

RHEOLOGICAL BEHAVIOUR OF CONCENTRATED SOLUTIONS OF SOME AROMATIC ESTER-IMIDE OLIGOMERS

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abstract: Aromatic ester-imide oligomers are transformed into high thermal class electric/electronic insulators by thermal curing. They are deposited on electric conductors from solutions of adequate concentration in a convenient solvent. Rheological behaviour of solutions must be known to be able to select the best solvent and the most adequate concentrations to obtain high quality insulators with uniform thickness and no defects. The rheological behaviour of solutions of two aromatic ester-imide oligomers - one containing neopentylglycol and the other one ethylene glycol - in cyclohexanone as solvent for concentrations ranging between 1 and 60% was studied. Given the low molecular weights and the relative rigidity of the chains, both ester-imide oligomers behave Newtonian. Viscosities of solutions increase very slowly with oligomer concentration for concentrations up to about 35%, then the increase is higher and a sudden increase produces when the concentration exceeds about 50% for both oligomers. According to the rheological measurements, the most convenient concentrations for deposition on electric conductors are 45%.

Introduction

High thermal class electric insulators are indispensable for the top electrical and electronic industries - aerospace and microelectronics. They are used especially for magnetic conductors functioning for a long time at high temperatures [1]. So the conventional temperature limit of functioning of electronic devices and circuits is 120⁰C [2], temperatures as 180 and even 200⁰C are necessary in many cases.

The application of insulating material is usually made by passing the electric conductors through an enamelling bath having a concentration of resin of 35÷55%, heating them to remove the solvent, followed by the thermal or catalytic curing to transform the thermoplastic insulator into an insoluble and infusible rigid thermosetting one. In industrial conditions curing is realized passing the conductors through ovens of pre-established length and temperature with a given speed.

A series of polymers and copolymers having the above thermal properties are known [1,2], but polymers having high heat resistance are usually insoluble and thus their application on wires from concentrated solutions is impossible.

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The polymers having the highest chemical and oxidative resistance and the best electrical and mechanical properties to be used as high thermal class electrical insulators are polyimides, obtained by the curing of imide oligomers [3]. In addition, the structure-properties relationships are relatively well established for this class of compounds [4,5], but they are highly insoluble.

Heat resistance and solubility are opposed properties and a slight decrease of heat resistance in the favour of solubility is generally accepted. Thus, ester-imide [6] or amide-imide [7] oligomers, with adequate heat resistance and improved solubility, determined by the flexibility of the functional groups (ester or amide) introduced into the main chains, were synthesized.

Compared to amide-imide, ester-imide oligomers have the following advantages [8÷10]: they are a bit more flexible and thus have improved solubility, better adhesion to different metals, higher resistance to solvents and environmental conditions, higher hardness and lower price. However, the commercial ester-imide oligomers have as solvents only cresols, solvents known as carcinogenic. That is why synthesis of ester-imide oligomers soluble in more solvents and/or mixtures of solvents is necessary.

Aromatic ester-imides oligomers are usually obtained by solution or melt polycondensation of polyalcohols (usually ethylene glycol, EG, and very seldom propyleneglycol), aromatic polycarboxylic acids or their derivatives and aromatic polyamines, comonomers able to form imide cycles [11]. Given their importance, information about this type of insulators may be finding only in patents.

Considering the structure-properties relationships established for polymers, we prepared more soluble ester-imide oligomers [12, 13]. Knowing that branching reduces the cohesion energy, and thus increases solubility, ester-imide oligomers containing a branched glycol – neopentylglycol (NPG) – were synthesised. Dimethylterephthalate (DMT) and trimellitic anhydride (TMA) were used as aromatic polycarboxylic monomers, diaminodiphenylmethane (DDM) as aromatic diamine, NPG and tris-(2-hydroxyethyl) isocyanurate (THEIC) as hydroxyl monomers. An increased number of aromatic rings into chains resulting in an increase of heat resistance (but a decrease of solubility), two molar ratios of DMT were used. To be able to make solubility comparisons, the corresponding oligomers containing EG were also prepared. Thus, four ester-imide oligomers, R₁ – R₄, were synthesised, two containing NPG and two EG, with two different molar ratios of DMT [12,13].

Thermal curing of oligomers deposited on electric conductors from concentrated solutions in a convenient solvent being practised in industry, the most convenient solvent/solvents must be selected. At the same time, the rheological behaviour of concentrated oligomer solutions in the selected solvent must be known in order to be able to choose the most adequate concentrations to obtain layers of uniform thickness, with no defects, that assure high quality insulators.

