stirred and refluxed for 6 h, the resulting sodium chloride was removed by suction filtration and the filtrate was evaporated to dryness using a rotary evaporator. The solid product was recrystallized from hot methanol, affording white crystals of PN-Et. The PN-Et was hydrolyzed to the corresponding acid with NaOH in aqueous 1,4-dioxane. The reaction mixture was poured into 250 cm^3 of ice water. After filtration, the mixture was acidified with 2N HCl. PN-COOH precipitated as a white solid, which was collected, thoroughly washed with water, and dried at 100 °C in a vacuum oven.

PN-Et: yield 88%, melting point 87 °C.

FT-IR (between KBr cells, $CHCl_3$), 3107, 3074 cm^{-1} (C-H arom.); 2982–2873 cm^{-1} (C-H of CH_3 and CH_2); 1719 cm^{-1} (C=O); 1603, 1503, 1412 cm^{-1} (C=C arom.); 1274 cm^{-1} (C-O-C); 1207, 1160 cm^{-1} (P=N); 1017 cm^{-1} (PO-Ar); 956 cm^{-1}(P-OAr); and 890 cm^{-1} (P=N) skeletal vibration.

^{31}P NMR ppm, ($CDCl_3$, H_3PO_4) (δ 7.54).

^1H NMR ppm, (δ 8.12–6.88, m, 24H, arom. H); (δ 4.36, q, 12H, O-CH_2-); and (δ 1.39, t, 18H, CH_3-).

^{13}C NMR ppm ($CDCl_3$, TMS), (δ 165.55, 153.73, 120.58, 131.29, 127.70, 61.17 and 14.31 ppm).

Elemental analysis C, H, N, calculated for $C_{54}H_{54}N_3O_{18}P_3$: C 57.60; H 4.83; N 3.73%. Found: C 56.153; H 4.832; N 3.146%.

PN-COOH: yield 86%, $T_{(dec)}$ 280–350 °C; IR (KBr dick), 3080 cm^{-1} (COO-H); 1698 cm^{-1} (C=O); 1602, 1506, 1425 cm^{-1} (C=C arom.); 1202, 1161 cm^{-1} (P=N); 1016 cm^{-1} (PO-Ar); 952 cm^{-1} (P-OAr); and 894 cm^{-1} (P=N) skeletal vibration.

^{31}P NMR ppm, (DMSO-d_6, H_3PO_4) (δ 8.39).

^1H NMR ppm, (6.91–7.37 and 7.78–8.08, m, 24H, arom.).

^{13}C NMR ppm, (δ 167.31, 153.21, 131.22, 128.20 and 120.48).

Synthesis of PN-acyl

Thionyl chloride (30 cm^3 in excess) was added to PN-COOH (5 mg, 5.22 mmole) in a 100 cm^3 round bottom flask fitted with a reflux condenser, a drying tube, and a magnetic stirrer. The flask was placed in an oil bath and the mixture was heated and stirred for 8 h under an atmosphere of nitrogen gas until a clear, colorless solution was formed; excess thionyl chloride was removed by distillation under vacuum. The whitish solid product was collected and stored under argon gas in a desiccator.

FT-IR (between KBr cells, $CHCl_3$), 3104, 3076 cm^{-1} (C-H arom.); 1776, 1741 cm^{-1} (C=O); 1595, 1497, 1413 cm^{-1} (C=C arom.); 1207, 1160 cm^{-1} (P=N); 1017 cm^{-1} (PO-Ar); 953 cm^{-1} (P-OAr); 890 cm^{-1} (P=N) skeletal vibration and 645 cm^{-1} [O=C(Cl)].

Synthesis of PN-acry

To a stirring solution of PN-acyl (4 mg, 3.74 mmol) in 50 cm^3 of 1,4-dioxane, a mixture of 2-hydroxyethyl acrylate (2.58 cm^3, 22.46 mmol) and triethylamine (3.13 cm^3, 22.46 mmol) in 20 cm^3 of 1,4-dioxane was carefully added over a period of 30 min. The mixture was stirred for 3 h, then heated for another 10 min. The precipitated salt was filtered and the solvent was removed by a rotary evaporator. The solid product was dissolved in methylene chloride, then washed twice with water in a separatory funnel. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The yellowish product, PN-acry, was collected and further dried in a vacuum oven at 80 °C.

PN-acry: Yield 82%; FT-IR (between KBr cells, $CHCl_3$), 3106, 3074 cm^{-1} (C-H arom.); 2958, 2857 cm^{-1} (C-H aliph.); 1725 cm^{-1} (C=O); 1635 cm^{-1} (-C=C of acrylate); 1602, 1503, 1411 cm^{-1} (C=C arom.); 1204, 1160 cm^{-1} (P=N) stretching; 1016 cm^{-1} (PO-Ar); 946 cm^{-1} (P-OAr) and 890 cm^{-1} (P=N) skeletal vibration.

^1H NMR ppm, ($CDCl_3$, TMS) (δ 8.05–7.20, b, 24H, arom. H); (δ 4.69, b, 24H, O-CH_2*-CH_2*-O); (δ 6.56, 6.02 trans and cis, b, 12H, C(O)-CH=CH_2*); (δ 6.31, m, 6H, C(O)-CH*=CH_2).

^{13}C NMR ppm, (δ 165.26, 164.50, 153.31, 131.50, 130.51, 127.72, 119.73, 128.39, 62.31 and 61.08).

Synthesis of PN-polyacry

To a stirring solution of PN-acry (4 mg, 2.25 mmole), an excess of 6 cm^3 of 2-hydroxyethyl acrylate in 30 cm^3 1,4-dioxane was added to a 100 cm^3 round bottom flask equipped with a reflux condenser, a drying tube, and a magnetic stirrer and placed in an oil bath. Benzoylperoxide (0.06 mg) was added and the contents of the flask were stirred at 100 °C for about 8 hours until a thick solution formed. The solution was filtered under vacuum pressure, and the solvent was removed with a rotary evaporator. The yellow solid product, PN-polyacry, was further dried under vacuum pressure.

PN-polyacry: FT-IR (KBr windows), 3454 cm^{-1} (alcoholic O-H); 3106 and 3073 cm^{-1} (C-H arom.); 2959, 2889, 2857 cm^{-1} (C-H aliph.); 1725 cm^{-1} (C=O); 1602, 1503, 1413 cm^{-1}, (C=C arom.); 1203, 1161 cm^{-1} (P=N); 1016 cm^{-1} (PO-Ar); 947 cm^{-1} (P-OAr) and 889 cm^{-1} (P=N) skeletal vibration.

Synthesis of PN-Ep

PN-COOH (5 cm^3, 5.22 mmole) in 50 cm^3 of pyridine was stirred and refluxed inside a 100 cm^3 round bottom flask until a clear colorless solution formed. Excess pyridine was distilled under vacuum and a white solid product precipitated and was dried in a vacuum oven. In a ceramic crucible, 15 mg of epoxy resin (EP) dissolved in 5 cm^3 of chloroform were mixed by spatula, added to the catalyzed PN-COOH, and the mixture was heated in an oven for about 30 min at 100 °C until a clear whitish, homogenous, sticky substance formed. The curing agent 1,6-hexamethylenediamine with a ratio equivalent to the epoxy resin of 1 : 1 was added and well mixed. The mixture gradually hardened over time. A semitransparent brown solid, cured PN-Ep, was obtained.

PN-Ep before curing: FT-IR (thin film on KBr cell), 3471 cm^{-1} (alcoholic O-H of epoxy resin); 3055 and

3034 cm^{-1} (str. C-H arom.); 2966, 2926, 2872 cm^{-1} (str. C-H aliph.); 1719 cm^{-1} (C=O); 1605, 1508, 1413 cm^{-1} (str. C=C arom.); 1161 cm^{-1} (P=N); 1016 cm^{-1} (PO-Ar); 937 cm^{-1} (P-OAr); 870 cm^{-1} (P=N) and 1298, 915, 830 cm^{-1} (oxirane) ring.

^{1}H NMR ppm, (DMSO-d$_6$ +1-2 drops TFA), (δ 7.83––6.82, m, arom. H); [δ 4.31 ppm, d, -CH$_2$*-CH(OH)--CH$_2$-O-]; [δ 4.20 ppm, b,-CH$_2$-CH* (OH)-CH$_2$-O-]; (δ 3.45 ppm, s, -CH$_2$-CH (OH*)-CH$_2$-O-); (δ 3.81 ppm, b, 12H-O-CH$_2$*-oxirane); (δ 2.90 ppm, b, 6H, -CH of oxirane); (δ 2.60 ppm, 12H, -CH$_2$* of oxirane); [δ 1.61 ppm, s, -CH$_3$ of 4,4'-(isopropoylidene)diphenoxy].

^{13}C NMR ppm, (δ 160.00, 156.46, 130.71, 128.51, 120.15, 143.37, 131.05, 127.86, 114.31, 78.06, 70.33, 69.84, 68.25, 50.16, 41.59, 44.14, 31.04), assignment of the ^{13}C NMR signals are given in results and discussion section.

