

DUAL-CURING PHTHALONITRILE-PROPARGYL ETHER RESINS FOR CFRP

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Introduction

Composite materials are becoming more important for aerospace industry and parts made with fiber reinforced plastics (FRP) comprise over 50 % of a modern civil aircraft mass. Whilst thermal stability of FRP allows their application for wings and body construction, turbines of engines are mostly made from metals. Thermal stability of FRP is limited by the polymer matrix while inorganic fibers possess much higher thermal stability.

Recently it has been reported that propargyl aryl ether blended with phthalonitriles could act as a polymerization activator of the latter, forming materials with high thermal properties inherent to phthalonitrile matrices [1]. Based upon these results, in this work we combined propargyl ether and phthalonitrile function in one molecule acquiring in new bifunctional self-curing monomers suitable for acting as matrices for CFRP.

Synthesis

Monomers 2m and 2p were synthesized according to a two-step scheme (Figure 1). In the first step precursors 1m and 1p were obtained by the reaction between 4-nitrophthalonitrile and resorcinol or hydroquinone respectively [2]. The second step was Williamson reaction between hydroxyl-containing semi-products 1m or 1p and propargyl chloride in DMAc in the presence of K_2CO_3 .

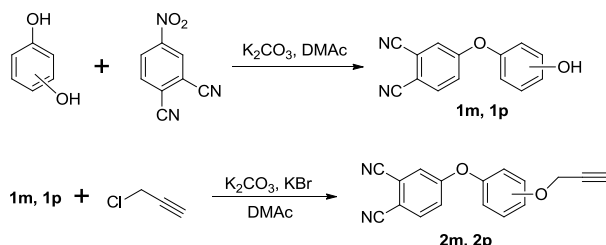


Figure 1: Synthesis of the monomers 2m and 2p.

To investigate polymerization of amine-propargyl/phthalonitrile monomer a synthesis of 4 was performed (Figure 2). The reaction between 4-aminophenol and 4-nitrophthalonitrile occurred at

room temperature with quantitative yield. Propargylation of the product 3 was also reached with quantitative yield at 60 °C and 10% excess of propargyl chloride.

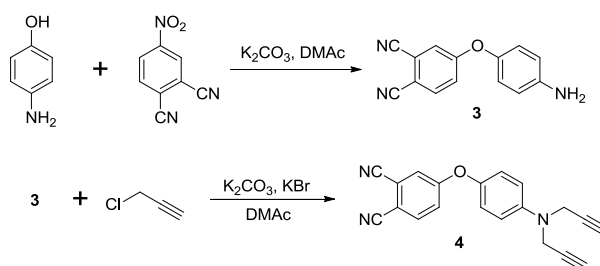


Figure 2: Synthesis of the monomer 4.

DSC analysis revealed melting points of monomers 2m = 117 °C and 2p = 98 °C which was a bit of surprise. In accordance with Carnelley rule [3] symmetric isomers melt at higher temperatures. Similar phenomena were reported for arylamine substituted phthalonitriles [4, 5]. Melting point of 4 was 129 °C higher than for 2m and 2p (Table 1). On all DSC curves collected for the monomers 2m, 2p and 4 exothermal peaks related to polymerization were observed ($T_{onset} \sim 244$ °C). As it is seen from Table 1, curing heat release for all the monomers was at a high level and the lowest value was observed for 2m.

Monomer	η at 130 °C, mPa·s	Curing parameters	
		T_{max} , °C	ΔH , J/g
2m	47	280	800
		307	
2p	39	282	1110
		297	
4	567	285	910
		305	

Table 1: Properties of the considered monomers.

Curing and thermosets testing

Due to the presence of two different thermosetting moieties in the molecule, curing of monomers 2m, 2p and 4 could be performed in several different ways (Figure 3).

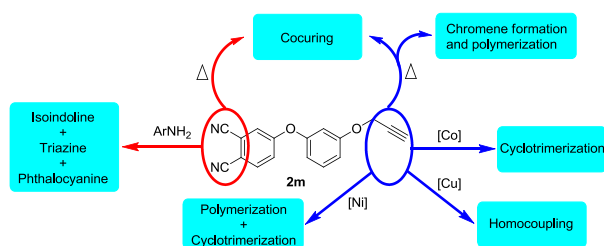


Figure 3: Potential ways of monomer 2m polymerization.

Self-curing of monomers 2m, 2p and 4 with the final temperature of 375 °C resulted in formation of thermosets possessing properties featured to phthalonitriles. Study of the polymer thermal properties (Table 2) showed that heat deflection temperatures (HDT) for all thermosets were higher than 400 °C which is much higher than for cured propargylated resins [10] and at the same time typical for phthalonitriles [11]. To estimate thermal and thermooxidative stabilities of the thermosets TGA in Ar and in air respectively was performed. Start of decomposition was defined as temperature at what 5 % mass loss occurred and designated as $T_{5\%}$ for decomposition in Ar and $TOS_{5\%}$ for decomposition in air. As it seen from Table 2 all the thermosets demonstrated similar values of $T_{5\%}$ and $TOS_{5\%}$ and char yields (Y_c) were found in range 75 – 80 %.

