Polyesterimide Resins with Built-In Polycyclic Compounds

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ABSTRACT: Polyesterimide (PEI) resins are used for the preparation of PEI varnishes, for copper wire enameling. They are usually manufactured from dimethyl terephthalate (DMT), ethylene glycol, bisphenol A (BPA), tris(2-hydroxyethyl) isocyanurate, trimellitic anhydride, and 4,4′-diaminodiphenylmethane. The synthesis involves condensation and imidization. DMT and BPA were partially or completely replaced with the polycyclic components: dimethyl 2,6-naphthalenedicarboxylate (NDC) and (*R*,*S*)-1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (TMC), respectively, to enhance the heat resistance and the thermal stability. The effect of NDC and TMC on the solubility, the glass transition temperature, the course of the thermal decomposition, and the properties of magnet wires, enameled with the thus-modified PEI varnishes, were investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4066–4073, 2006

Key words: polyesters; polyimides; structure-property relations; thermogravimetric analysis; thermal properties

INTRODUCTION

Polyesterimide (PEI) resins are the main component of PEI varnishes, which are used for copper wire enameling in the production of magnet wires. The PEI-insulated magnet wires are suitable for long-term use at high temperatures, usually up to 180°C. The threshold temperature is governed by two factors: the glass transition temperature (T_g) and the thermal stability of the crosslinked polymer.

EXPERIMENTAL

For the synthesis of PEI resins, the following starting materials were used: trimellitic anhydride (TMA), 4,4′-diaminodiphenylmethane (DADPM), ethylene glycol (EG), tris(2-hydroxyethyl) isocyanurate (THEIC), dimethyl terephthalate (DMT), and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA).

To enhance T_g and thermal stability of PEI resins, DMT and BPA were entirely or partially (50 mol %) replaced with dimethyl 2,6-naphthalenedicarboxylate (NDC) and (*R*,*S*)-1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (TMC), correspondingly.

NDC (Scheme 1) contains the condensed naphthalene ring system, which may be considered a fragment of the thermally stable ladder structure.[1,2] TMC (Scheme 2) comprises the tricyclic ring structure, with the spiro carbon atom, that is characteristic for the so-called cardo polymers.[3,4]

Synthesis of PEI resins and preparation of PEI varnishes

The PEI resins were synthesized in melt by an esterification–imidization method. TMA, DADPM, EG, THEIC; DMT and/or NDC; DPA and/or TMC; and zinc acetate were placed into a four-necked glass reactor, equipped with a stirrer, a thermometer, an inert gas inlet, a hole for sampling, and a condenser cooler. The reactor was heated in an electrical bath.

The molar ratios and the amounts of the aforementioned starting materials are given in Tables I and II. The schematic diagram of the formulations is presented in Table III.

After having charged the reactor with all the starting materials, the reaction mixture was heated slowly. The reaction mixture was stirred after the temperature reached 130°C. At 150°C, the evolution of the condensate (water and methanol) began. An abundant yellow precipitate of the TMA-DADPM diimido-dicarboxylic acid (Scheme 3) was formed, at 130–180°C. The precipitate disappeared at 180°C.

The esterification–imidization process was continued at 220°C. After the "melting point" (Boëtius apparatus) reached the value which was assumed for the given PEI resin sample, the reaction mixture was cooled down to 200°C, and the reaction was stopped

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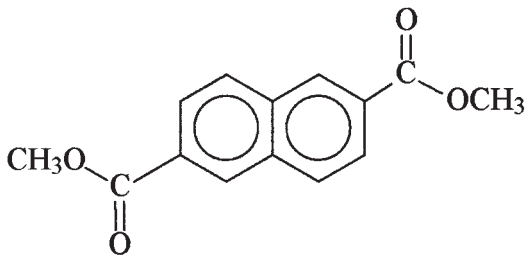


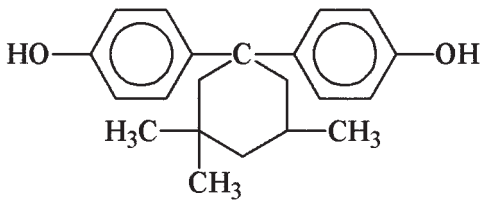
Scheme 1 NDC.

by adding 400 g of cool tricresol (a mixture of cresol isomers), and by further cooling.

Solution of PEI resin (590 g) in 400 g tricresol was diluted with 320 g of tricresol and 300 g of Solvesso 100; then, 1.8 g tetrabutyl orthotitanate, 67.8 g tetralin, and 16.2 g alkylphenolic resin were added.