Synthesis of PN-COOH/acry

In a mole ratio of 1 : 3, to a solution of PN-acyl (5 mg, 4.67 mmole) in 30 cm^3 of 1,4-dioxane, 2-hydroxyethyl acrylate (1.61 cm^3, 14.03 mmol) and triethylamine (1.96 cm^3, 14.03 mmol) in 1,4-dioxane (20 cm^3) were carefully added *via* an addition funnel over a period of 40 minutes in a 100 cm^3 round bottom flask fitted with a reflux condenser and a magnetic stirrer and placed in an oil bath. The contents of the flask were stirred for 4 h at room temperature before being refluxed for an additional 10 min under a nitrogen atmosphere. The solution was filtered, and the filtrate was dried under reduced pressure using a rotary evaporator. The resulting residue was reconstituted in 50 cm^3 methylene chloride and the solution was washed with distilled water in a separator funnel; the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and the solvent was evaporated to dryness; a solid pale white product, PN-COOH/acrylate, was obtained.

PN-COOH/acry. Yield 55%;

FT-IR (between two KBr cells, CHCl$_3$), 3170 cm^{-1} (COO-H); 3073 cm^{-1} (C-H arom.); 2959 cm^{-1} (C-H aliph.); 1724 cm^{-1} (C=O of acrylate); 1698 cm^{-1} (C=O of carboxylate); 1637 cm^{-1} (C=C acrylate); 1602, 1504, 1414 cm^{-1} (C=C arom.); 1203, 1160 cm^{-1} (P=N); 1016 cm^{-1} PO-Ar; 950 cm^{-1} (P-OAr) and 884 cm^{-1} (P=N) skeletal vibration.

^{1}H NMR ppm, (CDCl$_3$) (δ 8.41–6.80, b, 24H, arom. H); [δ 6.50–5.41, b, trans and cis, b, 12 H, C(O)-CH=CH$_2$]; (δ 4.45, b, 12 H, O-CH$_2$*-CH$_2$*-O).

^{13}C NMR ppm, (175.82, 166.93, 166.49, 155.56, 154.46, 133.29, 131.61, 129.47, 127.45, 121.96, 62.38, 61.08).

Synthesis of PN-Ep/polyacry

PN-COOH/acry (5 mg, 3.99 mmole) was dissolved in 50 cm^3 of 1,4-dioxane, excess of 6 cm^3 2-hydroxyethyl acrylate and 0.06 g of benzoyl peroxide were added. The flask contents were heated at 100 °C with continuous stirring for 8 h until a white, hazy gel formed and precipitated. The gel was isolated and excess solvent was removed under reduced pressure. The material obtained was stirred in pyridine, and refluxed for about 2 h before removing excess pyridine under reduced pressure; 7 mg in excess epoxy resin was added to the product and the components were mixed well before being heated in an oven at 100 °C for about 30 min. Brownish, homogenous, sticky material was formed. The curing agent 1,6-hexamethylenediamine was added and mixed in until the hard brown material PN-Ep/polyacry was formed.

FT-IR (thin film on KBr window) before curing of epoxy resin; 3457 cm^{-1} (O-H of epoxy resin), 3059 cm^{-1} (C-H arom.), 2960–2853 cm^{-1} (C-H aliph.), 1718 cm^{-1} (C=O of both ester groups), at 1250, 1160 cm^{-1} due to P=N stretching vibration, 950 cm^{-1} due to P-OAr bond and 1296, 915, 831 cm^{-1} (oxirane ring).

Methods of testing

Fourier-transform infrared (FT-IR) spectra in the range of 4000–400 cm^{-1} were recorded on a SHIMADZU 8400s FTIR spectrophotometer.

^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded using an Oxford Varian 300 NMR spectrometer operated at 300 MHz for proton and 75 MHz for carbon. Chemical shifts were recorded in parts per million relative to tetramethylsilane (TMS) (0.00 ppm) for ^{1}H NMR and ^{13}C NMR and to 85% H$_3$PO$_4$ (0.00 ppm) for ^{31}P NMR.

Thermal gravimetric analyses (TGA) were obtained on a TA Instruments–Discovery (TGA) at a heating rate of 10 °C/min in the range of ambient temperature to 700 °C in an atmosphere of N$_2$ gas.

Differential scanning calorimetry (DSC) analysis was performed on a NETZSCH DSC 204 F1 Phoenix (Germany) at a heating rate of 10 °C/min in an atmosphere of N$_2$ gas in a temperature range of 0–250 °C. Glass transition temperatures (T_g) were determined from the inflection point of the DSC thermogram.

EuroEA-3000 elemental analyzer was used to perform the C, H, N elemental analysis.

A Quanta 450 scanning electron microscope (SEM) (FEI, USA) was used to study the surface morphology of samples.

A Bruker energy dispersive X–ray (EDX) microanalyzer was used to obtain qualitative and semiquantitative information about the elements present in the specimens; a beam voltage of 20 kV was used for all specimens.

A limiting oxygen index (*LOI*) was determined using an instrument from Fangyuan Instrument (DG) Co., Ltd. according to the ASTM D-2863 Standard Test Method. Samples (3.5 × 6.5 × 100 mm) were held vertically by a clamp at the bottom end of the combustion column. Samples were ignited at the upper end of the column with a butane burner and allowed to burn like a candle from the top down in a mixture of oxygen and nitrogen gases passing through a bed of glass beads to smooth the flow of gas.

RESULTS AND DISCUSSION

Characterization of PN-Et

The condensation reaction of hexachlorocyclotriphosphazene with the sodium salt of 4-hydroxyethyl benzoate afforded a fully substituted hexakis(4-ethoxycarbonylphenoxy)cyclotriphosphazene, PN-Et (Scheme A).

The FT-IR spectrum (Fig. 1) shows characteristic bands of the phosphazene ring, mainly at 1207 and 1160 cm^{-1}, which represent the asymmetric and symmetric stretching of the (P=N) group, respectively. The band at 1017 cm^{-1} is attributed to the PO-Ar bond. The C=O and C-O-C absorption frequencies of ethoxycarbonylphenoxy appeared at 1719 and 1274 cm^{-1}, respectively. Absorption peaks at 600 and 526 cm^{-1}, characteristic of P-Cl bonds, are not discernible in the IR spectrum, suggesting that chlorine atoms had all been substituted, affording hexakis(4-ethoxycarbonylphenoxy)cyclotriphosphazene, PN-Et. The single resonance at 7.54 ppm on the ^{31}P NMR spectrum indicates a total replacement of the P-Cl bond. The elemental results are in good agreement with the theoretical data calculated based on the expected formula of PN-Et. These results indicate that six ester groups were successfully substituted on the cyclotriphosphazene ring, and no side products were formed.

