A PRELIMINARY STRUCTURE-FLAMMABILITY STUDY OF SOME POLYMERS

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Introduction

Flame retardants are added to plastic materials to inhibit or suppress the combustion process and to improve the ignition or burning performance. One of the most well known parameter of polymer flammability is the limiting oxygen index (LOI). It expresses the minimum percentage of oxygen required to sustain ignition and combustion. Flammability of commercial polymers became important in the last decades [1].

Aromatic polyesters have been found in the last years to be technically interesting as engineering plastics, especially the phosphoric polyesters (polyphosphonates and polyphosphates) because of their excellent mechanical, electrical and flame resistance properties and also because of their analogy with the nucleic acids [2, 3].

The phosphorous, halogen and nitrogen-containing polymers are the most widely used as commercial fire-retardant polymers [3].

The importance of structure of polymers deciding the flammability has been recognized in the literature. Knowledge in structure-flammability relationships is useful for developing the mechanism of flame retardancy and predicting the flammability of polymers. This paper presents a structure-property study for a series of polyphosphonates, modeled by their monomers.

In this paper two types of data mining approaches, MLR and ANN methods, were applied to model polymer flammability and results were compared.

Methods

A series of 14 polyphosphonates of various types was considered, having the limiting oxygen index (LOI) as dependent variable.

The studied polyphosphonates modelled by their monomer in a first approximation. The monomer molecular structures were built by the ChemOffice package [ChemBio3D Ultra 11.0, CambridgeSoft.Com, Cambridge, MA, U.S.A.] and energetically optimized by molecular mechanics calculations (MMFF94s force field) using the OMEGA software (OMEGA (version 2.3.2), OpenEye Science Software, 3600 Cerrillos Road, Suite 1107, Santa Fe, USA, 2008). Several 0D, 1D, 2D and 3D descriptors were calculated from the minimum energy conformations by the various programs [InstantJChem 5.9.2, Chemaxon Ltd., Budapest Hungary and Dragon Professional 5.5/2007, Talete S.R.L., Milano, Italy].

Multiple linear regression (MLR) calculations were performed by STATISTICA 7.1 [STATISTICA 7.1, Tulsa, StatSoft Inc, OK, USA] and MobyDigs [R. Todeschini, D.Ballabio, V.Consonni, A.Mauri and M.Pavan (2004) MOBYDIGS – Version 1 – Copyright (c) 2004 by TALETE srl, Milano, Italy] software.

The artificial neural networks (ANNs) calculations were carried out by using our inhouse program. The three-layer ANNs with the back-propagation errors were employed [J. Zupan, J. Gasteiger (1999) Neural Networks for Chemistry and Drug Design, 2nd Edition, Wiley-VCH, Weinheim]. The most commonly used log sigmoid function and the delta rule for the error correction formula were used in the networks.

Results and Discussion

Two types of chiral structures were found by conformational analysis for each compound and conformers of minimum energy were further used. Structural parameters were derived by InstantJChem and Dragon programs from the structures of minimum energy thus obtained. MLR calculations were performed for each type of isomer. Variable selection was carried out by the genetic algorithm, using the leave-one-out fit criterion as constrained function to be optimized. Following satisfactory MLR models was obtained for R isomer:

ID	Models	r^2	q^2	q^2_{boot}	$a(r^2)$	$a(q^2)$	r^2_{adj}	AIC	Kx	Kxy	SDEP	SDEC	F	s
MLR1R	Maximal Projection Area, ISH	0.883	0.825	0.802	0.364	-0.019	0.862	15.764	40.93	47.65	3.462	2.831	41.52	3.194
MLR 2R	Average Polarizability, ISH	0.848	0.765	0.751	0.249	-0.293	0.820	20.547	25.75	46.53	4.013	3.232	30.57	3.646
MLR 3R	Van der Waals Surface Area ISH	0.819	0.716	0.687	0.446	0.091	0.786	24.352	42.17	46.29	4.41	3.519	24.94	3.97
MLR 4R	ASA Hydrophobic, ISH	0.819	0.711	0.703	0.338	0.037	0.786	24.369	36.37	46.12	4.449	3.52	24.92	3.971
MLR 5R	ASA, ISH	0.811	0.712	0.690	0.245	-0.197	0.776	25.492	32.38	45.81	4.445	3.6	23.58	4.061
MLR 6R	Refractivity, ISH	0.855	0.782	0.721	0.300	-0.218	0.828	19.59	29.21	46.78	4.037	3.156	32.34	3.56
MLR 7R	Minimal Projection Radius, Mor02m	0.802	0.722	0.716	0.255	-0.194	0.767	26.623	27.02	45.6	4.366	3.679	22.34	4.151
MLR 8R	Average Polarizability, Mor03u	0.846	0.762	0.723	0.381	-0.012	0.818	20.785	47.08	47.18	4.04	3.251	30.16	3.667
MLR 9R	logP, ISH	0.887	0.830	0.822	0.166	-0.444	0.866	15.281	18.81	47.35	3.417	2.787	43.01	3.144
ANN9R	ANN	0.870												

