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Bis(4-cyanophenyl) phenyl phosphate as viscosity reducing comonomer for phthalonitrile resins

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ABSTRACT

Bis(4-cyanophenyl) phenyl phosphate (**CPP**) is introduced for the first time as a viscosity reducing comonomer for phthalonitrile resins. In comparison to the common phthalonitrile resins, the blends of **CPP** with 4,4′-[benzene-1,3-diylbis(oxy)]diphthalonitrile demonstrated advanced processing properties suitable for cost-effective injection processing (η as low as to 180 mPa·s at 100 °C). Thermal copolymerization was performed indicating complete inclusion of bis-benzonitrile **CPP** into the phthalonitrile network resulting in formation of thermosets with great thermal performance. Hydrolysis of **CPP** at pH 4, 7, and 10 was studied to confirm its suitability as a reactive diluent for phthalonitrile. Conversion vs. time plots were obtained via HPLC analysis, and pseudo-first order rate constants were determined in the range of 25–80 °C. The activation parameters were calculated from the Arrhenius equation.

1. Introduction

Fiber reinforced plastics (FRP) gradually replace common materials such as metals and alloys in aerospace industries. Modern aircrafts consist of polymer composites by > 50% and more new materials and techniques are developing to take their place in the industry. Contemporary trends in composites manufacturing are aimed to use cost-effective resin injection methods instead of autoclave processing. Thus, in emergent Russian aircraft MS − 21, the wingbox is constructed from 25 m long single CFRP parts produced by vacuum infusion. At the same time new materials are required to extend application range of the composites. One of the limitations of the polymer composites is quite low operation temperatures caused by the nature of matrices. Even typical heat-resistant matrices based on bis-maleimides [1,2], polyimides [3–5], benzoxazines [6–8], cyanate ether [9,10] and propargylated phenolics [11–13] can be used at temperatures up to 250–300 °C.

Polymer matrices based on phthalonitriles are known for their resistance to high temperatures (T_g > 400 °C, $T_{5\%}$ > 500 °C) [14–16], and at the same time for poor processability due to which the only possible way to manufacture composites was to use prepregs obtained from the resin solution [16–21]. One of the solutions to this problem was the development of low-melting monomers and oligomers. This was a long-term trend in a field of new chemistries in phthalonitrile resins [22–29]. In the case of oligomeric bis-phthalonitriles, a good processability suitable for cost-effective resin injection methods of composite manufacturing was reached, but at the same time a significant decrease in Young's modulus of the thermosets was observed in some cases [22,30]. With the development of siloxane- and phosphate-bridged bis-phthalonitriles [31–37] and hybrid phthalonitrile-propargyl ether monomer [38], manufacturing of carbon fiber reinforced plastics (CFRP) by cost-effective technologies, such as VIMP and RTM, was reported [39–41]. These results can widely extend the application range of composite materials in aerospace (for production of complex-shaped parts, e.g. jet engine blades or skin of ultrasonic vehicles) and other applications such as high-temperature composite tooling, flame-retardant materials for interior parts of submarines, engine cowls, exhaust pipes etc. The other approach aimed at improving processability of phthalonitrile resins is development of bis-phthalonitriles formulations with reactive plasticizers [32,42,43]. Bis-benzonitrile compounds were never considered as comonomers for bis-phthalonitriles, apparently due to a low reactivity in cyclotrimerization into triazines. Cyclotrimerization of nitriles needs rather harsh conditions of pressure (1000 atm) and temperature (300 °C) [44], or the use of rare metal catalysis [45–47]. Heat-resistant ring-chained polymers derived from bis(ether nitriles) and 1,4-dicyanobenzene were obtained in the presence of $ZnCl_2$ by heating in an oven at 295 °C for 12 h and then 365 °C for another 36 h

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under nitrogen atmosphere. At the same time, it is known that active monomers involve inactive ones in copolymerization [48,49]. It was suggested that an active isoindoline particle (neutral or anionic) formed after nucleophilic attack on phthalonitrile [50] could involve benzonitrile group in cyclotrimerization likewise it was reported for triflic anhydride [51].

Here we introduce bis(4-cyanophenyl) phenyl phosphate (**CPP**) as comonomer for common phthalonitirile 4,4′-[benzene-1,3-diylbis(oxy)] diphthalonitrile (**PN**). With an addition of **CPP** to **PN,** we anticipated to obtain easy-processable resin formulations for CFRP manufacturing. Therefore, an investigation of the blends of **CPP** and **PN**, their polymerization and the resulting polymers was an aim of the present study.