Solubility of the prepared oligomers in different solvents was determined as well as their global and partial solubility parameters [14] from solubility data using the Hansen's method [15,16]. To be able to select the most convenient solvent from the points of view of solubility, film-forming properties, price and human and environmental risk, the intrinsic viscosities of the most soluble oligomers, R₃, in the best solvents, selected according to the solubility parameters of the oligomer, were determined. With cyclohexanone as the most

convenient solvent from the above points of view, the rheological behaviour of solutions with concentrations ranging between 1 and 60% for the oligomer R₃ and for the corresponding oligomer containing EG, R₁, was determined and the most adequate concentration was selected.

Experimental

The oligomers' synthesis was realized by melting polycondensation of the following comonomers: DMT, TMA, DDM, THEIC and NPG or EG. It is described in detail in two previous papers [12, 13]. The oligomers R₁ and R₂ contain EG as dialcohol and different amounts of DMT (higher in the oligomer R₂, molar ratio 1.3) while R₃ and R₄ contain NPG and the same amounts of DMT, respectively.

To be dissolved, the oligomers were milled and sieved (sieve mesh 0.5 x 0.5 mm). The dissolution was done at room temperature for a solvent to oligomer ratio of 4/1 by weight.

The molecular weights of oligomers being small (between 1130 and 1350 g mol⁻¹ [12,13]), the intrinsic viscosities were determined using two Ubbelohde viscometers having the constants 0.00976 and 0.00488 at 25 ± 0.1^oC.

Rheological measurements were made, using cyclohexanone as solvent, for concentrations ranging between 1 and 60% at 25±0.1^oC. The viscosities were determined using adequate equipment: capillary viscometers having a range of constants (0.00488 ÷ 0.0945) for solutions with concentrations ranging between 1 and 9%, a Hoppler rheoviscometer for concentrations between 10 and 27% and a Kaake VT550 Viscotester, developing shear rates ranging between 0.3 and 1312.0 s⁻¹ and shear stresses between 1 and 10³ N s m⁻², for concentrations ranging between 28 and 60%.

Result and Discussion

It is well known that branching reduces the cohesion energy and increases polymer solubility, while an increased number of aromatic rings into the main chains increase polymer's heat resistance and decrease solubility.

The compounds given in Table 1 were used as solvents. The results of dissolution tests for a oligomer to solvent ratio of 4/1 by weight are given in the same Table, together with their global, δ , and partial - δ_d , δ_p and δ_h - solubility parameters of solvents.

Solubility data in Table 1 show that, indeed, NPG increases the solubility of oligomers both when the lower and the higher amount of DMT was used. Thus, oligomer R₃, combining the influence of branching produced by the presence of NPG in the molecule and of lower amount of DMT, is soluble or swells in all the solvents in Table 1, while R₁, containing the same amount of DMT but EG as glycol, is not soluble in acetone and methyldiethyleneglycol - with which R₃ swells - and swells in 1,2-dichlorethane in which R₃ dissolves. At the same time, oligomers containing the lower amount of DMT are more soluble than those containing the higher one as expected: R₁ swells in 1,2-dichlorethane while R₂ does not interact with it; R₃ swells in acetone and m-cresol and dissolves in

1,2-dichlorethane, while R_4 does not interact with the first two solvents and swells in 1,2-dichlorethane in which R_3 solves. Thus, R_3 is the most convenient oligomer from the point of view of solubility and R_2 the less convenient one. It is also convenient from the points of view of mechanical and electrical properties [18] as well as of thermal index [19] to be used as electrical and/or electronic insulator.

Table 1. Solvent tested, their global and partial solubility parameters and the result of dissolution tests

Solvent	Solubility parameters, MPa ^{1/2}				Oligomer solubility			
	δ	δ_d	δ_p	δ_h	R_1	R_2	R_3	R_4
Tetrahydrofuran	19.4	16.8	5.7	8.0	+	+	+	+
Dichlormethane	19.8	18.2	6.3	6.1	+	+	+	+
Acetone	20.0	15.5	10.4	7.0	-	-	±	-
1,2-Dichlorethane	20.0	18.8	5.3	4.1	±	-	+	±
Cyclohexanone	20.2	17.8	8.4	5.1	+	+	+	+
Morpholine	21.5	18.8	4.9	9.2	+	+	+	+
Pyridine	21.7	19.0	8.8	5.9	+	+	+	+
Methyldiethylenglycol	21.9	16.2	7.8	12.7	-	-	±	-
m-Cresol	22.7	18.0	5.1	12.9	+	+	+	+
Dimethylformamide	22.9	17.0	13.3	9.0	+	+	+	+
N-Methylpyrrolidone	22.9	17.0	12.3	9.2	+	+	+	+
Dimethylenetriamine	25.8	16.8	13.3	14.3	+	+	+	+
γ -Butyrolactone	26.0	19.0	16.6	6.5	+	+	+	+
Dimethylsulphoxide	28.4	18.4	16.4	10.2	+	+	+	+

- No interaction; ± Swelling; + Complete dissolution

Oligomer R_3 is also soluble in mixtures of methyldipropylene glycol and xylene or toluene 1/1 by weight at concentrations of 40% and higher. With usual concentrations for deposition ranging between 40 and 48%, such mixtures of solvents may be used for commercialization of oligomer R_3 .