* r^2 – Correlation coefficient, q^2 – leave-one-out crossvalidation param eter, q^2_{boot} – bootstrapping parameter, $a(r^2)$ and $a(q^2)$ – Y-scrambling variables, r^2_{adj} – adjusted r^2, SDEP – standard deviation error in prediction, SDEC – standard deviation error in calculation, F – Fischer test, s – standard error of estimate, AIC – Akaike Information Criterion, the multivariate K correlation indices (Kx – the multivariate correlation index of the matrix of X descriptors and Kxy – the multivariate correlation index of the matrix of X descriptors and Y response variable), FIT – the Kubinyi fitness function,

and for S isomer:

ID	Models	r^2	q^2	q^2_{boot}	$a(r^2)$	$a(q^2)$	r^2_{adj}	AIC	Kx	Kxy	SDEP	SDEC	F	s
MLR1S	Average Polarizability, ISH	0.778	0.648	0.579	0.113	-0.460	0.737	29.973	7.71	44.26	4.909	3.904	19.23	4.404
MLR2S	Minimal Projection Radius, GATS1m	0.678	0.510	0.463	0.104	-0.567	0.620	43.354	3.11	42.49	5.792	4.695	11.6	5.296
MLR3S	Minimal Projection Radius, Mor02m	0.841	0.790	0.777	0.249	-0.200	0.812	21.499	27.71	46.5	3.793	3.306	28.98	3.73
ANN3S	ANN	0.82												

* r^2 – Correlation coefficient, q^2 – leave-one-out crossvalidation param eter, q^2_{boot} – bootstrapping parameter, $a(r^2)$ and $a(q^2)$ – Y-scrambling variables, r^2_{adj} – adjusted r^2, SDEP – standard deviation error in prediction, SDEC – standard deviation error in calculation, F – Fischer test, s – standard error of estimate, AIC – Akaike Information Criterion, the multivariate K correlation indices (Kx – the multivariate correlation index of the matrix of X descriptors and Kxy – the multivariate correlation index of the matrix of X descriptors and Y response variable), FIT – the Kubinyi fitness function.

Best MLR model for R isomer was MLR9R and for S isomer: MLR3S. Better fitting results were noticed in case of R isomers models. GETAWAY (Geometry, Topology, and Atom-Weights AssemblY) descriptors encode both geometrical information given by the Molecular Influence Matrix (which in turn takes into account the relative position of atoms in a molecular structure optimized in some way) and the topological information given by the molecular graph, weighted by chemical information encoded in selected atomic weights.

The best set of molecular descriptors included in the above MLR model was used to develop nonlinear models by ANNs. ANNs gave worse results in comparison to the MLR model, indicating a preferred linear fitting. The obtained "tentative" models allow a rough estimation and important factors that influence the polymer flammability.

Conclusion

QSPR models were developed for 14 polyphosphonates by MLR and ANN. Increased hydrophobicity of the polymers favour higher flammability. Geometry of R isomer influences the flammability too.

References

[1]. Liaw D., and Wang D.-W., Reactive & Functional Polymers, 30, 1996, 309-315.

[2]. Sandler, S. R. and Karo, W. *Polymer Synthesis*, Vol. 1, Academic press, New York, 1974

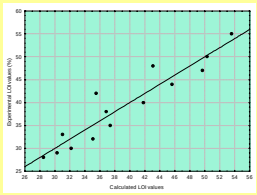
[3]. Iliescu, S., Ilia, G., Dehelean, G., Popa, A. and Macarie, L. *Polimeri organici cu fosfor*, Ed. Omega, Bucureşti, 1999

