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Modelling relation between oxidation resistance and tribological properties of non-toxic lubricants with the use of artificial neural networks

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Abstract The lubricants based on vegetable oils, as environmental friendly, are urgently sought. However, in addition to ecological characteristics, the lubricating properties have to be met. To meet these requirements the active additives influencing the lubricating properties and oxidation resistance are used. The useful lifetime of lubricants is determined largely by their abilities to resist oxidation. The article presented the results of new, ecological lubricants development. The oxidation performances of different developed lubricants have been tested. The experimentally determined oxidation stability of the compositions based on vegetable oils are presented. Analysed oxidation onset temperature was obtained from the differential scanning calorimetry (DSC) curves, which provides the rapid prediction of the oxidative stability of lubricants. Besides the lubricating composition based on vegetable oils, the developed greases-based mineral, or synthetic oil were investigated. The properties of these greases were evaluated using the measurement of parameters describing structure (penetration) and resistance to high temperature (dropping point). The lubricating properties of both the greases and vegetable oil compositions were tested on four-ball testing machine. In the results of the modelling of the lubricating properties the neural network models for the both types of the lubricants were developed. A discussion of the research results and analysis of models validity is given below. The experimental results are compared with the calculated using the neural models. An acceptable agreement was achieved.

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Introduction

Friction and wear are among significant factors that affected energy consumption. Therefore, the development of greases enabling the minimizing of power loss is of great importance [1]. Together with equipments development, lubricants have to meet new demands, for example, the ability to serve over a wide temperature range. The lubricating greases encompass a large group of products that together with oils are an important source of the environmental pollution. This is connected with the necessity of developing new technologies for creating lubricants. Therefore it is important to develop non-toxic and biodegradable grease, which after losing its maintenance properties will not be harmful to the ecosystem and will have a high-useful standard. Therefore, this grease can be applied in food industry and in other branches of industry too. Even though the studies on greases are widely conducted the performance of biodegradable greases is not yet well. Among these studies are: the influence of the greases properties on friction process [2–4], the wear and friction response of castor oil with respect to load, additive concentration and temperature [5], the interaction between base-oil and thickener [6], the thermo rheological behaviour of the greases [7] and the oxidation stability of lubricants [8, 9].

The development of new lubricants that meets both the environmental and tribological requirements needs a long-time for experimentations. Therefore, the prediction of lubricant properties in the way of modelling and using computational models is important to accelerate the design process. Thermal analysis, as studies show [10–13], is often helpful in modelling the properties of objects and processes, especially the oxidation resistance [12, 13]. The simulation procedure to enable precise evaluation of lubricant viscosity was developed by Konno et al. [14]. The authors used computational chemistry to accelerate the design of lubricants. The neural network success application for the development of computational models in the area of friction and lubrication is substantiated in literature [15–17]. Artificial neural networks are receiving increased attention in the ecological sciences as a powerful, flexible, statistical modelling technique for uncovering patterns in data [18]. Application of the neural networks for tribological properties prediction of composites was presented in [19].

In this article, the neural network method was applied to develop of the prediction model of tribological properties based on the properties of lubricants, among them the oxidation resistance.

The development of a new generation of lubricants with the elimination or considerable reduction of toxic chemical compounds was undertaken. Achievement of this aim was possible thanks to use of the non-toxic oil bases, ecologically safe thickeners and modifiers improving useful properties. The developed non-toxic greases are characterised by a beneficial set of physical-, chemical-, and tribological-properties.

Experiment

The research conducted encompassed development of two types of lubricant. The first group included lubricants based on vegetable oils with additives that improve lubricated properties and oil resistance to oxidation. The second group encompassed the greases developed based on: mineral or synthetic oils.

The vegetable compositions that were investigated are presented in Table 1. The rapeseed oil (R) has been used as a vegetable oil base. Three different kinds of additives were used namely: oil of milk thistle endosperm (OC) was used as antioxidant, phenol antioxidant (ETH), multifunctional additive (BCH), in addition to antioxidants, the corrosion inhibitors, and anti-seizure/-wear additives EP/AW.

Formulation of grease is shown in Table 2. The grease consists of synthetic and mineral oils as a base fluid, Lithium stearate (LiST), Lithium 12-hydroxystearate (LiOHST), and silica (SiO_2) as a thickener and polymer (PTFE) additive A (A1-5%, A2-10%) Table 1.