2. Experimental

2.1. Materials and methods

All the manipulations with oxidation and moisture sensitive compounds were carried out under inert atmosphere using the standard Schlenk technique. Dimethylacetamide (DMAA), dichloromethane (DCM), toluene and pyridine were purchased from Alfa Aesar Company. DMAA and DCM were used as received. Toluene and pyridine were distilled over P_4O_{10} twice and stored over CaH_2. Acetonitrile (HPLC grade), silica gel (0.04–0.065 mm seed), 4-nitrophtalonitrile (99% purity), phenyldichlorophosphate, resorcinol, 4cyanophenol, 3, 3′-(1,3-phenylenbis (oxy))dianiline (**APB**) and potassium carbonate were obtained from Sigma-Aldrich and used as received. 4,4′[benzene-1,3-diylbis(oxy)]diphthalonitrile (**PN**) was synthesized according to the known procedure [52] with quantitative yield (98%). Buffer solutions with pH 4, 7 and 10 were purchased from Panreac Applichem. According to the claimed description, the pH of these buffers was maintained in a temperature range from 20 °C to 100 °C.

Nuclear magnetic resonance (NMR) spectra were run on Bruker Avance 600 at 600 MHz for ^1H and 125 MHz for ^{13}C and ^{31}P with dimethyl sulfoxide-d_6 as solvent. Differential scanning calorimetry (DSC) was performed on Netzsch DSC 204 Phoenix, at a heating rate of 10 °C/min and an Ar purge rate of 50 mL/min and was applied for the determination of melting points of the monomers and the curing study. Thermal stability was evaluated by thermogravimetric analysis (TGA) on Netzsch TG 209 P3 Tarsus at a heating rate of 10 °C/min in range 40–1000 °C and Ar or air purge rate of 50 mL/min. Heat deflection temperature (HDT) was measured by the 3 point bending method on Netzsch TMA 402 with 1.82 MPa load (ASTM-E2092–03). Melt viscosity was measured with MCR 302 rheometer with cone 7 at 40 rpm. Dynamic mechanical analysis was performed on DMA Q800. Fourier Transform Infrared (FT-IR) spectra were recorded in the range of 4000–400 cm^{-1} on Bruker Tensor-27 spectrophotometer using KBr pellets.

HPLC analysis was performed at Agilent 1260 chromatographer (column ZORBAX Eclipse Plus C18; Tcolumn = 30°C; flow rate — 0,8 mL/min). Elution program is presented in Table 1. The obtained chromatograms were developed with Agilent ChemStation software. To study the kinetic parameters of the hydrolysis reaction at predetermined temperatures, the solutions were treated in sealed vials at the assigned time periods in the oil bath of the LAUDA Proline RP 845 thermostat.

Table 1
Elution program applied for LC analysis.

Time, min	Acetonitrile, %	H_2O, %
0–5	55	45
5–25	55–98	45–2
25–28	98	2
28–33	98–55	2–45
33–35	55	45

*2.2. Synthesis of bis(4-cyanophenyl) phenylphosphate (**CPP**)*

1 g (0.008 mol) of anhydrous potassium bromide and 6.32 g (0.08 mol) of pyridine were added to a solution of 9.52 g (0.08 mol) of 4-cyanophenol in 50 mL of dry toluene, and the mixture was stirred at 70 °C for 30 min under argon in a 100 mL three-neck flask. Then, 8.44 g (0.04 mol) of phenyl dichlorophosphate was added dropwise. The mixture was stirred at 70 °C for 24 h under argon. After that, the reaction mixture was cooled, filtered from pyridine hydrochloride, and the filtrate was washed with water (3 × 30 mL). The water layer was washed with toluene (3 × 10 mL) and the combined organic phases were dried over anhydrous sodium sulfate. The solution was then evaporated using a rotary evaporator and dried at 80 °C for 2 h under 5 mmHg. A yellowish solid was obtained with a yield of 95% (14.25 g). According to the NMR ^1H spectrum, the product purity was 95%. To obtain a purity > 99%, flash chromatography with silica gel was carried out (eluent – CH_2Cl_2:MeOH 29:1). 13.47 g (89.5% of total yield) of the product was obtained after evaporation of the solvent.

^1H NMR (600 MHz, DMSO-d_6) δ ppm 7.21–7.39 (m, 3H), 7.47 (t, $J = 7.79$ Hz, 2H), 7.53 (d, $J = 8.44$ Hz, 4H), 7.98 (d, $J = 8.53$ Hz, 4H).

^{13}C NMR (151 MHz, DMSO-d_6) δ ppm 109.14, 117.96, 119.93 (d, $J = 4.42$ Hz), 121.23 (d, $J = 5.53$ Hz), 126.39, 130.41, 134.97, 149.42 (d, $J = 7.74$ Hz), 152.74 (d, $J = 6.64$ Hz).

^{13}P NMR (243 MHz, DMSO-d_6) δ ppm −15.71.