[3]. Annakutty K. S., and Kishore K., Polymer 29, 1988, 756-761

Table 1. Calculated criteria for model predictivity of the MLR and ANN models

Model	RMSE	RMSEP	RMSENorm	RMSEPNorm	RMSECoef	RMSEPCoef	RSE	MAE	RSEP	MAEP
MLR1R	2.83	3.46	0.10	0.13	0.07	0.09	7.04	42.48	8.60	47.28
MLR 2R	3.23	4.01	0.12	0.15	0.08	0.10	8.04	43.99	9.97	49.57
MLR 3R	3.52	4.41	0.13	0.15	0.09	0.10	8.75	46.62	10.97	52.68
MLR 4R	3.52	4.45	0.13	0.16	0.09	0.11	8.75	47.20	11.06	36.44
MLR 5R	3.60	4.44	0.13	0.16	0.09	0.11	8.95	47.14	11.05	52.96
MLR 6R	3.16	4.04	0.12	0.15	0.08	0.10	7.85	43.28	10.04	49.31
MLR 7R	3.68	4.37	0.14	0.16	0.09	0.11	9.15	46.12	10.85	51.43
MLR 8R	3.25	4.04	0.12	0.15	0.08	0.10	8.08	45.31	10.04	51.03
MLR 9R	2.79	3.42	0.10	0.13	0.07	0.09	6.93	40.30	8.50	45.29
ANN9R	2.94	3.64	0.11	0.13	0.07	0.10	7.32	41.59	9.05	46.07
MLR1S	3.90	4.91	0.14	0.18	0.10	0.12	9.71	47.42	12.20	53.61
MLR2S	4.70	5.79	0.17	0.21	0.12	0.15	11.67	53.61	14.40	60.49
MLR3S	3.31	3.79	0.12	0.14	0.08	0.10	8.22	41.75	9.43	45.42
ANN3S	3.51	4.53	0.13	0.17	0.09	0.12	8.72	45.79	11.27	52.39

* RMSE – root mean squared error, RMSEP – root mean squared error of prediction (from LOO cross-validation), RMSENorm – Normalized RMSE, RMSEPNorm – Normalized RMSEP, RMSECoef – coefficient of variation of the RMSE, RMSEPCoef – coefficient of variation of the RMSEP, RSE (%) – relative standard error of fitting, RSEP (%) – relative standard error of prediction, MAE (%) – mean absolute error of fitting, MAEP (%) – mean absolute error of prediction



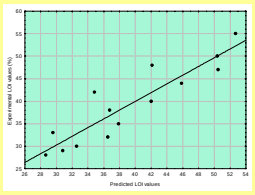
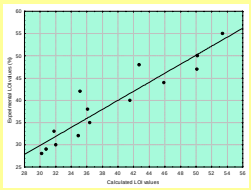


Fig. 1. Experimental versus calculated (left), respectively predicted (right) LOI values for the MLR9R model.



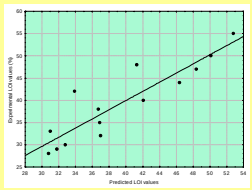


Fig. 2. Experimental versus calculated (left), respectively predicted (right) LOI values for the ANN9R model.

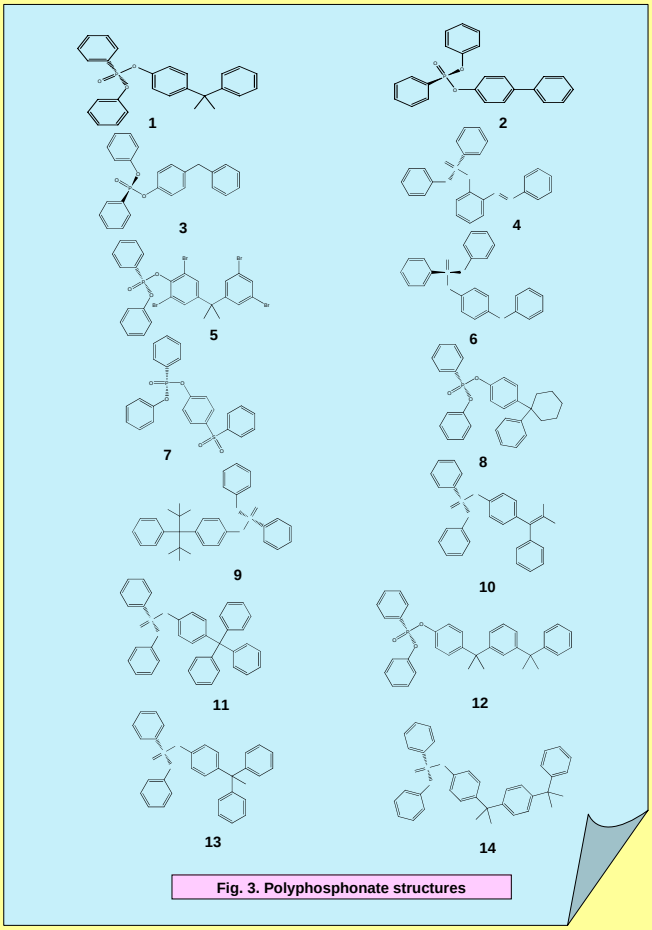


Fig. 3. Polyphosphonate structures