RESULTS AND DISCUSSION

PEI resins, with a partial or total replacement of DMT with NDC and BPA with TMC, were synthesized (Tables I–III). The PEI resins with an acid value (AV) in the range of 3.0–6.4 mg KOH (mostly 3.0–4.6 mg KOH/g) and a hydroxyl value (HV) in the range of 174.0–202.2 mg KOH/g were obtained. The number-average molecular weight (M_n) was for the most part in a relatively narrow range: 1270–1560. All M_n values were in the range of 1270–2005 (Table IV). The M_w values present a similar picture for the most part between 2765 and 3937 (all M_w values are within 2765–4795). The D (M_w/M_n) values between 2.04 and 3.00 point out an abnormal molecular weight distribution, with an assumedly high share of large molecules.



Scheme 2 TMC.

TABLE III
Effect of NDC and TMC on the Formulations

	TMC content		
NDC content	0	1	2
0	P-1	P-2	P-3
1	P-4	P-5	P-6
2	P-7	P-8	P-9

Content of NDC/DMT and TMC/PBA in the mixture of starting materials: "0" - no NDC and/or TMC, DMT and/or BPA only; "1" - 50 mol % DMT and/or BPA replaced by NDC and/or TMC; "2" - no DMT and/or BPA, NDC and/or TMC only. **Examples:** The formulations P-4 contain NDC and DMT in the molar ratio of 1 : 1, no TMC The formulations P-8 contain NDC; no DMT; BPA and TMC in the molar ratio of 1:1.

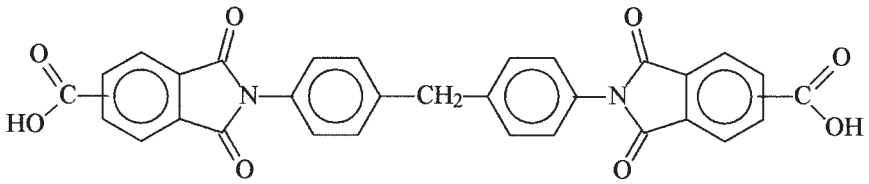
The "melting point" (Boëtius) values are in a relatively narrow interval of 100–121°C, supposedly, be-

TABLE I
Formulation (in moles) of the Starting Materials for the Synthesis of PEI Resins

Starting material	PEI samples								
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9
TMA	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
DADPM	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
EG	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51
THEIC	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DMT	1.0	1.0	1.0	0.5	0.5	0.5	—	—	—
NDC	—	—	—	0.5	0.5	0.5	1.0	1.0	1.0
BPA	0.62	0.31	—	0.62	0.31	—	0.62	0.31	—
TMC	—	0.31	0.62	—	0.31	0.62	—	0.31	0.62

TABLE II
Formulation (in grams) of the Starting Materials for the Synthesis of PEI Resins

Starting materials	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9
TMA	160.4	160.4	160.4	160.4	160.4	160.4	160.4	160.4	160.4
DADPM	82.3	82.3	82.3	82.3	82.3	82.3	82.3	82.3	82.3
EG	47.4	47.4	47.4	47.4	47.4	47.4	47.4	47.4	47.4
THEIC	130.6	130.6	130.6	130.6	130.6	130.6	130.6	130.6	130.6
DMT	97.1	97.1	97.1	48.6	48.6	48.6	—	—	—
NDC	—	—	—	61.5	61.5	61.5	123.0	123.0	123.0
BPA	70.8	35.4	—	70.8	35.4	—	70.8	35.4	—
TMC	—	48.1	96.1	—	48.1	96.1	—	48.1	96.1



Scheme 3 TMA-DADPM diimido-dicarboxylic acid.

cause the process of synthesis used to be stopped after the desirable "melting point" was reached.

There is rather no correlation between the starting composition of the PEI resins on one side and the average molecular weight values, "melting point," and *D* on the other side. Dependence of the "melting point" on the DMT : NDC and BPA : TMC molar ratio and HV or HV + AN is unclear or does not exist.

However, the effect of DMT replacement, with NDC and of BPA replacement with TMC on the thermal properties of PEI resins, can be clearly seen. The characteristic temperature values relating to the thermal decomposition process, namely

- end of the endothermic decomposition process,
- start of the exothermic decomposition process (SED), and
- end of the exothermic decomposition process
- rise with increasing NDC : DMT and TMC : BPA molar ratio.
- The resins differed in the DMT/NDC and BPA/TMC content in the mixture of the aforementioned starting materials (Table IV).