Anal. Calcd. for $C_{20}H_{13}N_2O_4P$: C 63.84, H 3.48, N 7.44, Found C 63.81, H 3.53, N 7.40

2.3. Blends preparation

Into a 250 mL three-neck flask equipped with magnetic stirrer, 30 g of **CPP** was placed and heated up to 140 °C under vacuum (1 mmHg). After the monomer was melted, the melt was stirred for 15 min and then vacuum was released, and 70 g of **PN** was added gradually under stirring. Then, 7 g of **APB** (10 wt% or 12.5 mol% to **PN**) were added to the mixture and it was stirred under vacuum at 140 °C to homogenate and degas the blend for 30 mins. Finally, the blend was poured to a metal box to cool down. PNDP-73 was obtained as dark resin. The other blends were obtained according to the same procedure using corresponding amounts of the components (Table 2).

2.4. Curing

To obtain molded plates, 20 g of the blend (**PNDP-73**, **PNDP-55** or **PNDP-37**) were placed into a 250 mL flask, then melted and degassed by stirring under vacuum (1 mmHg) at 140 °C. Next, the melt was poured into a metal mold (70 × 70 × 2 mm^3). The mold was placed into an air circulated heated oven and cured at 180 °C for 12 h. Next, the mold was disassembled, and the cured plates were post-cured by heating (10 °C/h) to 330 °C or 375 °C and held at final temperature for 8 h.

3. Results and discussion

3.1. Synthesis

In our previous works, it was shown that linking of bis-

Table 2
Mass ratios of the comonomers and the properities of considered blends.

Name	**PN**, mass %	**CPP**, mass %	T_m/T_g, °C
PN	100	0	185
CPP	0	100	88
PNDP-37	30	70	-2
PNDP-55	50	50	10
PNDP-73	70	30	21

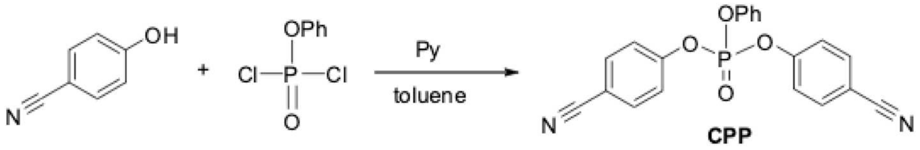

Fig. 1. Synthesis of **CPP**

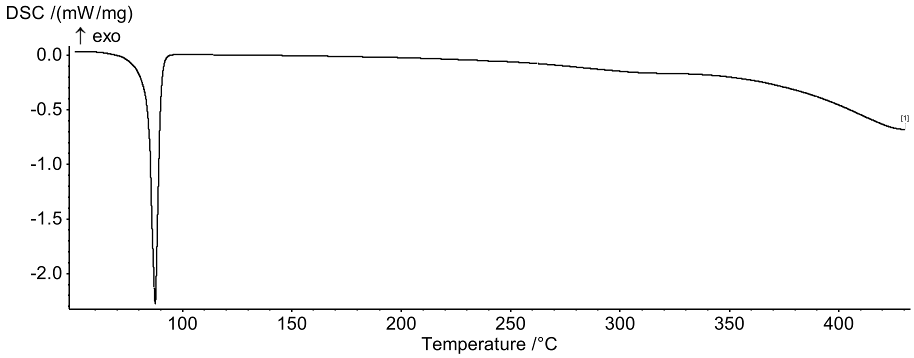

Fig. 2. DSC curve obtained for **CPP** doped with 5% of APB.

phthalonitriles with phosphate bridges improved the processability of the resulting monomers, as well as increased thermal oxidative stability of the thermosets [32]. Based on this idea and in an attempt to simplify the synthesis procedure, phosphate-bridged bis-nitrile monomer **CPP** was synthesized for the first time to be studied as a prospective reactive plasticizer. The reaction between 4-cyanophenol and phenyl dichlorophosphate was performed by refluxing in toluene with pyridine as a base (Fig. 1). The reaction mixture was separated from pyridine hydrochloride, washed with water and, after elimination of the solvent, the desired product was separated from the reaction mixture with a high yield of 95%. At the same time, the content of the aimed compound in the product was only 95%. To obtain pure **CPP**, flash chromatography on SiO_2 was performed. **CPP** appeared to be a white crystalline compound with melting point $T_m = 88\,^\circ C$ (Fig. 2).

3.2. Curing and thermosets properties

An attempt to polymerize **CPP** in the presence of 5–20 mol% of **APB** (Fig. 3) was performed, but in all the cases no thermosets were formed during the overnight heating up to 375 °C. DSC data demonstrated no exothermal peak related to polymerization (Fig. 2). Endothermal effect at temperature above 300 °C indicated decomposition of the monomer. During the curing experiment, condensation of white crystals on the top part of the vial was observed. NMR study of the substance confirmed 4-cyanophenol structure.

Further, the blends consisting of **CPP** and **PN** (Fig. 3) in three different rations and APB as curing initiator were prepared for a curing study (Table 2). **APB** was taken in 10 wt% ratio to **PN** monomer because **CPP** did not undergo polymerization initiated by the amine.