Catlyst	HDT, °C	$T_{5\%}$, °C	Y_c , %, Ar	$TOS_{5\%}$, °C
2m	428	499	75	503
2p	405	519	79	497
4	412	504	80	512

Table 2: Thermal properties of thermosets derived from 2m, 2p and 4.

Based on the properties (curing parameters, rheological behavior and thermal properties of the cured matrices) monomer 2m was chosen for further investigations.

Curing of monomer 2m in the presence of various initiators was studied. It was shown that catalyst do affect curing process (shape of DSC curve) and properties of the resulting thermosets (Table 3). Aromatic diamine (APB), cobalt triphenylphosphine dichloride and 2-ethylhexanoates of Cu and Ni were tested. The best results regarding thermal and therooxidative stability were demonstrated by thermosets cured in the presence of APB which is connected to an increase of phthalonitrile polymerization share [12].

Mechanical properties of the 2m blends with APB were investigated (Table 4). With an increase of APB content Young modulus of the cured matrix increases. The same trend can be mentioned in the case of fracture toughness parameters. For these reasons formulation consisting of 2m and 10 % APB which is referred to as PPN in further experiments was set up for CFRP

manufacturing. DMA was performed for PPN revealing no clear transition but a drastic decrease of the storage modulus above 400 °C.

Catlyst	HDT, °C	$T_{5\%}$, °C	Y_c , %, Ar	$TOS_{5\%}$, °C
None	428	499	75	503
4 % APB	415	502	79	504
1 % $Co(Ph_3P)_2Cl_2$	450	474	77	470
1 % $CuEh_2$	434	499	79	490
0.1 % $NiEh_2$	428	490	77	415
0.5 % $NiEh_2$	335	386	68	382

Table 3: Properties of monomer 2m cured with different catalysts.

Matrix	Flex. Strength, MPa	Flex. Modulus, GPa	G_{IC} , J/m ²
2m	73±8.5	4.5±0.24	52±2
2m + 4 % APB	60±7.8	4.9±0.65	106±6
PPN	85±7.3	5.1±0.26	97±3

Table 4: Mechanical properties of the resin 2m cured in different conditions.

CFRP manufacturing and characterization

Impregnation was performed in an oven equipped with outlets for a vacuum pump at 130 °C and took about 15 minutes. After the resin showed up in outlet tube outside the oven it was sealed and heated for 6 hours at 180 °C. The sample was disassembled and post-cured at 375 °C resulting in high-temperature CFRP formation with the matrix content of 28–30 %.

Mechanical characteristics of CFRP are shown in Table 5.

Parameter		Post-curing T, °C	
		375	330
Tensile	σ_{11}^+ , MPa	548±14	742±15
	E, GPa	67±1.9	62±0.9
Compressive	σ_{11}^- , MPa	325±22	485±39
	E, GPa	63±3.6	59±8.4
Interlaminar shear	τ_{13} , MPa	32±2.8	32±2.2
In plane shear	τ_{12} , MPa	57±3.6	72±1.5

Table 5: Mechanical properties of the obtained CFRP samples.

Sample cured at 375 °C demonstrated average mechanical properties and high porosity was detected by SEM.

It was suggested that matrix partially decomposed during curing. Another sample was post-cured at 330 °C and tested. No porosity was detected by SEM and significant increase of mechanical properties was observed after tests.

Thermal behavior of the composites was estimated by shear strength tests at elevated temperatures (Table 6). As it is seen, the materials retain up to 96 % of mechanical properties at 300 °C and 70–75 % of the interlaminar shear strength at 400 °C.

T, °C	Curing at 375 °C		Curing at 330 °C	
	τ_{13} , MPa	τ_{12} , MPa	τ_{13} , MPa	τ_{12} , MPa
250	–	–	31±2,2	62±2,3
300	25±3.1	54±2.5	30±1,7	59±3,0
350	25±2.7	47±2.7	–	–
400	23±1.8	37±0.95	–	–

Table 6: Mechanical properties of the composites at elevated temperatures.

Inflammability tests

Samples of the cured matrix and CFRP were tested for LOI according to the Russian GOST- 21793-76. Both materials showed high LOI values in comparison to the known materials (Table 7).

Sample	LOI, %
PPN	41
CFRP (PPN based)	75

Table 7: Flammability of CFRP with matrices of different types.

Conclusions

The novel monomers containing two thermosetting groups, namely propargyl ether and phthalonitrile, were synthesized. Propargyl ether groups provided self-curing of the monomer not only by homopolymerization but also by initiation of phthalonitrile polymerization. Influence of catalysts with different action mechanisms such as APB, Co, Ni and Cu salts on curing behavior was studied. Thermal properties of the considered differently cured matrices were found at the high level characteristic to phthalonitriles, which in addition to the relatively low melting point and melt viscosity make this monomer prospective for high-temperature composite formation by vacuum infusion molding processing. The samples of CFRP were obtained and demonstrated high thermal stability. LOI of CFRP samples were found at the level of 75 %. Thus, such materials could find possible application in aerospace or any other fields that require materials with extended thermal performance.

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