Solubility of PEI resins in organic solvents

PEI varnishes are 28–40 wt % solutions of PEI resins in organic solvents. Usually, a mixture of cresol isomers, as a solvent, and aromatic hydrocarbons (e.g., solvent naphtha), as a diluent, are used. PEI manufacturers try to replace cresols with other solvents, because of its toxicity and unpleasant odor. According to the patent application,[5] cresols can be replaced by methyl benzoate and isophorone.

The Hansen method of solubility parameters is helpful for designing the compositions of solvent/diluent systems, for varnishes.[6] We applied that method using the simplified two-parameters system ($\delta_p - \delta_h$), viz., polarity/hydrogen bonds, to develop without-cresol formulations for PEI varnishes.[7,8]

Within this study, the effect of replacement of DMT with NDC and of BPA with TMC on the solubility area, was investigated (Fig. 1). It was found that the solubility areas of all tested PEI resins are similar. Notwithstanding, the use of both NDC and TMC results in a limitation of the solubility area, in which the effect of NDC is more pronounced.

Investigation of the behavior of PEI resins at elevated temperatures

Thermogravimetric (TG) measurements were performed on uncrosslinked PEI resins, using a thermobalance TGA-7 (Perkin–Elmer), at a constant heating rate of 5°C/min. Temperatures were recorded at which the weight loss reached 10, 15, and 20% (Tables V–VII).

Thermoanalytical investigations were made on uncrosslinked PEI resins by means of a Derivatograph OD-102 (MOM, Budapest, Hungary). TG, differential thermogravimetric (DTG), and differential thermoanalytical (DTA) curves were recorded in air, at a constant heating rate of 5°C/min. The exemplified derivatographic diagram is shown on Figure 2. Thermal decomposition of the PEI resins was best characterized by the temperatures of the end of the fast weight loss (EFL, DTA curve) and by the SED process (DTG curve), and of the end of the fast decomposition

TABLE IV
Properties of the PEI Resins

Properties	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9
DMT : NDC molar ratio	2 : 0	2 : 0	2 : 0	1 : 1	1 : 1	1 : 1	0 : 2	0 : 2	0 : 2
Acid value (mg KOH/g)	3.5	4.2	6.4	4.2	4.6	3.0	3.2	5.3	3.5
Hydroxyl value (mg KOH/g)	200.0	182.6	180.0	186.4	198.8	200.2	174.0	192.0	196.5
"Melting point" (Boëtius) (°C)	100	116	121	118	107	114	112	118	116
Molecular weight									
M_0	1,560	1,515	1,435	1,345	1,395	2,005	1,810	1,345	1,270
M_w	3,935	4,795	4,265	3,655	3,585	3,980	4,475	3,250	2,765
M_z	7,215	9,940	8,590	7,090	6,705	6,820	8,140	5,845	5,125
$D = M_w M_n$	2.54	3.19	3.00	2.75	2.56	2.04	2.49	2.43	2.49

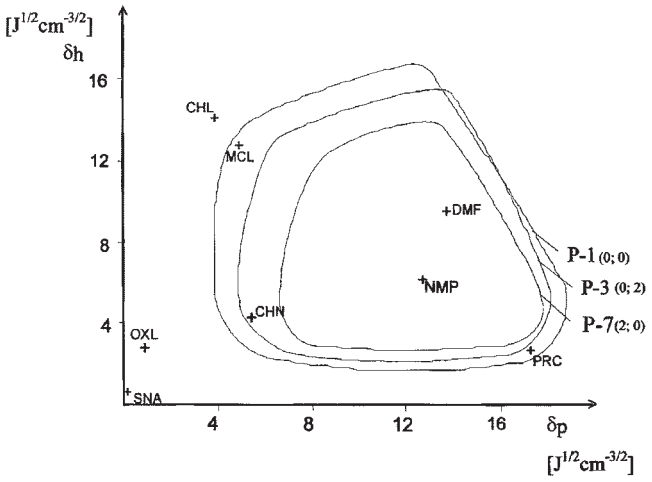


Figure 1 Solubility areas of PEI resins (Hansen method). 1-Sample P-1; 2-Sample P-3; 3-Sample P-7; δ_p, polarity parameter; δ_h, hydrogen bonds parameter, $J^{1/2}/cm^{3/2}$; CHL, cyclohexanol; MCL, methylcyclohexanol; CHN, cyclohexanone; DMF, dimethylformamide; NMP, *N*-methylpyrrolidone; PRC, propylene carbonate; OXL, *ortho*-xylene; SNA, solvent naphtha.

process (EXD; DTG curve). The dependence of the EFL and end of the endothermic decomposition (END) values on the NDC and TMC content in the formulations can be seen in Tables VIII and IX.