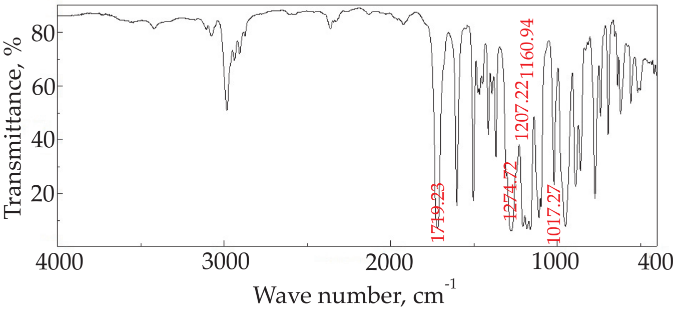
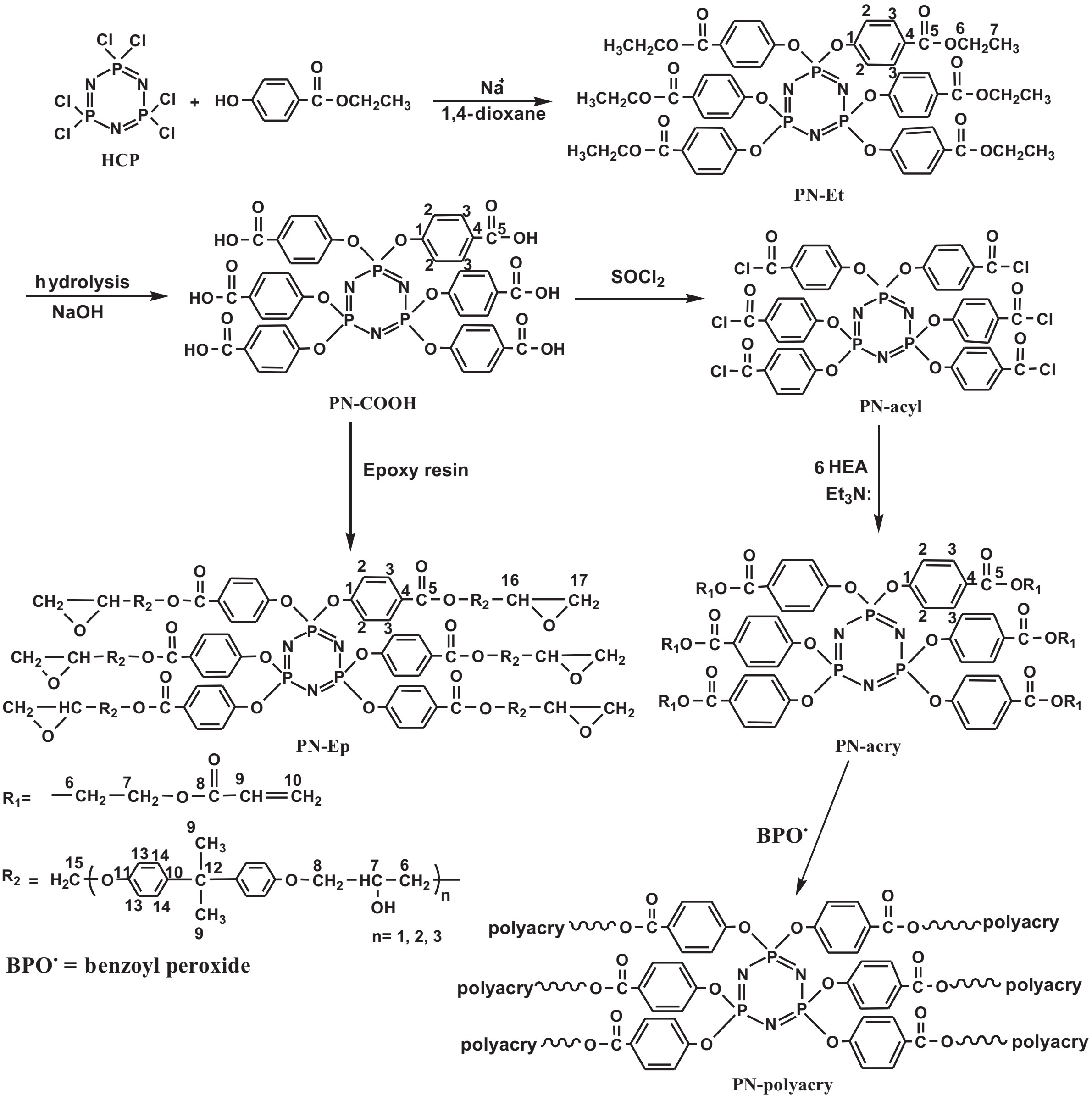


Fig. 1. FT-IR spectrum of PN-Et



Scheme A

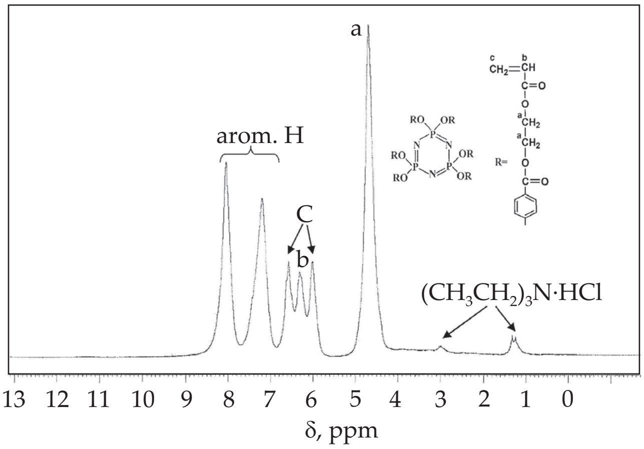


Fig. 2. ^{1}H NMR spectrum of PN-acry

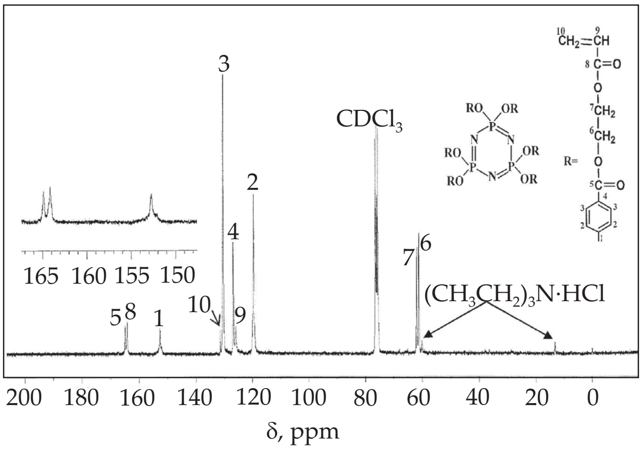


Fig. 3. ^{13}C NMR spectrum of PN-acry

The product PN-Et was hydrolyzed with NaOH to the corresponding carboxylic acid PN-COOH. The procedure we used, according to Miyata *et al.* [21], afforded a complete hydrolysis to PN-COOH and the phosphazene ring remained intact, as indicated by the presence of characteristic peaks at 1202 and 1161 cm^{-1}due to P=N of phosphazene ring. Other peaks due hydroxyl stretching (O-H) and C=O of the carboxyl group were appeared at 3080 and 1698 cm^{-1} in FT-IR spectrum.

Characterization of PN-acry

PN-acry was synthesized from the condensation of PN-acyl with 6 moles of 2-hydroxyethylacrylate in the presence of triethylamine as an HCl scavenger (Scheme A). The FT-IR spectrum of PN-acry shows strong peaks at 1725 cm^{-1} due to C=O carbonyl groups in 4-carbonyl phenoxy and acrylate. Absorption frequencies at 1635 cm^{-1} due to the -CH=CH$_2$ of the acrylate group, 1204 and 1160 cm^{-1}

Table 1. ^{13}CNMR spectral data of products

Labeled[a]	PN-Et δ ppm	PN-COOH δ ppm	PN-acry δ ppm	PN-Ep δ ppm	PN-COOH/acry δ ppm
1	153.73	153.21	153.31	156.46	154.46
1″	–	–	–	–	155.56
2	120.58	120.48	119.73	120.15	121.94
3	131.29	131.22	130.51	130.71	133.29
4	127.70	128.20	128.39	128.51	129.47
5	165.55	167.31	165.26	160.00	166.93
5″	–	–	–	–	175.82
6	61.17	–	61.08	68.25	61.08
7	14.31	–	62.31	69.84	62.38
8	–	–	164.50	78.06	166.49
9	–	–	127.72	31.04	127.45
10	–	–	131.50	131.05	131.61
11	–	–	–	143.37	–
12	–	–	–	41.59	–
13	–	–	–	114.31	–
14	–	–	–	127.86	–
15	–	–	–	70.33	–
16	–	–	–	50.16	–
17	–	–	–	44.14	–

[a] Carbon atoms numbered according to the overall structure of products given in Scheme A, B.

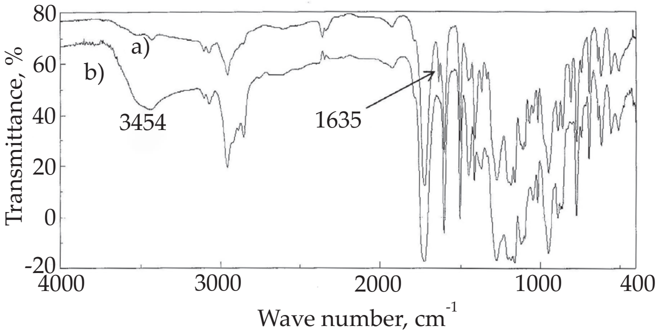


Fig. 4. Stack plot of the FT-IR spectra of: a) PN-acry, b) PN-polyacry

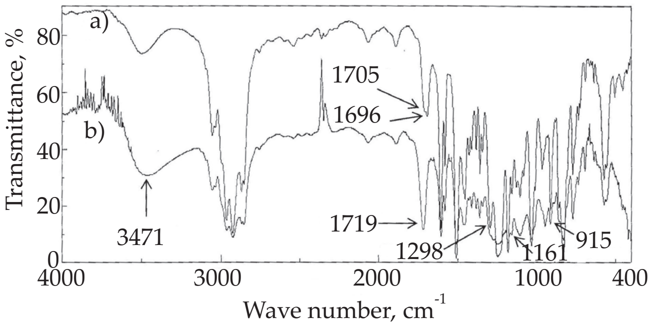


Fig. 5. Stack plot of the FT-IR spectra of reaction of: a) uncatalyzed, b) catalyzed, PN-COOH with epoxy resin

due to P=N, and 946 cm^{-1} due to P-OAr were apparent. The ^{1}H NMR spectrum (Fig. 2) exhibited broad resonances with no splitting. This might be due to self-aggregation of molecules in deuterated, low-polar solvents such as $CDCl_3$; it could also reflect the distribution of molecules in similar environments. Signals at 8.05–7.20 ppm and 4.69 ppm were attributed to aromatic protons and methoxy groups $-O-CH_2^*-CH_2^*-O-$, respectively. Trans and cis isomers of the methene group $C(O)-CH=CH_2^*$ appeared at 6.56 and 6.02 ppm, respectively, while the signal at 6.31 ppm was assigned to the methane group $C(O)-CH^*=CH_2$.

