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# Structure Thermal Stability and Thermal Stabilization of the Engineering Polyimide and Polysulfone Resins

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Thermal stability and thermal stabilization of the engineering resins of polyimide and polysulfone types was investigated. It is shown, that polyalkaneimide (PAI) and polysulfone (PSF) degradation in the melt at processing temperature is caused by autooxidation which is responsible for loss of materials performance. Analysis of PAI and PSF degradation and stabilization has allowed us to develop approaches to improve stability of these resins and also solve similar problems of other resins with high heat deflection temperatures, such as polyethersulfone, polysulfones, polyamidoimides, polyetherketones.

*Keywords:* Thermal stability; polyimides; polysulfones; stabilizers; degradation mechanisms; oxidation

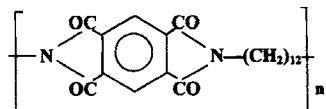
These polymers are exposed to 300–360°C temperatures for short times during production and processing stages and for long periods of times in articles at 150–250°C [1–4]. At temperatures over 300°C these organic polymers start showing thermodynamic instability. The thermal stability at high processing temperatures when complex parts are formed becomes an important requirement for organic thermo-stable polymers. Destructive damages occurring at processing affect aging of polymers during the parts operation. The analysis of structural and technological factors influencing the polysulfone (PSF) and polyalkaneimides (PAI) thermal stability is therefore, an important technological task.

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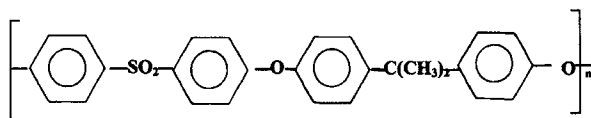
\*Corresponding author.

The following materials were studied:

- laboratory and industrial samples of PAI based on pyromellitic dianhydride and dodecamethylenediamine [5]:



- laboratory and industrial samples-bisphenol A polysulfones based on 4,4'-dichlorodiphenyl sulfone [6]:



- PAI with various methylene chain length based on diamines  $C_6-C_{13}$ . These were products of laboratory synthesis;
- low molecular compounds, modelling the main fragments of PAI backbone, *e.g.*, 1,12-dodecamethylene bis-phthalimide;
- polyethersulfone (PES), based on 4,4'-dichlorodiphenyl sulfone and 4,4'-dihydroxydiphenyl sulfone or bis (chlorophenylsulfonyl) biphenyl;
- PSF model compounds such as its monomers and dimers.

The commercial polymers contain in contrast to ideal high-molecular models impurities and backbone defects. It is necessary to estimate their effects on the degradation kinetics. From the practical point of view such approach allows us to develop requirements to purity and structural perfection in order to upgrade the products.

The analysis of many PSF samples showed the presence of such impurities as Na, K, Mg, Ca, Ba, Cr, Fe, Ni, Cu, Zn-containing compounds in concentrations (metal ion)  $(0.1 - 600)10^{-5}\%$  by weight, solvent residues of  $10^{-3} - 10^{-2}\%$  monomer residues as well hydrolysis product of sulfone monomer-hydroxychlorodiphenyl sulfone in concentrations of  $10^{-3} - 10^{-1}\%$ , anions  $Cl^-$  and  $SO_4^{2-}$  in concentrations of  $(2 - 400)10^{-3}\%$  by weight. The contents of OH end groups (blocked and unblocked PSF) were 0.006–0.096% by weight.

Molecular weight distributions (MWD) of PSF samples were characterized by ranges of  $M_n$ -12000–18000,  $M_w$ -30000–40000 and  $M_z$ -60000–82000 [7–11]. These data were compared with those of tests on PSF thermal stability measured by  $O_2$  absorption, discoloration and melt flow index (MFI) stability when PSF is exposed in the channel of rheoviscosimeter for 10 and 20 min. PSF thermal stability depends first of all on the contents of phenol (OH) end groups, Fe compounds and bisphenol A content also.  $M_z$  value showing the high molecular weight contents in MWD is also important. Evaluation of the hydroxyphenyl end groups activity at the initiation of thermal oxidation in  $PH + O_2 \rightarrow P$  reaction in comparison with the similar process in the isopropylidene  $CH_3$  groups bisphenol A units also indicate the lability of the hydroxyl end groups. We can neglect the OH-groups contribution in the initiation of oxidation as their content is only about 0.005% by weight.