All the blends were amorphous resins and, according to DSC study, blends containing 50% and 70% of **CPP** demonstrated the no endothermic effects related to melting of the single components (Fig. 4). Glass transition temperature rises with the rising of **PN** mass content. For **PNDP-73**, effects related to the crystallization and melting of **PN** were observed in the range of 100–180 °C that may be caused by excessive content of **PN** for the formation of eutectic system.

The processing is limited by matrix viscosity, and defined as the time for the resin to reach a viscosity of 300 mPa·s. The experimental data are presented on Fig. 5. It's easy to see, the viscosity values of every mixture allows them to be applied in cost-effective injection methods at temperatures above 150 °C. The widest processing window was observed for blend PNDP-37 with the highest **CPP** content and with increase of **PN** content a processing window diminished.

The curing process of the prepared resin samples was investigated by DSC (Fig. 6). The curing temperatures and thermal effects were found (Table 3). For the blend with the predominant content of **CPP**, very weak exothermal peak was observed. With an increase of **PN** content, T_{onset} shifted to lower temperatures and a growth in ΔH was observed. This data is in good accordance with the suggestion that **CPP** was involved in polymerization by active **PN** comonomer. Nevertheless, low thermal effect in all the cases can be considered as a technological advantage of the blends, allowing for the obtainment of composite parts without the risk of overheating.

Bimodality of the curing peak, which can be distinguished in the case of **PNDP-73**, can be attributed to two different processes. The peak at 252 °C can be related to phthalonitrile polymerization, whilst broad peak at higher temperatures in our suggestion is related also to copolymerization of **CPP** and **PN**.

The samples of the blends were cured with a final hold at 330 °C for 8 h. The resulting thermosets were grounded into fine powders, placed into a Soxhlet extractor, and continuously washed with acetonitrile to find out if some of the monomers were not included in the polymer network. In all the cases, weight decrease after extraction was < 0.2% of the initial weight. Therefore, it was concluded that all the monomers were involved in the polymerization.

The cured resins (poly(**PNDP-37**), poly(**PNDP-55**) and poly(**PNDP-73**)) were also investigated by FT-IR spectroscopy. It has been reported that phthalonitrile monomers may form polytriazine, polyisoindoline and phthalocyanine structures. Absorption bands at 1708 cm^{-1} and 1525 cm^{-1} (pyrrole ring), indicating formation of isondoline structures, were observed [30] and the highest intensity was predictably detected for poly(**PNDP-73**) with the highest **PN** content. No strong phthalocyanine absorption bands at 1010 cm^{-1} [53] were found in all the mixtures, which indicates that most of the curing occurred through

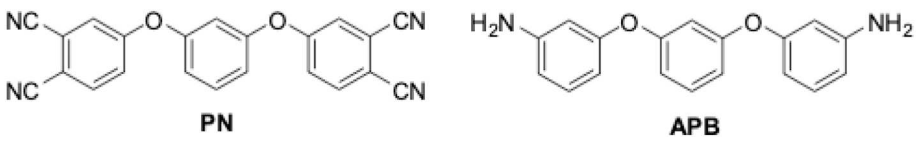

Fig. 3. Monomer PN and curing initiator APB.

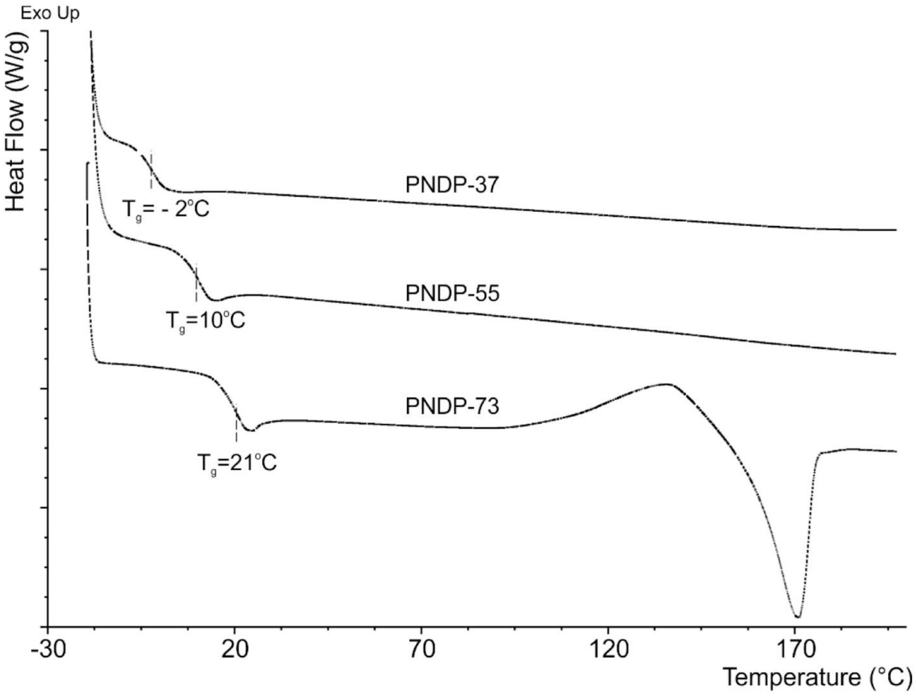

Fig. 4. DSC-curves obtained for the considered blends.