Table 2. Partial and global solubility parameters and radii of interaction sphere of the four oligomers

Oligomer	δ_d , MPa ^{1/2}	δ_p , MPa ^{1/2}	δ_h , MPa ^{1/2}	δ , MPa ^{1/2}	R, MPa ^{1/2}
R_1	18.2	9.6	8.2	22.1	7.6
R_2	18.0	10.0	8.6	22.3	7.2
R_3	17.8 ^a 18.0 ^b	9.6 ^a 11.1 ^b	8.4 ^a 8.8 ^b	21.9 ^a 22.9 ^b	7.6 ^a 8.6 ^b
R_4	18.0	9.6	8.2	22.1	7.6

^aHansen's method; ^bOriginal method

Solubility data were used to determine the partial (δ_d - due to the dispersion forces, δ_p - due to the dipole-dipole and dipole-induced dipole forces and δ_h - due to hydrogen bonds) and global (δ) solubility parameters of the oligomers as well as of the radii of their interaction spheres (R) using Hansen's method [15,16]. The obtained results are given in Table 2

together with those obtained using an original - more accurate - method, but only for oligomer R₃ [14].

As expected, the lowest solubility parameter was obtained for oligomer R₃ - containing NPG and the lowest amount of NPG - and the highest one for R₂ - containing EG and the highest amount of DMT. At the same time R₁ - containing EG and the lowest amount of DMT - has the same solubility parameter as R₄ - containing NPG and the highest amount of DMT. They have also the same values for δ_p and δ_h and radii of interaction spheres. The influence of NPG is reflected into the values of δ_d , a little bit lower for R₃ and a little bit higher for R₁. The oligomer containing EG and the higher amount of DMT (R₂) has the lowest radius of interaction sphere, while the others three have identical values. This explains the lower number of solvents for oligomer R₂ (less solvents are included into the oligomer's solubility sphere). The new original method [14] gives higher values for all the above quantities but it was proved only for oligomer R₃.

Determination of intrinsic viscosities, $[\eta]$, being time consuming, they were determined only for the most soluble oligomer, R₃, in the solvents given in Table 3 in the order of increasing of their global solubility parameters. The solvents were selected according to the solubility parameters of the oligomer R₃.

Table 3. Intrinsic viscosities of oligomer R₃ in the specified solvents

Solvent	Cyclohexanone	Morpholine	Dimethyl- formamide	N-Methyl- pyrrolidone	γ -Butyro- lactone	Dimethyl- sulphoxide
$[\eta]$, dl/g	0.0075	0.1045	0.0990	0.1014	0.0700	0.0190

As it is well known, the intrinsic viscosity is a measure of the size of the macromolecules in the given solvent: the higher the polymer-solvent interaction (the better the solvent), the higher the macromolecule size. The oligomers having very low molecular weights and pretty rigid molecules, due to the aromatic and imide cycles from their main chains, the intrinsic viscosities have low values, as can be seen in the Table.

Considering the values of intrinsic viscosities, the best solvent may be considered morpholine, followed by N-methylpyrrolidone, but they are not usual solvents in the paint or varnishing industry. Thus, the third solvent from the point of view of the value of intrinsic viscosity - cyclohexanone - was selected as solvent for concentrated solutions in view of deposition and determination of rheological behaviour.

Rheological measurements were performed for solutions of the most soluble oligomer R₃, containing NPG and the lower amount of DMT, and - for comparison purposes - for the corresponding oligomer containing EG - R₁. Because of the low viscosities, capillary viscometers with different constants were used to determine the viscosities of solutions having the concentration ranging between 1 and 9%, a Hoppler rheoviscometer for concentrations ranging between 10 and 27% and a rotational viscometer for higher concentrations (28 ÷ 60%).

Rheological measurements shown that even the most concentrated solutions behave Newtonian, so their rheograms are not shown. This can be explained by the low molecular weight of oligomers and their relatively rigid molecules.

The dependence of viscosity on concentration for the oligomer R_3 is shown in Fig. 1.