The acceptable stability of the melt viscosity is found with samples with  $M_z$  below 70000. As far as the limited concentration of other impurities are concerned one must follow our experimental data using the artificial impurities introduction into PSF: Fe-0.0005, 4,4'-dichlorodiphenyl sulfone-0.005, NaCl-0.005% by weight. The sample with lesser contents of impurities and hydroxyphenyl OH-groups may be regarded as approximately "ideal" PSF [10–12].

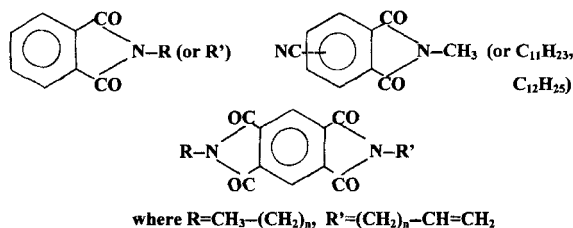
The similar approach to the problem of "impurities–thermal stability" relationship was used for PAI for which we first determined with the high temperature gel chromatography their MWD moments. Critical for PAI quality is the Fe content does not exceed 0.005% by weight. For good thermal stability PAI polydispersity must not exceed 3.0 [10].

## PAI DEGRADATION AND STABILIZATION

During processing cycle at 300–350°C the weight losses of PAI are not noticeable. The degradation is followed by Yellow Index (YI) increase, gel fraction formation and increase MFI from 0.6 to 2.5 g/10 min. The unstability of PAI macromolecules in melt at  $O_2$  absence conditions becomes noticeable at 300°C through gel content increase and decrease of sol- fraction molecular weight with effective activation energy  $E_a$  of

$50 \pm 10$  kJ/mol. Thermolysis of PAI at processing temperatures is followed by evolution of  $C_1$ – $C_3$  hydrocarbons having  $E_a$  of 160–240 kJ/mol and correlates with  $E_a$  of mass losses  $-232$  kJ/mol [10–11].

The increase of temperature to  $350^\circ\text{C}$  and above leads to formation of homologous of phthalimide, nitrilephthalimide and pyromellite diimide.



The ratios of mass-spectral peaks intensities of homologues indicate that the primary scissions break in PAI methylene chains occurs along  $\alpha - C - C -$  bonds or in the middle of aliphatic chain ( $R = C_5 - C_7$ ). Methylene chains as the most thermally unstable fragments of macromolecule begin to decompose at PAI melting point. At temperature appr.  $300^\circ\text{C}$  the thermolysis rate is small: in 1 hour about 0.1% of aliphatic chains are damaged. The ratios of hydrocarbons and carbon oxides (the products of imide cycles degradation) yields indicate that even at  $350^\circ\text{C}$  the rate of heterocycle degradation is by one order of magnitude smaller than that of methylene chains. At further temperature increase ( $400 - 450^\circ\text{C}$ ) the heterocycles degradation is noted in IR-spectra where absorption bands of imide cycle carbonyls ( $1720$  and  $1780 \text{ cm}^{-1}$ ) first decrease and then disappear completely at simultaneous growth and then domination of nitrile absorption band ( $1620 \text{ cm}^{-1}$ ). The thermolysis of PAI has signs of a radical chain process: high values of activation energy and relative variety of degradation products. Calculated by means of CNDO/2 molecular orbital method molecular diagram of dimethylpyromellite diimide shows the developed conjugative system into which methyl substituents are included.

TGA data demonstrate a serious threat of oxidation when PAI is heated in air with dynamic regime which models processing steps (heating to melting). Instead of weak endothermic DTA peaks (in argon flow) which are connected with the phase transition and melting of

PAI (275–300°C), the DTA curve shows an intensive exothermic peak with maximum at 290°C which is very close to the temperature of weight losses onset during dynamic TGA. Other less intensive exothermic DTA peaks with maximum at 350°C and 450°C correspond to the deep PAI thermooxidative degradation. Dynamic heating of PAI in the air to the temperature of the first exothermic peak does not cause degradation, whereas after a short time after melting the polymer discolors, gel fraction content increases to 15% intrinsic viscosity of sol fraction decrease by 40%, MFI increase from 0.6 to 2.0 g/10 min.