The temperature values, at which the weight loss reached 10, 15, and 20%, are the measures of thermal stability of the resins. Moreover, the temperature values relating to the start of the slow weight loss (TG curve), to the end of slow weight loss (TG curve), and to the start of endothermic decomposition (DTA curve) can be estimated.

TABLE V
Effect of NDA and TMC on $I_{10\%}$[a]

	TMC content		
NDC content	0	1	2
0	286 (P-1)	306 (P-2)	312 (P-3)
1	301 (P-4)	310 (P-5)	
2	310 (P-7)	308 (P-8)	307 (P-9)

[a] $I_{10\%}$ indicates the temperature at which there was 10% weight loss.

TABLE VI
Effect of NDC and TMC on $I_{15\%}$[a]

	TMC content		
NDA content	0	1	2
0	318 (P-1)	341 (P-2)	360 (P-3)
1	337 (P-4)	339 (P-5)	341 (P-6)
2	376 (P-7)	356 (P-8)	340 (P-9)

[a] $I_{15\%}$ indicates the temperature at which there was 15% weight loss.

TABLE VII
Effect of NDA and TMC on $I_{20\%}$[a]

	TMC content		
NDC content	0	1	2
0	371 (P-1)	408 (P-2)	417 (P-3)
1	411 (P-4)	411 (P-5)	
2	417 (P-7)	417 (P-8)	408 (P-9)

[a] $I_{20\%}$ indicates the temperature at which there was 20% weight loss.

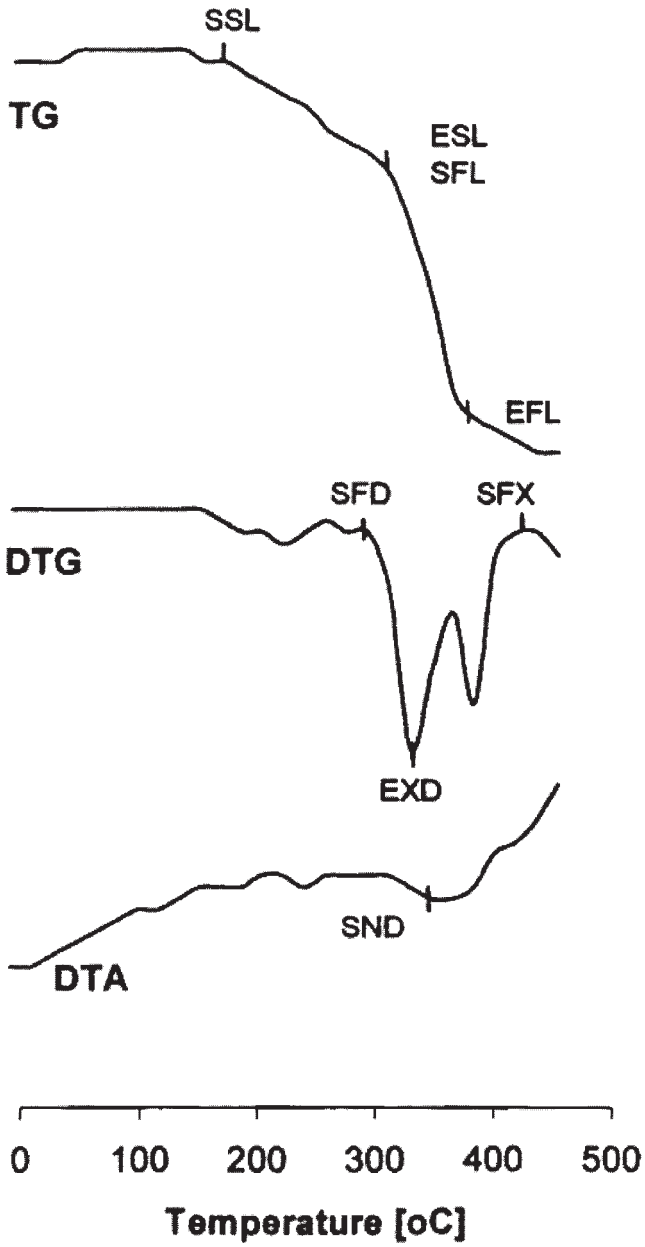


Figure 2 Exemplified curves from the derivatograph (thermal decomposition). SSL, start of the slow weight loss; ESL, end of the slow weight loss; SFL, start of the fast weight loss; EFL, end of the fast weight loss; SFD, start of the fast decomposition; EXD, end of the fast decomposition; SND, start of the endothermic decomposition; END, end of the endothermic decomposition.