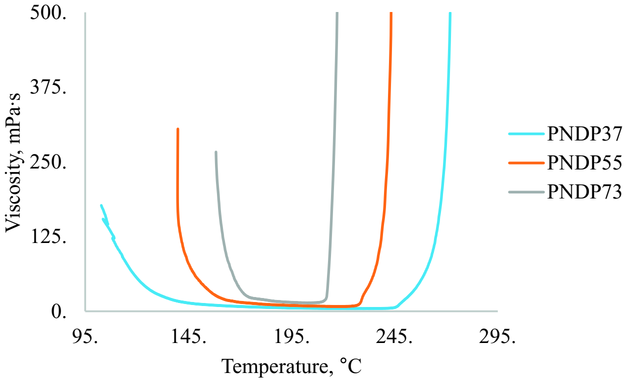

Fig. 5. Temperature dependence of the viscosity of considered resin blends.

triazine rings. In all the obtained spectra, absorption bands at 1508 cm^{-1}, 1355 cm^{-1} related to triazine rings were observed (Fig. 7). Unreacted nitrile groups (absorption at 2223 cm^{-1}) were present in all the samples and could be related to cylotrimerization of phthalonitrile groups in which only one of the vicinal nitrile groups is involved due to a steric hindrance. Poly(**PNDP-37**) derived from the blend with the highest **CPP** content intensity of C≡N groups is lower than in the other blends, indicating almost complete involvement of nitriles in polymerization.

Thermal properties of the thermosets were investigated by DMA and TGA tests. The performed DMA tests showed that the elasticity modulus of all samples steadily decreased with temperature growth, and glass transitions of the samples were above 300 °C (Table 4). In the case of poly(**PNDP-37**), no clear transition was observed. It is worth noting that the highest modulus in the glassy state (420 MPa) was found for this thermoset, indicating the highest degree of cross-linking. This is a natural result because **CPP** can participate in polymerization only through cyclotrimerization leading to cross-linking, while **PN** polymerizes also with a formation of linear poly(isoindoline) chains. Therefore, poly(**PNDP-73**) demonstrated the lowest T_g and storage modulus in the glassy state among the considered thermosets. However, it is still higher than reported for phthalonitrile matrix PNT cured at 330 °C (T_g = 320 °C) [54]. More importantly, the T_g is higher than curing temperature which allows to fabricate composites without devitrification. As far as it is known, phthalonitriles demonstrate the best thermal properties after curing at 375 °C [55]. Therefore, the samples were cured with a hold at a final temperature of 375 °C for 8 h. In the case of **PNDP-37**, the sample cracked after high-temperature post-curing, probably because of a high shrinkage. For the other two samples, DMA tests were performed and showed no glass transition up to 450 °C (Fig. 8). Also, it is worth highlighting the more smooth character of storage modulus decrease of the samples cured at 375 °C, indicating an obvious increase of cross-linking density with increasing curing temperature.

At the same time, thermal stability of thermosets cured at 330 °C ($T_{5\%}$ and $TOS_{5\%}$) increased with an increase of **PN** content in the blends, which could be explained by the predominant formation of heat resistant phthalonitrile network. The best stability was found for the thermoset originating from the **PN** rich blend **PNDP-73** (Table 4). The presence of phosphate moieties in the thermosets improved their oxidation stability: none of the samples completely combusted during TGA experiments. The highest mass residue among the samples cured at 330 °C in air was found for poly(**PNDP-55**)-330,[1] despite lower phosphate content than in poly(**PNDP-37**)-330. This can be explained by lower decomposition temperature of poly(**PNDP-37**)-330 and as far as oxidation is a heterogeneous process of different surfaces of the samples. Post-curing of the thermosets at 375 °C predictably resulted in an increase of the thermal stability of the samples. Char yield (Y_c) values grew up to 80% due to an additional cross-linking of the phthalonitriles which occurred at an elevated temperature. Degradation temperatures in inert atmosphere and on air ($T_{5\%}$ and $TOS_{5\%}$ respectively) grew up to 516 °C which is at the same level as for common phthalonitriles. On air, the samples also did not completely combust in the experimental conditions, and it was noticed that Y_c is higher for thermosets with higher phosphate-containing thermosets.

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[1] Designation poly(**PNDP-55**)-330 corresponds to thermoset obtained from resin **PNDP-55** cured at 330 °C. Further the same principle was used to designate the other thermosets obtained from **PNDP** resins at 330 °C or 375 °C.