The PAI melt absorbs O<sub>2</sub> with CO<sub>2</sub>, CH<sub>2</sub>O, CO and H<sub>2</sub>O evolution. Kinetics of O<sub>2</sub> absorption at 300–350°C has two stages. The initial rapid stage having a sigma type form of kinetic curve stage follows the first kinetics order. Further, there is a slow stage with the constant O<sub>2</sub> absorption rate. The first stage depending on temperature takes 2–5 hours with absorption of 8 mol O<sub>2</sub>/monomer unit; the second stage is observed during tens of hours with the additional absorption to 2 moles of O<sub>2</sub> per monomer unit. Activation energy of PAI melt state oxidation which was determined through initial rates of O<sub>2</sub> absorption is 57 kJ/mol. Activation energy of CO<sub>2</sub> and CO evolution are 135 and 163 kJ/mol, respectively. CO<sub>2</sub>, CH<sub>2</sub>O are the main gas products of PAI high temperature oxidation. For instance, their yield resulting from one hour PAI oxidation at 350°C are 0.55 and 0.53 moles/monomer unit respectively. CO and especially H<sub>2</sub>O yields are significantly smaller. Balance of oxygen consumption and evolution shows that the main part of absorbed O<sub>2</sub> is bonded by polymer into polymer products. NMR, FT-IR and mass-spectrometry data indicate that degradation leads to imide cycles and appearance of heavy products in the forms of backbone fragments when methylene chains or heterocycles decompose [11].

Oxidation of PAI in solid state the polymer thermal aging is followed by oxygen absorption and carbon oxides, water and pyromellite diimide evolutions. FT-IR data confirm the methylene group consumption and accumulation of aliphatic C=O-groups. Formal kinetics of solid state oxidation is presented as a complete oxidation of aliphatic chains into carbon oxides and formation at 200–250°C of pyromellite imide backbone fragments in form of pyromellite diimide. PAI thermal oxidative aging is followed by H<sub>2</sub>

evolution. The kinetics of  $H_2$  formation correlates with gel fraction accumulation during the PAI solid phase oxidation.

PAI thermal oxidation in melt and in solid state is inhibited by small additives such as metal and phosphorous compounds. These high temperature stabilizers sharply decrease all forms of PAI degradation:  $O_2$  absorption, gas and heavy products evolutions, gel formation *etc.*

Discussing the mechanism of PAI thermal oxidation on processing and aging, we considered the experimental data and unexpected cluster type paramagnetism of PAI and its magnetic susceptibility with the effective moment  $\mu_{ef} = 0.77 - 0.94$  M.B. We consider radical chain process of high temperature oxidation of  $O_2$  molecular complex with conjugated  $\pi$ -system of PAI macromolecules.

The optimal formulations for PAI processing and aging were established. Additives were introduced into PAI powder before extrusion and granulation. The stabilized PAI has improved processing ability (the melt viscosity is lower) which allows us to decrease the processing temperature by  $10^\circ C$  or decrease the extrusion pressure. Material tests by Gettferd rheoviscometer showed that the extrusion of stabilized PAI can be decreased by two times in comparison with a non-stabilized polymer. By examination of strands, pellets and articles the stabilized material looks more flowless and its mechanical characteristics are by 10–20% higher than those of non stabilized material. Stabilization effect is noted also at accelerated thermal aging. During 90 days of aging  $200^\circ C$  and  $250^\circ C$  the stabilized PAI keeps about 70% of the initial properties level whereas non-stabilized PAI has almost completely failed.

## DEGRADATION AND STABILIZATION OF POLYSULFONE

PSF processing causes polymer degradation. When separating from the reaction mass and after granulation PSF discolors and its  $M_z$  moment, which limits the material processing ability increases by 5000–10000. Injection molding causes additional yellowing and  $M_z$  growth. In a number of cases processing is followed by partial PSF crosslinking. These changes correlate with the decrease of such quality parameters as elongation, MFI and its stability during exposition in rheoviscometer channel. Comparison of PSF molecular mass char-

acteristics changes during processing or testing in rheoviscometer with shear forces  $(0.13 - 5.6)10^6$  dyne/cm shows that the main degradative factor during processing is thermal oxidation but not mechanical degradation [13–19].