Small signals at about 3.0 and 1.1 ppm were assigned to a residual side product, triethylamine hydrochloride ($Et_3N{\cdot}HCl$).

The ^{13}C NMR spectrum (Fig. 3) confirms the structure of PN-acry. Signals at 165.26 ppm (labeled 5) and 164.50 ppm (labeled 8) can be assigned to carbonyls adjacent to phenoxy and acrylate groups, respectively. Signals at 131.50 (labeled 10) and 127.72 (labeled 9) ppm were assigned to $-CH=CH_2-$ groups. However, the signal at 167.31 ppm (labeled 5 in the PN-COOH, Table 1) due to carbonyl of the carboxyl group completely disappeared, implying that the six carboxyl groups were successfully substituted with acrylate units.

PN-acry was polymerized to the corresponding homopolymer PN-polyacry using benzoyl peroxide as an initiator. For comparison, a stack plot of FT-IR spectra of PN-acry and PN-polyacry is depicted in Fig. 4. An important feature is the disappearance of the absorption band at 1635 cm^{-1} which represented the $CH=CH_2$ in acrylate groups. This implies that the polymerization of acrylate groups was achieved under the given conditions, affording PN-polyacry.

Characterization of PN-Ep

PN-Ep was prepared by reacting PN-COOH with epoxy resin *via* an oxirane ring opening. The reaction took place slowly at room temperature and most of the epoxy resin did not react even after the temperature was raised to 150 °C for 72 h. The reaction of an oxirane ring with a carboxyl group can proceed in the absence of a catalyst, however, Blank *et al.* reported the catalytic activity of different bases to be pyridine > isoquinoline > quinoline > N,N-dimethylcyclohexylamine > tributylamine > *N*-ethylmorpholine > dimethylaniline > potassium hydroxide [29]. Therefore, when catalyzed PN-COOH was added to an epoxy resin, the oxirane ring opening reaction proceeded at about 80 °C and was nearly complete in 30 minutes at 100 °C. Figure 5 shows a stack plot of FT-IR spectra of uncatalyzed and catalyzed reactions of the PN-COOH with epoxy resin. The shoulder peaks at 1696 cm^{-1} and 1705 cm^{-1} indicate carbonyl groups; the for-

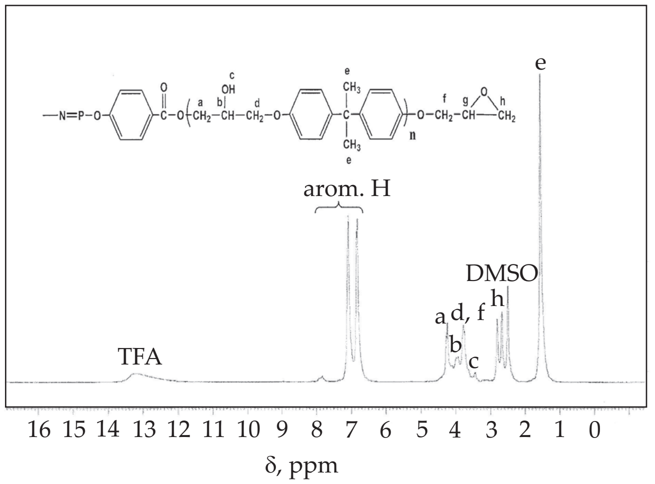


Fig. 6. ^{1}H NMR spectrum of PN-Ep

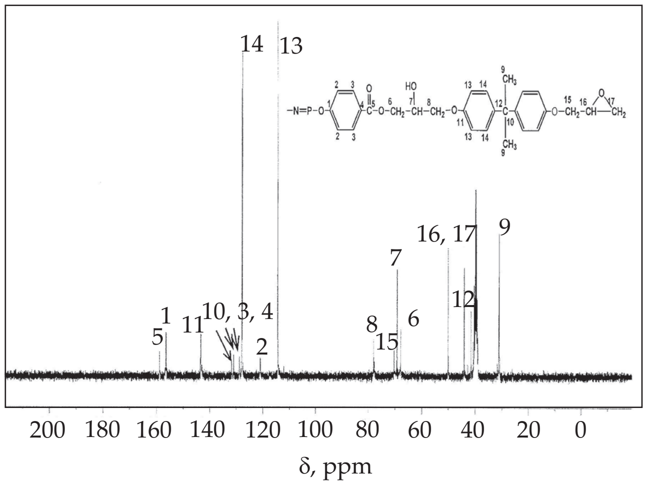


Fig. 7. ^{13}C NMR spectrum of PN-Ep

mer is assigned to unreacted carbonyl groups, while the latter is assigned to partial reactions with epoxy rings (Fig. 5a). The completed carboxyl-epoxy resin reaction is represented by a single carbonyl ester at 1719 cm^{-1} (shifted by about δ = 21 cm^{-1} from that of neat PN-COOH) (Fig. 5b) suggesting a complete reaction between the six COOH groups on the cyclotriphosphazene core with the epoxy ring in PN-Ep. Other important peaks discernible in the spectrum are at: 3471 cm^{-1} due to the hydroxyl of methine-CH_2-CH(OH)-CH_2-, 1161 cm^{-1} due to the symmetric P=N, 1016 cm^{-1} due to PO-Ar, and 1298, 915, 830 cm^{-1} due to the terminal oxirane ring stretching vibration.

The ^{1}H NMR spectrum (Fig. 6) exhibited aromatic proton resonances at 7.83–6.82 ppm. A strong single resonance at 1.61 ppm was assigned to methyl groups of 4,4′-isopropylidenediphenoxy. Resonances due to the reacted oxirane ring appeared as weak signals at 4.31, 4.20, and 3.45 ppm and were assigned to the protons of methylene (-CH_2^*-CH(OH)-CH_2-O-), methine (-CH_2-CH*(OH)-CH_2-O-), and hydroxyl (-CH_2-CH(OH*)-CH_2-O-) groups, respectively. Resonances of the unreacted terminal oxirane group appeared at 3.81 ppm, d, (-O-CH_2^*-oxirane), 2.90 ppm, b, (-CH of oxirane), and 2.60 ppm, b, (-CH_2 of oxirane). The ^{13}C NMR spectrum in Fig. 7 supports the proposed chemical structure of PN-Ep.

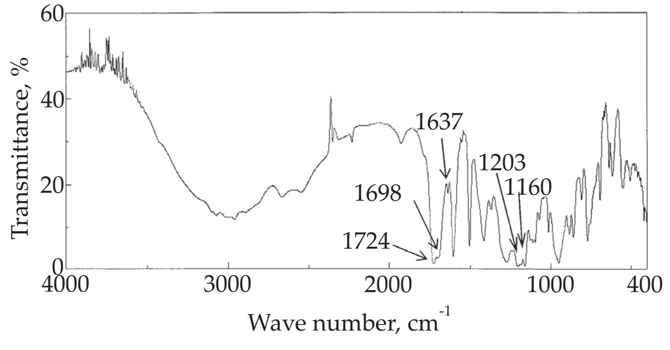


Fig. 8. FT-IR spectrum of PN-COOH/acry

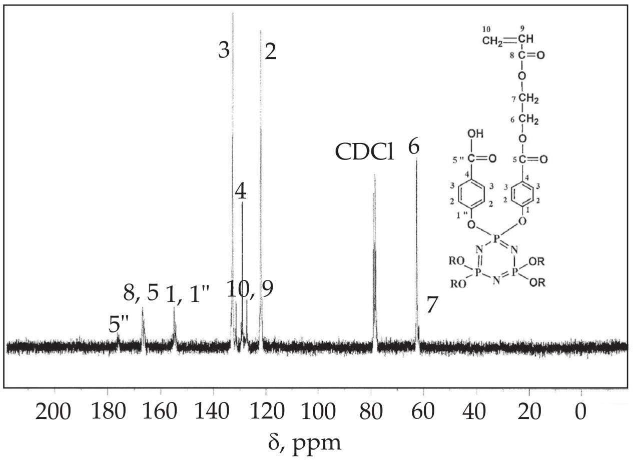


Fig. 9. ^{13}C NMR spectrum of PN-COOH/acry

Characterization of PN-COOH/acry

PN-COOH/acry was synthesized by reacting PN-COOH with three moles of 2-hydroxyethyl acrylate to form an intermediate compound consisted of three 4-carboxyphenoxy groups and three acrylate groups attached to a cyclotriphosphazene ring. The unreacted carboxyl groups were used in the next step to incorporate the epoxy resin into the polymeric system.

The FT-IR spectrum of PN-COOH/acry (Fig. 8) shows the carbonyl of the acrylate and carboxylic groups at 1724 and 1698 cm^{-1}, respectively, suggesting presence of both carboxyl and acrylate groups. The broad band centered at 3170 cm^{-1} represents unreacted (COO-H), the band at 1637 cm^{-1} represents -CH=CH_2 groups of acrylates, and bands at 1203 and 1160 cm^{-1} represent P=N stretching vibrations.