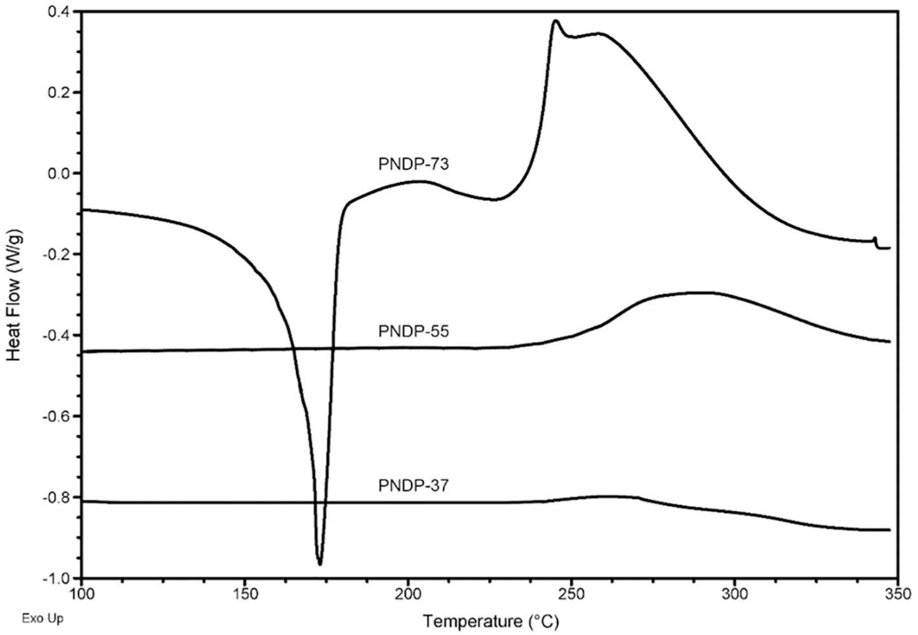

Fig. 6. Curing peaks (DSC) of the studied blends.

Table 3
Curing parameters of investigated blends.

Name	T_{onset} °C	$T_{1,\ max}$ °C	$T_{2,\ max}$ °C	ΔH, J/g
PNDP-37	–	264	–	5.6
PNDP-55	236	252	289	42.2
PNDP-73	228	244	257	115.1

Thus, it was shown that the considered mixtures of **CPP** and **PN** possess improved processability in comparison to phthalonitriles, and could be cured with the formation of heat-resistant thermosets. It can be concluded that excessive concentration of the diluent can affect the properties of the thermoset. Based on thermal properties data and processability of the uncured resins, **PNDP-55** can be admitted as the most prospective composition for composite fabrication. At the same time, the presence of phosphate ester groups in **CPP** structure raises some concerns related to possible applications of this compound as a reactive plasticizer. To solve these concerns, a hydrolysis study was performed.

3.3. Hydrolysis study

Data related to the hydrolysis of triesters of phosphoric acid is barely presented in literature [56,57] but the basic experimental approaches were reported. Here, the hydrolysis kinetics data for **CPP** at three different pH values (4, 7 and 10) are presented, including rate constants and activation parameters calculated from the Arrhenius equation.

Hydrolysis was performed for a 1 mg/mL monomer solution in acetonitrile/buffer mixture (50:50% vol.). Taking into account the slow hydrolysis rates in acidic media [58,59], it was decided to start the experiments at pH 4 to estimate the possibility of acidification of the reaction media, with the aim of stopping hydrolysis in further experiments at higher pH values. First, it was found that with ^{31}P NMR and HPLC, the hydrolysis of **CPP** occurred only with elimination of 4-cyanophenol. There is another possible pathway for the reaction – with elimination of phenol. Nevertheless, no phenol was found in all the solutions after treatment and the only phosphorus-containing product **CPPA** of the reaction was observed after 100% conversion of the initial triester CPP (Fig. 9). The reaction mixture was evaporated and then freeze-dehydrated to obtain a solid. In the ^{31}P NMR spectrum of this solid, only one resonance at −9.28 ppm (See Data in Brief related article) was observed, demonstrating a shift to the weak field area (−15.71 ppm for 1), which is in correspondence with literature data for chemical shifts of di- and triarylphosphoric esters [60]. Hydrolysis was also performed with H_2O^{18} (95% isotopic purity) to reveal whether the reaction occurs via phosphorus-oxygen or carbon-oxygen bond fission. It was shown that in the acidic medium, the hydrolysis proceeds with phosphorus-oxygen bond fission similarly to what is reported for hydrolysis of arylphosphates in dioxane-water 75:25 *v*/v [58]. The reaction mixture was analyzed by LC/MS chromatography and only one product corresponding to **CPPA** was detected and had $M + H^+ = 278$, which indicated that the labeled oxygen was present only in the phosphoric species (See Data in Brief related article, M = 275 for neutral molecule without tracer). In contrast, no excess abundance of the tracer was observed in the formed 4-cyanophenol (See Data in Brief related article). Thus, hydrolysis of **CPP** at pH = 4 could be described by the following reaction scheme (Fig. 9).