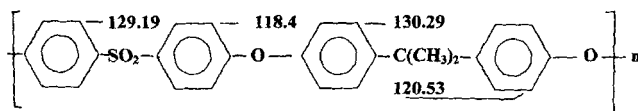
Weight losses during dynamic heating of PSF in  $O_2$  absence and presence are characterized by rate constants of  $2.4 \cdot 10^{13} \exp(-190/RT)$  and  $4.3 \cdot 10^7 \exp(-92/RT) \text{ min}^{-1}$ , respectively, *i.e.*, in  $O_2$ -presence PSF degradation is sharply increased. PSF heating at  $300-350^\circ\text{C}$  is followed by  $O_2$  absorbtion and  $CO_2$ ,  $H_2O$  and  $CH_2O$  evolution. PSF high temperature oxidation is characterized by two-stage kinetics with the first stage lasting 2–4 hours and then the slow stage with the constant rate  $O_2$  consumption followed to 10 hours of total  $O_2$  absorbtion from the start of oxidation (depending on temperature) of 1–2 mol/monomer unit with effective activation energies 72 and 11 kJ/mol for the first and second stage respectively.

At PSF thermal oxidation at  $300-350^\circ\text{C}$  for 1.5–3.0 hours lead to gel formation. But from the very beginning of process the PSF molecular weight increases. The MWD curve and all its moments ( $M_n$ ,  $M_z$ ,  $M_w$ ) shift to higher values. These changes are realized by branching of PSF macromolecules. A new mode of gel chromatography combining viscometry and on line refractometry detection gives information which treatment by Zimme-Stockmayer theory with computer solution of the inverse problem allows us to evaluate the polymer branching. Initially linear PSF macromolecules are branched as result of thermal oxidation. Branching frequency  $\lambda$  grows together with exposure, reaching value of 0.25–0.36 per monomer unit near the gel point. The number of side branches per the macromolecule follows the exponential function of its molecular weight so that from MWD moments  $M_z$  is the most sensitive to high temperature oxidation. PSF exposure in the melt state in  $O_2$  absence results in weak decrease molecular weight and very weak growth of branching number. For instance, the gel point in  $O_2$  absence at  $320^\circ\text{C}$  is not detected within 10 hours. The resulting branching in this case is characterized by  $\lambda = 0.0055$ , whereas the similar experiment in  $O_2$  presence (air) already in 10 min gave  $\lambda = 0.008 - 0.015$ . The effect of shear forces on PSF branching during thermal oxidation conditions is relatively weak. For instance increasing of loads at test in rheoviscometer by 10 times increases  $\lambda$  only by 20%.

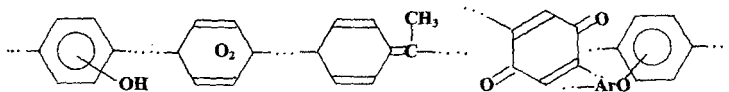


In oxidized PSF  $^{13}\text{C}$  NMR spectra we observed new signals of substituted and unsubstituted aromatic C atoms with chemical shifts in the intervals of 140–150 and 110–120 ppm. IR data also confirm new substitutions in aromatic nuclei and consumption of the main paraphenylene structure in the melt state oxidized PSF. The appearance of new substituted aromatic C atoms was connected with branching of macromolecules at high temperature PSF oxidation, *i.e.*, these atoms become presumably points of backbone branching in reactions of phenyl and phenoxy macroradicals. This model has allowed us to introduce conception of polar effects on homolytical reactions, which is known in kinetics of radical polymerization, and homolytical arylation into the discussion of PSF degradation.

The combination of heterogroups of various electrical negativity; In PSF backbone strong electron accepting sulfonyl (Hammett constant  $\sigma_n = +0.72$ ), electron donating ether ( $\sigma_n = -0.32$ ) groups, and weak electron-donating isopropylidene groups ( $\sigma_n = -0.197$ ) affects the electron density on aromatic C atoms which is reflected in values of chemical shifts of  $^{13}\text{C}$  NMR-spectra for aromatic and aliphatic moieties of PSF macromolecule:



Similarity of kinetics of PSF and completely aromatic polyether-sulfone high temperature oxidation indicates the participation of the backbone aromatic nuclei in the process. As a result of high temperature oxidation the linear PSF macromolecule is converted into branched or crosslinked structures partially losing the initial structure with development of new elements of conjugation blocks which lead to PSF discoloration:



For analysis of degradation mechanism the information about the affect of additives on the process is very useful. High temperature

oxidation of PSF is inhibited by small additives which in concentrations of 1–5 mmoles/kg decrease by 1.5–2.0 times the rate of O<sub>2</sub> absorption, and volatile products evolution, while suppressing discoloration and branching.