The ^{13}C NMR spectral data are in good agreement with FT-IR data. In the spectrum depicted in Fig. 9, signals due to the carbonyl of unreacted carboxyl groups and due to acrylate units appear at 175.82 ppm (labeled 5″) and 166.49 ppm (labeled 8), respectively. Peaks due to the methene –CH=CH_2 group are discernable at 131.61 ppm (labeled 10) and 127.45 ppm (labeled 9). Assignments of other resonances are listed in Table 1.

Characterization PN-Ep/polyacry

The final product, PN-Ep/polyacry block copolymer, was prepared by coupling the unreacted carboxylic groups of PN-COOH/acry with excess epoxy resin (Scheme B). The FT-IR spectrum depicted in Fig. 10 clearly shows the disappearance of the peak at 1637 cm^{-1} characteristic of the double bond in –CH=CH_2 groups, indicating that polymerization of acrylate groups has taken place. Disappearance of the broad absorption centered at 3170 cm^{-1} of unreacted carboxyl groups indicates that unreacted carboxyl groups have been coupled with epoxy resin. Other important features in this spectrum are the absorption peaks at 3457 cm^{-1} and 1718 cm^{-1} representing the O-H of the open oxirane ring and the carbonyl groups, respectively.

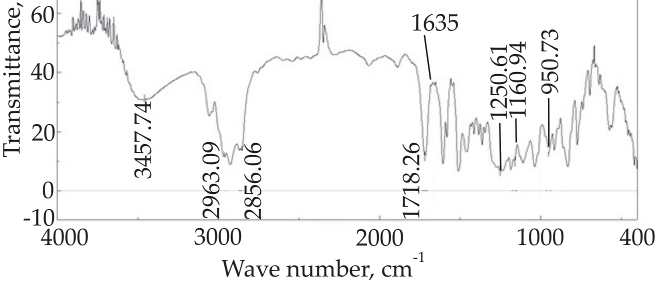
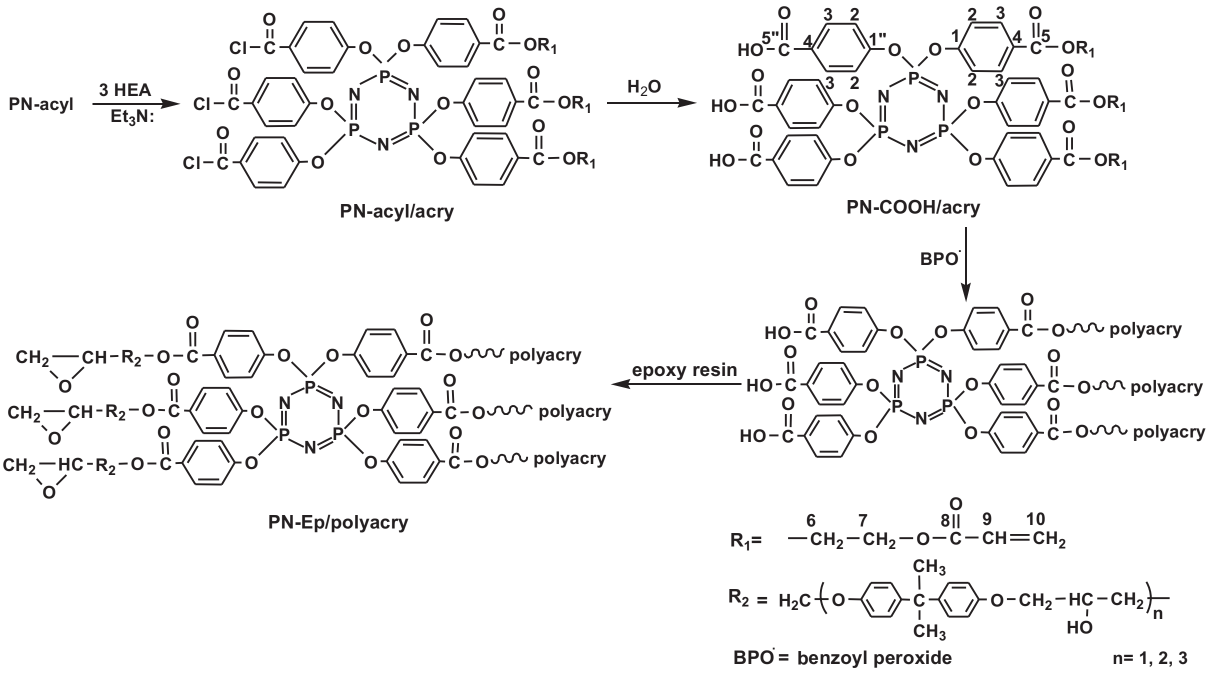


Fig. 10. FT-IR spectrum of PN-Ep/polyacry



Scheme B

Thermal analysis

The glass transition (T_g) is an important parameter, especially for epoxy containing polymers, because the materials are covalently cross-linked during the curing process. Unlike thermoplastic materials, the cured epoxy does not melt or flow when heated, but undergoes a slight softening at high temperatures. Therefore, the T_g value is strongly dependent on the curing procedure. Cures at low temperature, such as room temperature, will result in a low T_g. Very high T_g values are not achievable in room temperature curing [30].

Although curing of PN-Ep was performed at a relatively low temperature, the PN-Ep thermogram reveals a single endothermic transition at 77 °C due to the glass transition (T_g) (Fig. 11). This somewhat high T_g for a cured epoxy at room temperature is due to the incorporation of a multifunctional cyclotriphosphazene ring into the epoxy molecules, which decreases the molecular motion of the polymer chains and thus increases the T_g. The thermogram of PN-polyacry shows a T_g at 118 °C, which may be due to a rather flexible structure of the cyclotriphosphazene-based polyacrylate system. Furthermore, the thermogram of the PN-Ep/polyacry copolymer shows a clear transition at 97 °C. A T_g transition at 97 °C, which it is between the T_gs of PN-Ep and PN-polyacry is likely due to the formation of compatible copolymers system containing epoxy resin and polyacrylate with cyclotriphosphazene core. The thermogram of PN-Ep/polyacry shows another small transition at about 117 °C is might be due to the some of the polyacrylate chains.

A stack plot of the TG curves of PN-COOH, PN-polyacry, PN-Ep, PN-Ep/polyacry, and the control sample (polyacrylate/epoxy resin, formed from the in situ polymerization of 2-hydroxyethylacrylate in the presence of epoxy resin followed by curing with 1,6-hexamethylenediamine at 70 °C) is depicted in Fig. 12. The thermogram of PN-COOH showed moderate thermal stability and we-

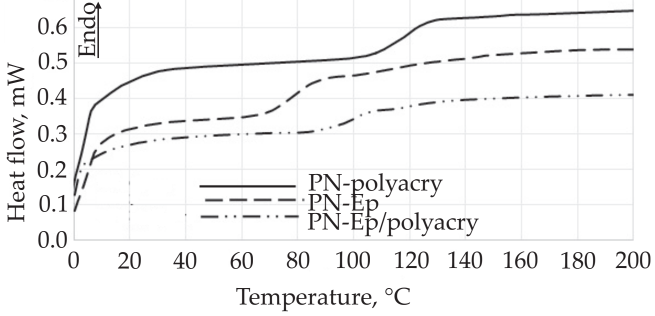


Fig. 11. Stack plot of the DSC thermograms of PN-polyacry, PN-Ep and PN-Ep/polyacry

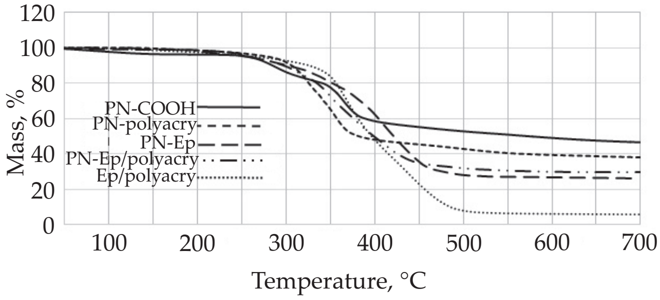


Fig. 12. Stack plot of TG curves of PN-COOH, PN-polyacry, PN-Ep and PN-Ep/polyacry

T a b l e 2. Thermal and fire retardant properties of products

Sample name	T_g, °C	1st decomp. step		*LOI*, vol %	Char, wt %	
		°C	wt %		600 °C	700 °C
PN-COOH	–	300	18	–	50.4	47.3
		360*)	21*			
PN-polyacry	118	350	40	30.5	39.4	38.4
PN-Ep	77	415	60	27.2	27.8	26.5
PN-Ep/polyacry	97, 117	380	50	28.0	32.8	30.3
Control sample	–	410	90	20.3	6.1	5.2
Cured epoxy resin	–	–	–	21.5a)	0	0
Neat polyacrylate	–	–	–	18.0b)	0	0

*) Values due to second major decomposition step.

a) Data reported by Liang *et al.* [32]; b) Data reported by Laoutid *et al.* [34].

ight loss commenced at over 240 °C. The main thermodegradation steps occurred at 300 and 360 °C with weight losses of 18% and 21%, respectively. The first step is likely due to the loss of bulky COOH, while the second step can be assigned to the cleavage of P-OAr bonds.