TABLE VIII
Temperature (in °C) of the End of the Fast Decomposition Process (EXD)

NDC content	TMC content		
	0	1	2
0	458 (P-1)	472 (P-2)	467 (P-3)
1	465 (P-4)	478 (P-5)	468 (P-6)
2	476 (P-7)	478 (P-8)	484 (P-9)

TABLE IX
Temperature (in °C) of the End of the Endothermic Decomposition Process (END)

NDC content	TMC content		
	0	1	2
0	397 (P-1)	408 (P-2)	420 (P-3)
1	408 (P-4)	410 (P-5)	
2	417 (P-7)	419 (P-8)	420 (P-9)

Glass transition temperature

PEI films, which are deposited on the surface of a copper wire, have a maximum working temperature close to the glass transition temperature (T_g) of the crosslinked film. The T_g values were determined using differential scanning calorimetry (DSC). Moreover, T_g was determined from the temperature dependence of the dielectric loss factor (tan δ) of the crosslinked PEI film, measured directly on the magnet wire (see Fig. 3).

The dependence of T_g (DSC) on the NDC and TMC content in the PEI formulation is presented in Figure 4. An approximate trend of T_g increase, with increasing NDC and TMC content, can be seen, although some irregularities and some deviations from that general tendency are observed.

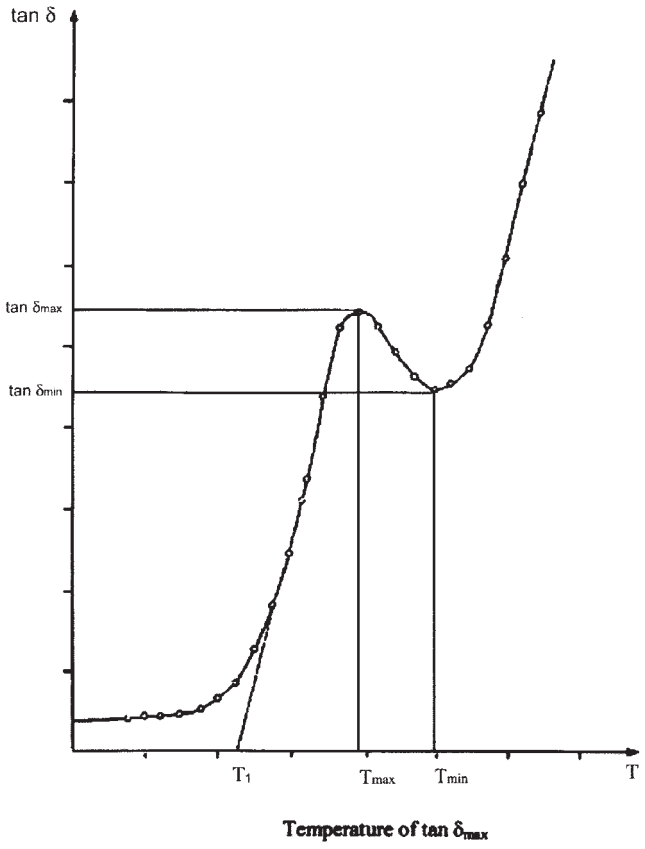


Figure 3 T_g δ determination based on the temperature dependence of tan δ.