Hydrolysis kinetics in acidic medium were studied in the temperature range of 25–80 °C. All samples were immediately frozen by being placed in liquid nitrogen after exposition for a certain period at the assigned temperature to stop all the reactions in the solution. The samples were defrosted immediately before the HPLC analysis. Concentrations of the substrate were measured and then plotted versus time (See Data in Brief related article).

Since the hydrolysis was studied at a water concentration significantly exceeding the substrate concentration, data analysis for the hydrolysis of the test substances was considered as a pseudo-first order reaction:

$$V_1 = k_1 \cdot C = -\frac{dC}{d\Gamma^+} \qquad (1)$$

It is more convenient to work with the linear form of this equation. For this, a logarithm was taken on both sides of the equation:

$$\ln C = \ln C_0 - k_1 \cdot \Gamma \qquad (2)$$

According to Eq. (2), when considering the linear dependence of ln *C* from τ, the value of the angular coefficient will be numerically equal to the reaction rate constant *k*. The obtained data is presented in

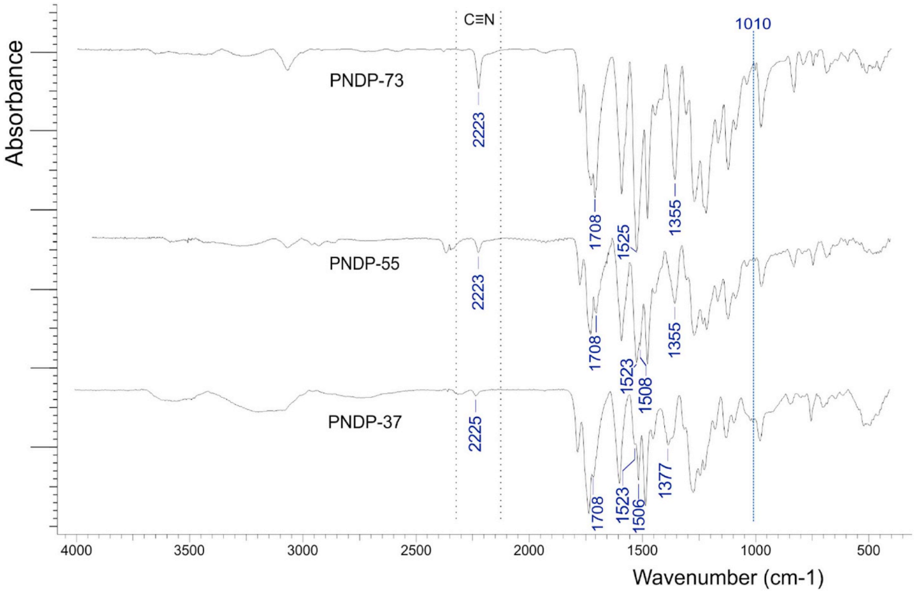

Fig. 7. FT-IR spectra of investigated cured resin blends.

Table 4
DMA and TGA data for used thermosets curing at 330 °C and 375 °C.

Thermoset	T_g, °C	$T_{5\%}$, N_2 (°C)	Y_c, N_2 (%)	$TOS_{5\%}$ (°C)	Y_c, air (%)	Ref.
Curing at 330 °C						
Poly(**PNDP-37**)	–	384	68	377	10	This work
Poly(**PNDP-55**)	343	412	65	434	18	This work
Poly(**PNDP-73**)	332	467	68	463	2	This work
Curing at 375 °C						
Poly(**PNDP-37**)	–	509	80	527	45	This work
Poly(**PNDP-55**)	> 450	510	78	502	35	This work
Poly(**PNDP-73**)	> 450	516	79	503	28	This work
PN	441	523	75	504	0	[31]

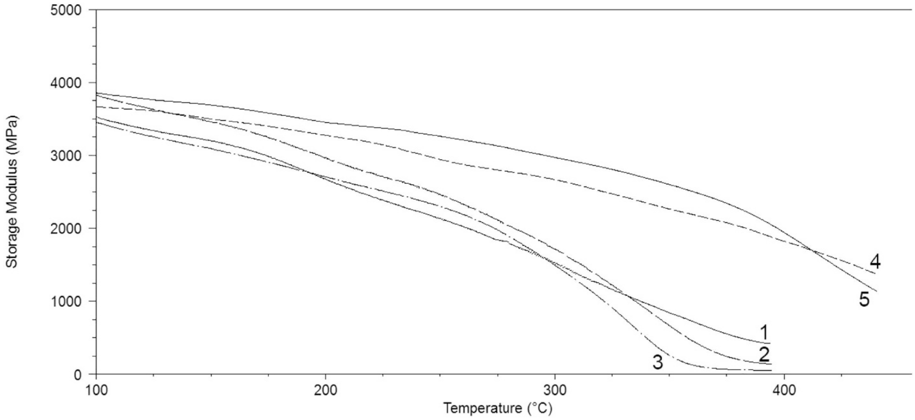

Fig. 8. DMA curves of the considered thermosets curied at 330 °C from: **PNDP-37** (1), **PNDP-55** (2) and **PNDP-73** (3), and at 375 °C: **PNDP-55** (4), **PNDP-73** (5).