The homopolymer PN-polyacry thermogram exhibited one major decomposition step at 350 °C (within a temperature range of 300–450 °C) with total weight loss of 40%. This step is attributed to the decomposition of major components of PN-polyacry. The homopolymer PN-Ep thermogram showed slightly better thermal stability than that of PN-polyacry, as the main decomposition occurred at 415 °C (within the range of 300–480 °C) with a total weight loss of 60%. The enhanced thermal stability of PN-Ep is likely due to the cross-linking density of cured phosphazene-based epoxy resin.

The block copolymer PN-Ep/polyacry thermogram exhibited one decomposition step at 380 °C (within the range of 300–450 °C) with a total weight loss of 50%. The appearance of one decomposition step suggests the formation of a compatible copolymers with a cyclotriphosphazene core.

The thermograms of all the formulated polymeric systems showed minor decomposition steps at 460–550 °C with weight losses less than 10%. This minor decomposition is likely due to the scission and partial volatilization of P=N, which may play important role in disrupting the combustion in the vapor phase.

Note that the thermal stabilities of PN-polyacry, PN-Ep, and PN-Ep/polyacry are slightly lower than that of the control sample (polyacrylate/epoxy resin) because the P-O-Ar and C-O-C bonds of phosphazene containing polymeric materials are less stable than those of nonphosphazene compounds when heated [31]. However, the homo- PN-polyacry, PN-Ep, and co-polymers PN-Ep/polyacry exhibited higher char content than the control sample; this result is attributed to the formation of covalently cross-linked and thermally stable phosphorus and nitrogen species.

The char residues discernible from the TG curves of PN-COOH, PN-polyacry, PN-Ep, PN-Ep/polyacry, and the control sample (polyacrylate/epoxy resin) at 700 °C are 47.3%, 38.4%, 26.5%, 30.3% and 5.2%, respectively (Table 2). The presence of a substantial amount of char residue is likely a result of the breaking and repolymerizing of cyclotriphosphazene rings with a subsequent increase in crosslinking density attributable to inter- and intra-reactions of the resulting polymeric chains. The formation of highly crosslinked products during the pyrolysis of cyclotriphosphazene containing materials has been reported by other researchers [32, 33].

Flammability characteristics

The flammability characteristics of the products were evaluated by limiting oxygen index (*LOI*) measurements; the results are summarized in (Table 2). The test result of a conventional cured epoxy resin and polyacrylate are presented for comparison. The limiting oxygen index test is widely used by researchers to semiquantitatively evaluate the ignitability and burning behavior of polymeric materials. This method is based on the fact that many materials, once ignited, will burn continuously in an atmosphere containing sufficient oxygen but not in an atmosphere of pure nitrogen. The limiting oxygen index value denotes the minimum amount of oxygen in an oxygen-nitrogen mixture that will just sustain the burning of the product, in a candle-like manner, continuously for three minutes. Since one fraction of air contains approximately 21 vol % of oxygen, materials with a limiting oxygen index value ≤ 21 will probably support burning to completion in normal atmospheric conditions once they are ignited [34].

The *LOI* value of the control sample (polyacrylate/epoxy resin) was found to be 20.3 vol %; this low value is expected because both polymers are oxygenated hydrocarbons and have no inherent fire retardant properties. From the *LOI* values of the products given in (Table 2), it can be seen that the *LOI* of PN-polyacry, PN-Ep, and PN-Ep/polyacry are higher than the *LOI* of the conventional epoxy resin, neat polyacrylate and the control sample. This in agreement with the generally accepted notion that the presence of phosphazene moieties may provide

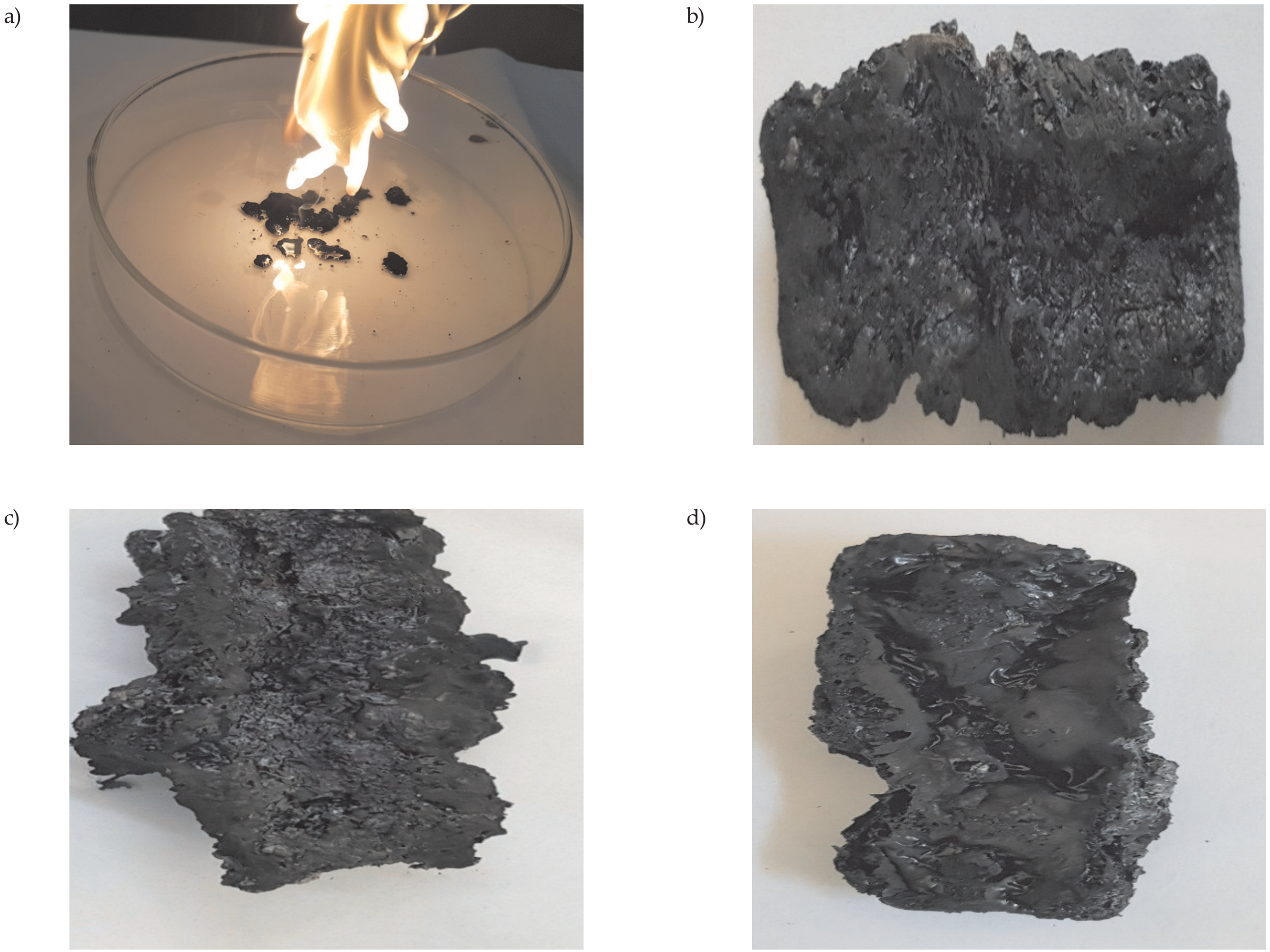


Fig. 13. Digital photos of the: a) burning of cross-linked epoxy resin at atmospheric conditions, b) char residue of PN-polyacry after burning at *LOI* = 30.5 vol %, c) char residue of PN-Ep after burning at *LOI* = 27.2 vol %, d) char residue of PN-Ep/polyacry after burning at *LOI* = 28.0 vol %

acid sources during pyrolysis that promote dehydration of the matrix, leading to the formation of an unbroken char layer which can act not only as an insulative barrier to further heat transfer to the underlying polymeric materials but also can obstruct the ease of diffusion of flammable gases into the combustion zones and inhibit combustion in the condensed phase. Meanwhile, the burning of a solid material occurs in a complicated series of free radical reactions which may release radical scavengers that can react with •H, •O, •OH free radicals and their quenching effect to gaseous phase and hence inhibit combustion [34, 35].

Digital photos of the residues in Fig. 13 show that when the neat cured epoxy catches fire under normal atmospheric conditions it drips heavily, affording a black viscous tar, whereas the control sample (polyacrylate/epoxy resin) leaves an ash residue but not a solid char. PN-polyacry, and PN-Ep/polyacry formed intumescent, thick, unbroken compact char layers, which prevented heat-transfer from the burning zone back to the underlying polymeric material and also provided barriers to diffusion of combustible species to the gas phase, thus delaying pyrolysis. Further, the relatively low thermal stability of the inorganic core might have accelerated the production of solid residue at the commencement of decomposition and thereby significantly insulated polymeric chains from combustion.