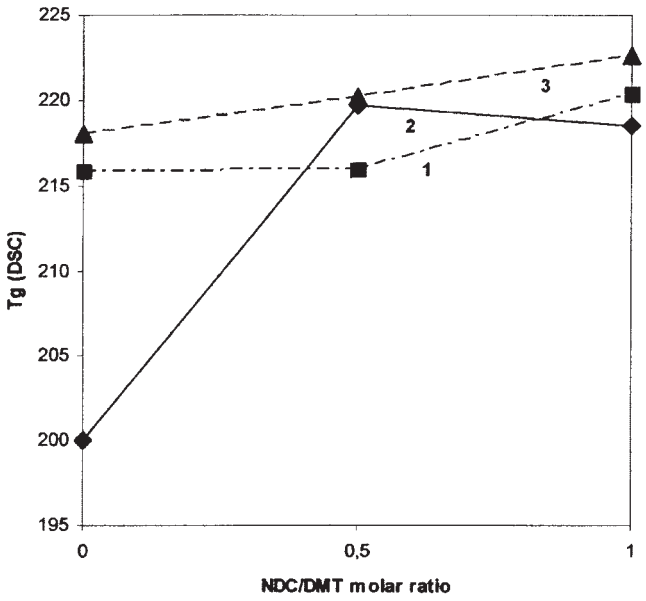


Figure 4 Effect of the NDC/DMT molar ratio on T_g (DSC). 1-no TMC; 2-TMC:BPA = 1 : 1; 3-no BPA.

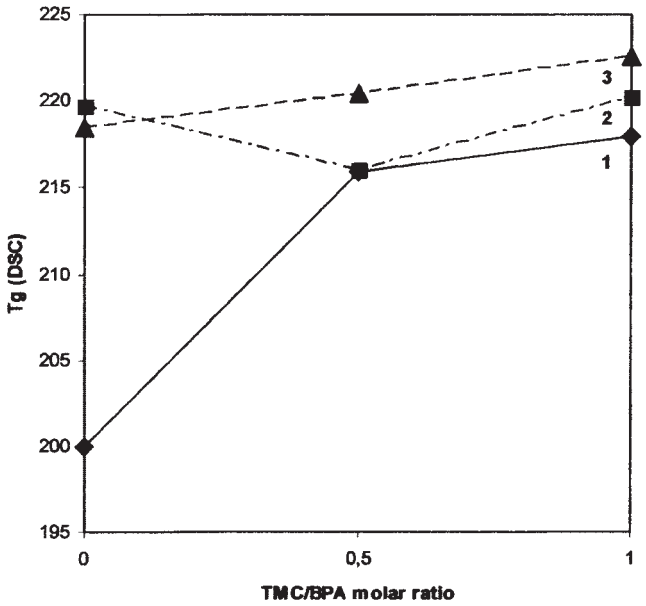


Figure 5 Effect of the TMC/BPA molar ratio on T_g (DSC). 1-no NDC; 2-NDC:DMT = 1 : 1; 3-no DMT.

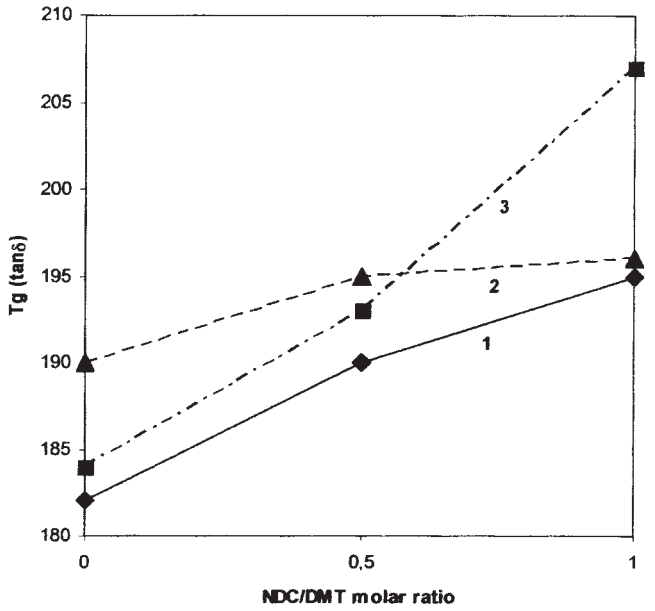


Figure 6 Effect of the NDC/DMT molar ratio on T_g (tan δ). 1-no TMC; 2-TMC : BPA = 1 : 1; 3-no NDC.

Similar dependencies are shown in Figure 5 for T_g (tan δ). The conclusions are similar, as mentioned earlier. Increase in T_g (tan δ) is generally observed at increasing NDC and TMC content in the formulations (Figs. 6 and 7). The dependencies for T_g (tan δ) are more regular than those for T_g (DSC), the increase in T_g being stronger, with increasing NDC content, in comparison with an increase in TMC content in the PEI formulation.