High temperature stabilization of PSF with additives has the characteristics of radical chain inhibition: small effective concentrations, dependence on O<sub>2</sub> pressure, inhibition of homolytical process of macromolecules branching. Additives decrease the initiation effect of some impurities, for example dimethylsulfoxide (DMS) on PSF thermal oxidation. Mass spectral and GLC-analysis show the radical character of DMS pyrolysis.

By analogy with photooxidation of aromatic and heterocyclic compounds thermal oxidation of completely aromatic polyheteroarylenes we proposed as a model of initiation a direct O<sub>2</sub> addition to aromatic nuclei with formulation of peroxides or peroxyradicals.

This model can explain the known high oxidation stability of aromatic polymers with SO<sub>2</sub> linkage where powerful electron acceptor sulfonyl groups prevent formation of molecular complex with O<sub>2</sub>.

PSF thermal aging at 150–180°C is followed by O<sub>2</sub> absorption, CO<sub>2</sub> and H<sub>2</sub>O evolution, accumulation of aliphatic C=O groups in oxidized polymer, discoloration, little decrease of molecular weight and practical absence of macromolecules branching and hydroperoxides formation. Almost linear character of kinetics curve with the constant rates O<sub>2</sub> absorption (observation during 400 days) correlates with the course of mechanical properties changes. The data of X-ray and electron microscopy indicate disorder of solid PSF morphology in the beginning of thermal treatment: the globular formations with dense domains packing of about 1000Å sizes is changed into a sponge type loose packing. The further aging is connected with solid-phase PSF oxidation which takes place on side methyl groups of isopropylidene moieties. Addition of thermostabilizers inhibits PSF low-temperature oxidation with decreased rates of O<sub>2</sub> absorption, evolution of volatile products and discoloration. The additive effectiveness should be attributed to radical inhibition.

Testing of stabilizers was carried out with experimental batches PSF. The screening was accomplished by examining the processability with and without additives and determination of volatility at vacuum-extrusion. The analysis of more than 50 batches showed the

TABLE I Quality of PSF experimental batch

<i>Sample</i>	<i>MFI at 300°-g/10 min</i>	<i>MFI<sub>10 min</sub>/MFI<sub>20 min</sub> at 320°</i>	<i>Elongation, %</i>	<i>Tensile Strength, Mpa</i>	<i>Heat deflection temperature</i>	<i>Translucence, %</i>
Control	2.6	0.86	45.0	68.0	175°	50.2
Stabilized	2.9	0.96	64.0	75.0	184°	68.5

effectiveness of thermostabilizers use, as shown in Table below where the batch was divided into two parts: control and stabilized).

The comparison of PSF aging kinetics during one year has showed a two times slower drop of stabilized batches strength in comparison with non-stabilized ones.

The PAI and PSF degradation in the melt at processing temperatures is caused by autooxidation which is responsible for loss of material performance. Although in vacuum extrusion and injection molding the direct contact of polymers with atmosphere is absent, the high processing temperatures stimulate oxidation even at rather insignificant O<sub>2</sub> content (30–70 torr). Formally, PAI and PSF are related to different chemical polymer classes, these two polymers but essentially are have a similar structure: aromatic polymers with strong electron accept or sulfonyl and imide groups which activate the neighbour structures. At low operating temperatures, the oxidation of PAI and PSF affects aliphatic and aromatic moieties. The signs of aromatic fragments oxidation of PAI and PSF structure and likely of some other high temperature thermoplastics (polyethersulfone, polyetherimide, polyetheretherketone) are branching and chain cross-linking. Strong electron acceptor sulfonyl and imide groups participate also in conjugation which stabilizes the macroradicals. It is likely that resins with only electron donor heterogroups are unstable. PAI and PSF thermal stability at processing increases with additives. An important function of additives is deactivation of impurities such as iron compounds. The more polymer is contaminated, the more thermal stabilization is necessary.

The analysis of PAI and PSF degradation and stabilization has allowed us to develop an approach to solve similar problems of other resins with high heat deflection temperatures such as polyethersulfone, polysulfones, polyamidoimides and polyetherketones.

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