The *LOI* values of 27.0–30.5 vol % for PN-polyacry, PN-Ep, and PN-Ep/polyacry are above the threshold value of 26.0 vol %, which renders the polymers as self-extinguishing materials. Therefore, PN-polyacry, PN-Ep, and PN-Ep/polyacry have the potential for applications requiring good flame retardancy.

SEM photomicrographs of the char residue (Fig. 14) show a spread of pores and tunnels over the surface of PN-polyacry and PN-Ep/polyacry. The porous surface is a result of the discharge of different gases such as, CO, CO_2, H_2O, N_2, and NH_3 that can be generated during combustion [36]. However, the char morphology of PN-Ep showed a dense block of nonporous surface, possibly due to the formation of highly cross-linked char product that could act to reduce flammability by covering the outer layer of the polymer and thereby blocking the source of fuel (volatile combustible gases).

Quantitative elemental analysis of the char residue surface was determined with EDX analysis and is described

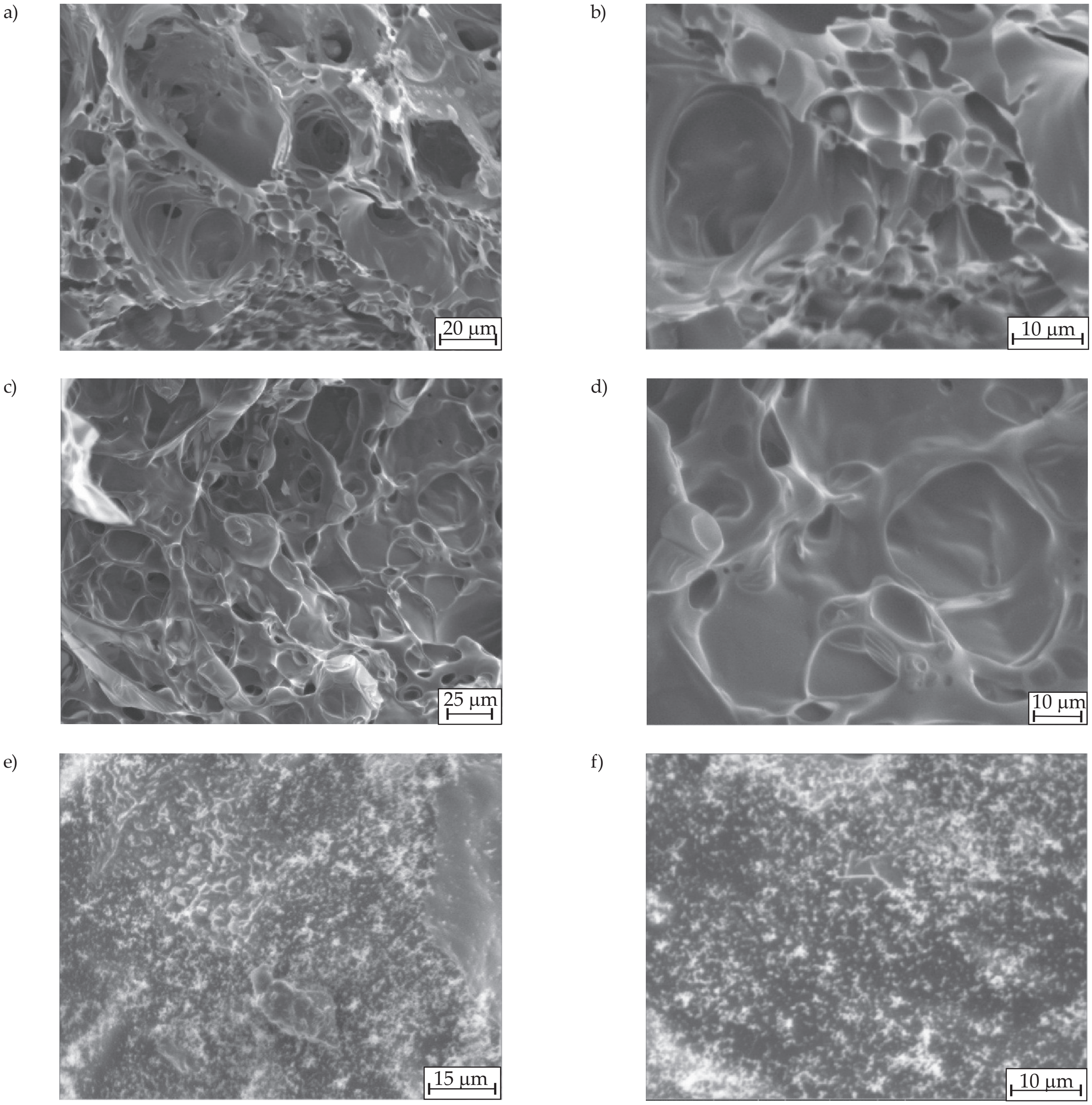


Fig. 14. SEM photomicrographs of the residual char obtained after burning determined *LOI* of: a), b) PN-polyacry, c), d) PN-Ep/polyacry, e), f) PN-Ep

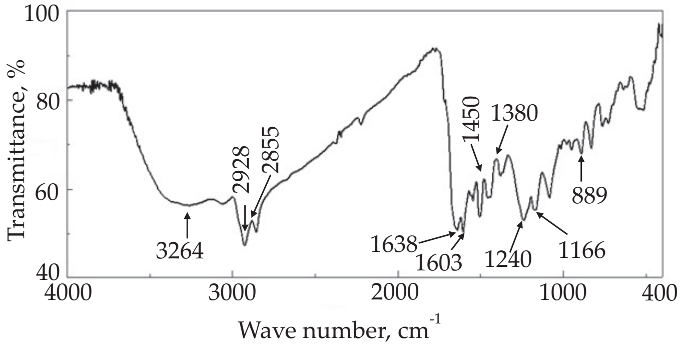


Fig. 15. FT-IR spectrum ot the char residue obtained from burning of PN-Ep/polyacry

in (Table 3). A high content of phosphorus and nitrogen compounds were present, which agrees with the FT-IR analysis of the char residue.

The FT-IR of char residue obtained from burning PN-Ep/polyacry at a limiting oxygen index value of 28.0 vol %, as depicted in Fig. 15, clearly shows a broad peak at about 3264 cm^{-1}, reflecting the stretching vibration of hydroxyl bonds, at 1638, 1603, and 1505 cm^{-1} due to C=C bonds of aromatic moieties. The peaks at 1240 and 1166 cm^{-1} are the major absorptions attributed to P=N stretching vibrations and that at 889 cm^{-1} is assigned to P–O–P bonds. These two absorptions bands are due to formation of phosphorous oxynitrides [37]. Absorption

T a b l e 3. EDX elemental analysis data of solid char residue of products

Element	PN-polyacry wt %	PN-Ep wt %	PN-Ep/polyacry wt %
C	52.83	19.43	67.70
	72.43	30.67	78.60
P	31.72	37.64	14.62
	16.87	23.04	6.58
O	4.12	15.25	2.19
	4.25	18.07	1.91
N	5.36	10.48	10.31
	6.45	14.18	10.27

*) Traces of another elements are appeared but not recorded in the table, this is due to contamination of the samples during burning test.

bands at 2928 and 2855 cm^{-1} indicate the presence of organic species present in the multiporous solid pyrolysis product.

CONCLUSIONS

Polyacrylate, epoxy resin homo- and block copolymers with cyclotriphosphazene cores were synthesized and characterized by FT-IR and ^{1}H, ^{13}C, and ^{31}P NMR. Oxirane ring opening to produce the homopolymer PN-Ep was much faster in the presence of PN-COOH and epoxy resin when carboxyl groups were catalyzed. A partial reaction of PN-acyl with 2-hydroxyethylacrylate and the reaction of unreacted carboxyl groups with the oxirane ring afforded a new block copolymer composed of epoxy resin and polyacrylate. The incorporation of a cyclotriphosphazene core to the polymeric system significantly enhanced char formation at elevated temperatures, increasing from about 0 % to 30–38 wt %. Limiting oxide index (*LOI*) values of the homo- and block copolymers were above the threshold value of 26 vol % to render the polymeric system self-extinguishing. An SEM morphology study revealed intumescent solid char in PN-polyacry and PN-Ep/polyacry, as indicated by pores and tunnels on the product surface, while PN-Ep produced a solid dense char with a nonporous surface. FT-IR and EDX analyses of char residue indicated that phosphorus-nitrogen are the main components present in the condensed phase.

Funding for this work was provided by a research grant from the Department of Chemistry and the Polymer Research Unit, Mustansiriyah University, Baghdad, Iraq.