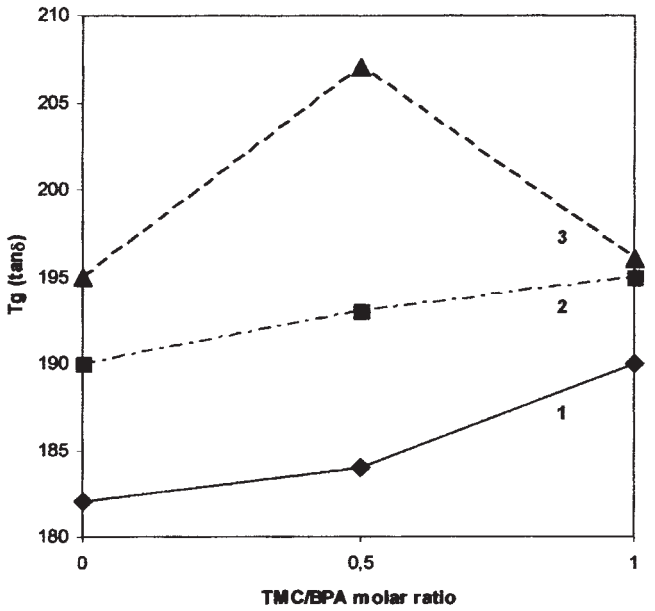


Figure 7 Effect of the TMC/BPA molar ratio on T_g (tan δ). 1-no NDC; 2-NDC : DMT = 1 : 1; 3-no DMT.

TABLE X
Properties of Magnet Wires[a] Enameled with PEI Varnishes

Sample No. (see Table I)	Molar ratio DMT:NDC	Molar ratio BPA:TMC	Flexibility[b] number of cracks 1*d*	Flexibility[b] number of cracks 2*d*	Elasticity[c] number of cracks 1*d* + 10%	Resistance to abrasion[d] (N)	Breakdown voltage (kV)	Thermal shock resistance (200°C/0.5 h) Number of cracks 1*d*	Thermal shock resistance (200°C/0.5 h) Number of cracks 2*d*	T_{max} (tan δ)[e] (°C)	Appearance of the film[f] Smoothness	Appearance of the film[f] Fluidity	Appearance of the film[f] Gloss	Appearance of the film[f] Glide
P-1	2:0	2:0	1	0	0	7.7	>4	6	0	182	2	1	2	2
P-2	2:0	1:1	0	0	1	9.9	>4	0	0	184	2	1	1	1
P-3	2:0	0:2	0	0	1	12.0	>4	7	0	194	1	1	2	1
P-4	1:1	2:0	0	0	2	10.3	>4	1	0	190	2	2	1	2
P-5	1:1	1:1	2	0	2	11.0	>4	6	0	193	2	1	1	1
P-6	1:1	0:2	0	0	0	12.6	>4	0	0	195	2	3	2	2
P-7	0:2	2:0	3	0	3	11.3	>4	1	0	195	2	2	1	2
P-8	0:2	1:1	0	0	0	13.0	7.5	2	0	207	1	1	1	1
P-9	0:2	0:2	0	0	0	13.0	>4	0	0	196	1	1	1	1

[a] Tested according to IEEC 851, the nominal diameter of the conductor: 1.0 mm.
[b] Winding on a mandrel; 1 *d* = diameter of the mandrel is equal to the diameter of the wire; 2 *d* = diameter of the mandrel is equal to the double diameter of the wire.
[c] Winding on a mandrel of a prestretched wire (10% elongation).
[d] *N*, pressure load; the higher values correspond to higher abrasion resistance.
[e] Temperature of a maximum on the curve tan δ = *f(t)*; tan δ, dielectric loss factor; *T*, temperature; T_{max} is close to T_g; see Fig 3.
[f] 1 = very good; 2 = fair, 3 = unsatisfactory.

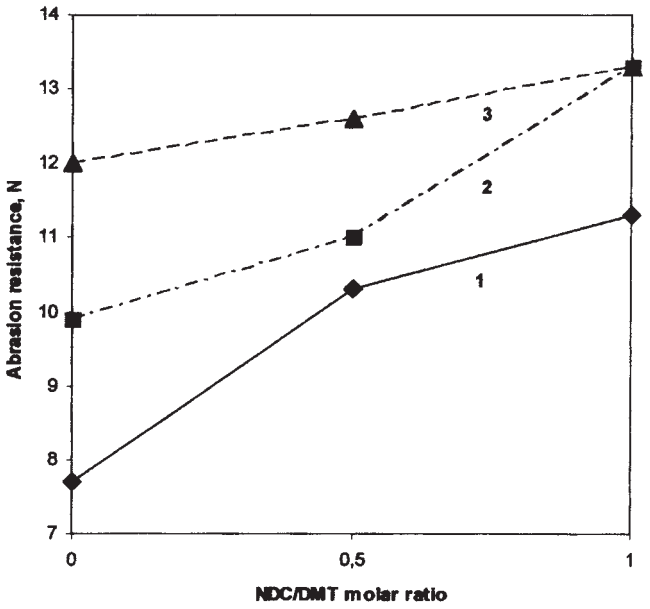


Figure 8 Effect of the NDC/DMT molar ratio on the abrasion resistance. 1-no TMC; BPA only; 2-TMC : BPA = 1 : 1; 3-no BPA.