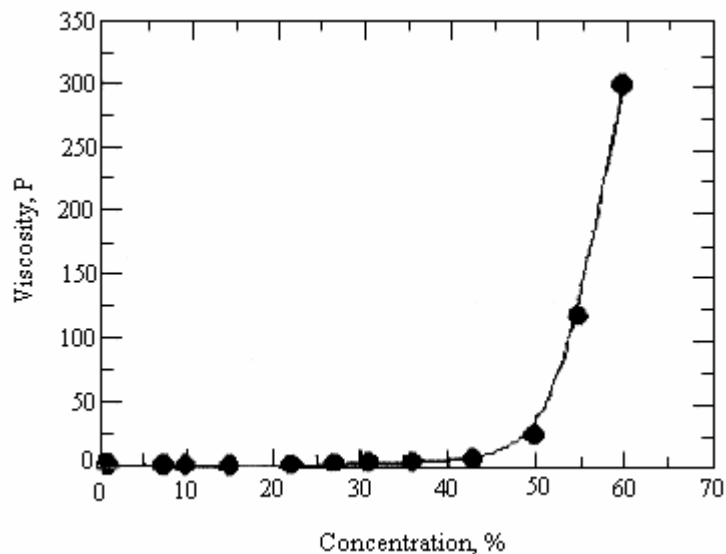


Fig.1: Dependence of viscosity on concentration for oligomer R_3 .

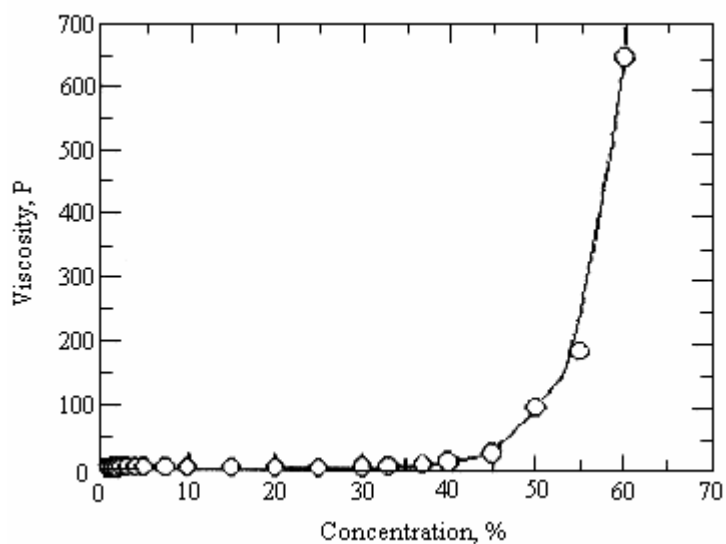


Fig. 2: Dependence of viscosity on concentration for oligomer R_4 .

As can be seen from the Fig. 1, the viscosity increases very slowly with concentration until it is about 35%, the increase is more pronounced between 35 and about 45% and it is very high for concentrations exceeding about 50%.

The equation fitting the best the experimental data is:

$$\eta = 0.011 \cdot \exp(0.165 \cdot c) \quad (1)$$

The dependence of viscosity on concentration for the oligomer R₁ (Fig. 2) is similar, but the viscosities of solutions are higher for all the concentrations (about 2.2 higher for 60 %), so the molecular weights of the two oligomers are comparable (about 10% lower for oligomer R₁). The equation describing the best its behaviour is:

$$\eta = 0.124 \cdot \exp(0.125 \cdot c) \quad (2)$$

The differences of viscosity may be explained by the shape of molecules of the oligomer R₃ that are more bulky than those of the oligomer R₁, due to the presence of NPG - a branched dialcohol - in the molecule.

Figs. 1 and 2 show that concentrations of about 45%, and no higher than 48%, must be used in order to obtain films of convenient thickness by deposition from an enamelling bath on electric conductors from cyclohexanone solutions. If the concentration exceeds 48% the viscosity is excessively high and the deposition from cyclohexanone solutions cannot be done.

Conclusions

The most convenient oligomer from the point of view of solubility for application from concentrated solutions on electrical insulators is R₃, containing neopentylglycol and the lower amount of dimethylterephthalate.

Both the oligomer R₃ and the corresponding oligomer containing ethylene glycol, R₁, has Newtonian behaviour in cyclohexanone as solvent for concentrations ranging between 1 and 60% due to their low molecular weight.

Viscosities of solutions increase very slowly with concentration within the concentration range 1÷35%, the increase is more pronounced between 35 and about 45% and is very high for concentrations exceeding about 50%.

The rheological measurements show that in the case of cyclohexanone as solvent the most convenient concentration for deposition on electric conductors by passing them through an enamelling bath to obtain high quality insulators is 45%. If the concentration exceeds 48% the viscosity is excessively high and the deposition from cyclohexanone solutions cannot be done.

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