REFERENCES

[1] Lu S., Hamerton I.: *Progress in Polymer Science* **2002**, *27* (*8*), 1661. https://doi.org/10.1016/S0079-6700(02)00018-7

[2] Schäfer A., Seibold S., Walter O., Döring M.: *Polymer Degradation and Stability* **2008**, *93*, 557. https://doi.org/10.1016/j.polymdegradstab.2007.11.016

[3] Sudhakara P., Kannan P.: *Soft Materials* **2009**, *7*, 198. https://doi.org/10.1080/15394450903172814

[4] Sun D., Yao Y.: *Polymer Degradation and Stability* **2011**, *96*, 1720. https://doi.org/10.1016/j.polymdegradstab.2011.08.004

[5] Huang Z., Shi W.: *Polymer Degradation and Stability* **2007**, *92*, 1193. https://doi.org/10.1016/j.polymdegradstab.2007.04.008

[6] Bai Y., Wang X., Wu D.: *Industrial and Engineering Chemistry Research* **2012**, *51*, 15064. https://doi.org/10.1021/ie300962a

[7] Maaskant E., Gojzewski H., Hempenius M.A. *et al.*: *Polymer Chemistry* **2018**, *9*, 3169. https://doi.org/10.1039/c8py00444g

[8] Liu R., Wang X.: *Polymer Degradation and Stability* **2009**, *94*, 617. https://doi.org/10.1016/j.polymdegradstab.2009.01.008

[9] Yang R., Wang B., Han X. *et al.*: *Polymer Degradation and Stability* **2017**, *44*, 62. https://doi.org/10.1016/j.polymdegradstab.2017.08.008

[10] Li J., Pan F., Xu H. *et al.*: *Polymer Degradation and Stability* **2014**, *110*, 268. https://doi.org/10.1016/j.polymdegradstab.2014.08.027

[11] Guo Y.-N., Qiu J.-J., Tang H.-Q., Liu C.-M.: *Journal of Applied Polymer Science* **2011**, *121*, 727. https://doi.org/10.1002/app.33806

[12] Wang C., Hu F., Yang K. *et al.*: *RSC Advances* **2015**, *5* (*107*), 88382. https://doi.org/10.1039/c5ra15598c

[13] Xu G.-R., Xu M.-J., Li B.: *Polymer Degradation and Stability* **2014**, *109*, 240. https://doi.org/10.1016/j.polymdegradstab.2014.07.020

[14] Yang S., Wang J., Huo S. *et al.*: *Polymer Degradation and Stability* **2016**, *126*, 9. https://doi.org/10.1016/j.polymdegradstab.2016.01.011

[15] Zhao B., Liang W.-J., Wang J.-S. *et al.*: *Polymer Degradation and Stability* **2016**, *133*, 162. https://doi.org/10.1016/j.polymdegradstab.2016.08.013

[16] Yang Y., Kong W., Cai X.: *Polymer Degradation and Stability* **2016**, *134*, 136. https://doi.org/10.1016/j.polymdegradstab.2016.09.021

[17] Qian L., Feng F., Tang S.: *Polymer* **2014**, *55*, 95. https://doi.org/10.1016/j.polymer.2013.12.015

[18] Yang R., Hu W., Xu L. *et al.*: *Polymer Degradation and Stability* **2015**, *122*, 102. https://doi.org/10.1016/j.polymdegradstab.2015.10.007

[19] Chandrasekhar V., Athimoolam A.P., Vivekanandan K., Nagendran S.: *Tetrahedron Letters* **1999**, *40*, 1185. https://doi.org/10.1016/s0040-4039(98)02560-x

[20] Zhao Z.P., Guo Q., Li X. *et al.*: *Express Polymer Letters* **2012**, *6* (*4*), 308. https://doi.org/10.3144/expresspolymlett.2012.34

[21] Miyata K., Watanabe Y., Itaya T. *et al.*: *Macromolecules* **1996**, *29*, 3694. https://doi.org/10.1021/ma951698h

[22] He Q., Dai H., Tan X. *et al.*: *Journal of Materials Chemistry C* **2013**, *1* (*43*), 7148. https://doi.org/10.1039/C3TC31371A

[23] Qian L.-J., Ye L.-J., Xu G.-Z. *et al.*: *Polymer Degradation and Stability* **2011**, *96*, 1118. https://doi.org/10.1016/j.polymdegradstab.2011.03.001

[24] Chen Y., Wang W., Qiu Y. *et al.*: *Polymer Degradation and Stability* **2017**, *140*, 166. https://doi.org/10.1016/j.polymdegradstab.2017.04.024

[25] Kook H.J., Tae K.S., Jung K.H., Kwon Y.: *Journal of Nanoscience and Nanotechnology* **2006**, *6*, 3446. https://doi.org/10.1166/jnn.2006.031

[26] Liu J., Tang J., Wang X., Wu D.: *RSC Advances* **2012**, *2* (*13*), 5789. https://doi.org/10.1039/c2ra20739g

[27] Yuan W., Tang X., Huang X., Zheng S.: *Polymer* **2005**, *46*, 1701. https://doi.org/10.1016/j.polymer.2004.12.040

[28] Guo Y.-N., Zhao C., Liu S.-Z. *et al.*: *Polymer Bulletin* **2009**, *62*, 421. https://doi.org/10.1007/s00289-008-0035-6

[29] Blank W.J., He Z.A., Picci M.: *Journal of Coatings Technology* **2002**, *74*, 33. https://doi.org/10.1007/BF02720158

[30] Yile X., Dayo A.Q., Jun W. *et al.*: *Materials Chemistry and Physics* **2018**, *203*, 293. https://doi.org/10.1016/j.matchemphys.2017.10.004

[31] Zhou L., Zhang G., Li J., Jing Z.: *Journal of Thermal Analysis and Calorimetry* **2017**, *129*, 1667. https://doi.org/10.1007/s10973-017-6319-z

[32] Liang W.-J., Zhao B., Zhao P.-H. *et al.*: *Polymer Degradation and Stability* **2017**, *135*, 140. https://doi.org/10.1016/j.polymdegradstab.2016.11.023

[33] Jin W., Yuan L., Liang G., Gu A.: *ACS Applied Materials Interfaces* **2014**, *6*, 14931. https://doi.org/10.1021/am502364k

[34] Laoutid F., Bonnaud L., Alexandre M. *et al.*: *Materials Science and Engineering R: Reports* **2009**, *63*, 100. https://doi.org/10.1016/j.mser.2008.09.002

[35] Levchik G.F., Grigoriev Y.V., Balabanovich A.I. *et al.*: *Polymer International* **2000**, *49*, 1095. https://doi.org/10.1002/1097-0126(200010)49:10<1095::aid-pi405>3.0.co;2-b

[36] Qu L., Zhang C., Li P. *et al.*: *RSC Advances* **2018**, *8*, 29 816. https://doi.org/10.1039/c8ra05911j

[37] Zhang T., Cai Q., Wu D.-Z., Jin R.-G.: *Journal of Applied Polymer Science* **2005**, *95*, 880. https://doi.org/10.1002/app.21295

Received 20 II 2019.

W kolejnym zeszycie ukażą się m.in. następujące artykuły:

A. Dworak, A. Utrata-Wesołek, Ł. Otulakowski, M. Kasprów, B. Trzebicka – Polimery w medycynie – kierunki rozwoju (*j. ang.*)

M. Bhuvaneshwaran, P.S. Sampath, S. Balu, S. Sagadevan – Właściwości fizykochemiczne i mechaniczne naturalnych celulozowych włókien *Coccinia Indica* i ich kompozytów na osnowie żywicy epoksydowej (*j. ang.*)

N. Mohd Nurazzi, A. Khalina, S.M. Sapuan, R.A. Ilyas – Wpływ zawartości włókien i obróbki alkalicznej na właściwości mechaniczne kompozytów z nienasyconej żywicy poliestrowej wzmacnianych włóknem szklanym i włóknem palmy cukrowej (*j. ang.*)

M.A.R. Saat, R. Rasid, M.A. Bakar, A. Jalar, E.M. Salleh – Właściwości mechaniczne mieszanek PE-PET-PS-PP wytwarzanych w warunkach dużej szybkości ścinania (*j. ang.*)

M.S.N. Atikah, R.A. Ilyas, S.M. Sapuan, M.R. Ishak, E.S. Zainudin, R. Ibrahim, A. Atiqah, M.N.M. Ansari, R. Jumaidin – Degradacja i właściwości fizyczne bionanokompozytów skrobi palmy cukrowej wzmocnionej nanowłóknami celulozowymi tej palmy (*j. ang.*)

M. Chorobiński, Ł. Skowroński, M. Bieliński – Metodyka wyznaczania wybranych charakterystyk barwienia polietylenu z wykorzystaniem systemu CIELab

W. Głuszewski – Zastosowanie chromatografii gazowej do oznaczania radiolitycznego cząsteczkowego wodoru, którego oderwanie inicjuje wtórne zjawiska w radiacyjnej modyfikacji polimerów (*j. ang.*)