Properties of enameled wires

The magnet wires were prepared by the enameling of copper wires. A laboratory enameling machine was used to apply the PEI varnishes, to evaporate the solvent–diluent mixture and to bake the film.

The properties of magnet wires are presented in Table X.

Flexibility of the specimens is generally very good. The few cracks may be incidental. The flexibility test on the prestretched specimens points out a positive effect of TMC.

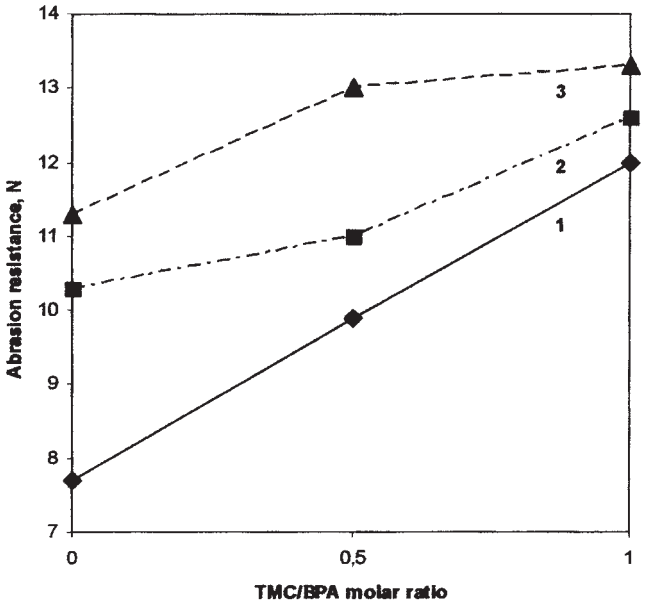


Figure 9 Effect of the TMC/BPA ratio on the abrasion resistance. 1-no NDC; 2-NDC : DMT = 1 : 1; 3-no DMT.

TABLE XI
Effect of NDC and TMC on T_g (DSC)

	TMC content		
NDC content	0	1	2
0	200 (P-1)	216 (P-2)	218 (P-3)
1	220 (P-4)	216 (P-5)	216 (P-6)
2	219 (P-7)	220 (P-8)	223 (P-9)

The advantageous effect of NDC and TMC on the abrasion resistance is well pronounced. It can be best seen on Figures 8 and 9.

There seems to be rather no distinct effect of NDC and TMC on the thermal shock resistance. The effect of the aforementioned components on the T_{max} (tan δ) value is well pronounced. There are, however, some irregularities.

There is some uncertainty, as far as conclusions from the results presented in Table XI are concerned. The properties of the films depend not only on the chemical composition of the PEI resins, but also on other factors, mainly on the baking parameters (i.e., on the crosslinking degree) and on the quality of the surface of the bare copper wire, before applying the varnish.

In general, the magnet wire P-8 (full replacement of DMT by NDC; 50 mol % BPA replaced by TMC) exhibits outstanding properties (Table XII).

CONCLUSIONS

NDC and TMC can be used for the synthesis of PEI resins in the same way as DMT and BPA. The partial (50 mol %) or entire replacement of DMT by NDC and of BPA by TMC affects some important properties of PEI resins and varnishes and of the PEI-enameled copper wires. The solubility area of the PEI resins is diminished. The temperatures, which characterize the thermal decomposition and the glass transition temperature (T_g), are shifted toward higher values. The same concerns the temperature, which corresponds to a maximum on the dielectric loss tangents versus temperature curve. Abrasion resistance of the crosslinked PEI films is distinctly increased.

TABLE XII
Effect of NDC and TMC on T_g (tan δ)

	TMC content		
NDC content	0	1	2
0	182 (P-1)	184 (P-2)	190 (P-3)
1	190 (P-4)	193 (P-5)	195 (P-6)
2	195 (P-7)	207 (P-8)	196 (P-9)

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