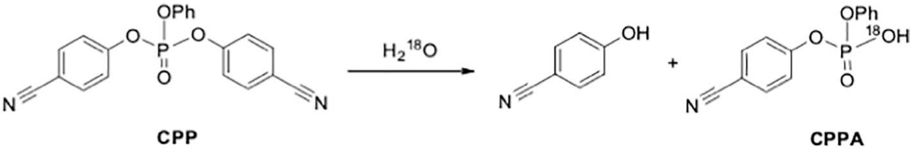

Fig. 9. Established hydrolysis reaction of CPP under pH = 4, 7 and 10.

Table 5. It can be seen that hydrolysis takes place in an acidic environment to a considerable extent in contrast to the reported ethers [59]. This circumstance did not allow us to use only acidification of the samples to stop the hydrolysis process at higher pH values. Therefore, the samples were additionally frozen in liquid nitrogen.

Then, hydrolysis was carried out in a neutral and basic media. In

Table 5
Rate constants and conversion for hydrolysis of CPP at various pH values.

T, °C	pH 4		pH 7		pH 10	
	k, s^{-1}	Conversion, %	k, s^{-1}	Conversion, %	k, s^{-1}	Conversion, %
25	1.20×10^{-6}	20 (48 h)	9.72×10^{-6}	80 (48 h)	1.36×10^{-4}	91 (5h)
35	2.70×10^{-6}	40 (48 h)	2.47×10^{-5}	100 (48 h)	4.28×10^{-4}	100 (3 h)
50	7.31×10^{-6}	68 (48 h)	8.33×10^{-5}	100 (12*h*)	2.15×10^{-3}	97.5 (30 min)
60	1.89×10^{-5}	73 (24 h)	2.21×10^{-4}	100 (6 h)	4.94×10^{-3}	99 (15 min)
80	6.45×10^{-5}	58 (4 h)	9.69×10^{-4}	100 (1.5 h)	–	100 (3 min)

Table 6
Activation parameters of **CPP** hydrolysis.

pH	E_A, kcal/mol	A, s^{-1}
4	15.22	1.73×10^5
7	17.52	6.87×10^7
10	20.43	1.31×10^{11}

both cases, it was also found with ^{31}P NMR and HPLC that the hydrolysis of **CPP** occurred only with elimination of 4-cyanophenol, and the reactions could be described in the same way as those occurring at pH = 4 (Fig. 9). Hydrolysis with H_2O^{18} showed that no excess abundance of tracer was observed by LC/MS in the formed 4-cyanophenol, and the reactions proceeded only with P—O bond fission. The kinetic parameters were determined for the hydrolysis in both media. It was shown that the hydrolysis rate increases with an increase of pH (Table 5). Under pH 10 at 80 °C, full conversion was reached in 3 min and it was not possible to define the rate constant. It is worth noting that even in this condition, the product **CPPA** appeared to be stable to further hydrolysis.

Activation parameters were calculated using the Arrhenius equation from the rate constants collected at different temperatures. The results are listed in Table 6, and these dependencies are presented in the supporting materials (See Data in Brief related article). According to the hydrolysis study, **CPP** is more sensitive to moisture than phosphate-bridged phthalonitrile reported previously, but still resistant enough at acidic and neutral media at room temperature. As far as **CPP** is stable to hydrolysis on air, it can be used as a diluent for phthalonitriles, but storage limitations concerning a risk of hydrolysis should be composed based on the present data.

4. Conclusions

In this work, we introduced a new concept aimed at improving the processability of phthalonitriles by the addition of bis-benzonitrile phosphate ether **CPP**. Copolymerization of benzonitrile with phthalonitrile was demonstrated for the first time and the resulting thermosets were characterized by FT-IR and thermal analysis indicating inclusion of bis-benzonitrile molecule to phthalonitrile network, resulting in heat resistant polymers formation. By adjusting **CPP**/**PN** ratios, it is possible to adjust the processability of the resins and thermal performance of thermosets. Based on the combination of resin processability/thermoset, performance of **PNDP-55** blend can be assumed as the most prospective for composites fabrication.

Hydrolysis of **CPP** was investigated for the first time. Hydrolysis rate grows with an increase of pH, and in alkali media **CPP** is unstable even at room temperature. At all the considered pH values, hydrolysis occured through P—O bond fission and only with 4-cyanophenol elimination. Based on the collected experimental data, we can conclude that the newly presented approach allows to sufficiently cut the price of phthalonitrile CFRP fabrication by using cheaper resin formulations and cost-effective techniques.

Supplementary materials containing chromatograms, NMR spectra and detailed experimental procedures are presented in Data in Brief article.

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