The study included an assessment of the impact of the thermo-oxidation controlled process on changes of resistance to oxidation and the tribological parameters of the vegetable oils without and with the additives. The content

Table 1 Vegetable oil compositions

The kind of the composition	Symbol	Concentration of additive/%
Vegetable oil	R	0
Vegetable oil with BCH	R-BCH-1.5	1.5
	R-BCH-2	2
	R-BCH-2.5	2.5
	R-BCH-5	5
Vegetable oil with OC	R-OC-05	0.5
	R-OC-1	1
	R-OC-2	2
	R-OC	50
Vegetable oil with ETH	R-ETH-01	0.1
	R-ETH-0.2	0.2
	R-ETH-0.5	0.5
	R-ETH-1	1

Table 2 Composition of developed ecological greases

Developed grease	Thickener	Thickener concentration/%	Additive concentration/%
Base fluid type—mineral oil			
Grease I	Li St	12.5	–
Grease I_1	Li St	15	–
Grease I_2	Li St	20	–
Grease I_A1	Li St	12.5	A1
Grease I_A2	Li St	12.5	A2
Grease II	Li 12-OH	12.5	–
Grease II_1	Li 12-OH	15	–
Grease II_2	Li 12-OH	20	–
Grease II_A1	Li 12-OH	15	A1
Grease II_A2	Li 12-OH	15	A2
Base fluid type—synthetic oil			
Grease III	SiO2	7	–
Grease III_A1	SiO2	7	A1
Grease III_A2	SiO2	7	A2

and kind of the additives have been selected in such a manner that both properties of the dispersion phase and ecological character of the grease remained unchanged. Their proper selection must minimise the unfavourable influence of oxygen on the stability of the base oil.

Oxidation resistance was determined based on of the oxidation onset temperature (OOT). The results that obtained for samples using LABSystem SETARAM TG/DSC apparatuses provided information about the temperature at which oxidation begins while heating in the presence of oxygen (OOT).

The oxidation onset temperature is determined as the intersection point of two tangents. The effectiveness of the additives oils was investigated in DSC method conditions.

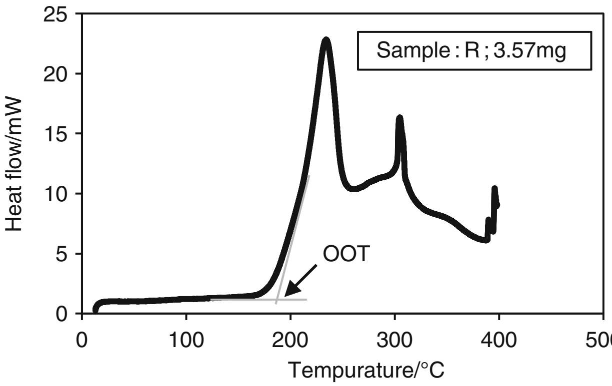

Fig. 1 Typical DSC curve showing the determination of the OOT on the example of rapeseed oil

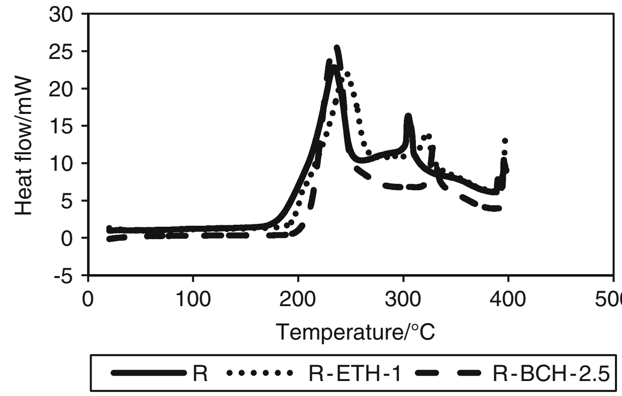

Fig. 2 DSC curves for rapeseed oil, with and without the additives

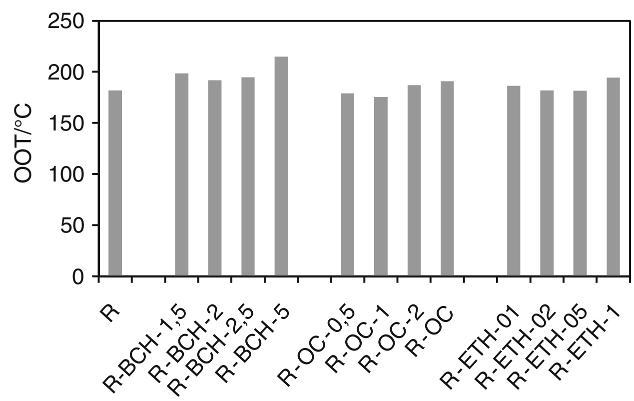

Fig. 3 Influence of the antioxidant concentration on a OOT of rapeseed oil, measured every 10 K/min

Characteristic parameters were extracted from the DSC curve and used for assessment of the oxidative resistance of the base oils and compositions. The mean of the determination of the beginning of oxidative degradation from the DSC curve is presented in Fig. 1.

The following parameters were used for DSC: sample 3.5 ± 0.3 mg, the range of the temperature 20–400 °C, the speed of warming 10 °C/min, and an atmosphere O_2.

In order to evaluate the effectiveness of used antioxidants, the lubricants of vegetable oil were oxidised in Stanhope-Seta oxidative baths under specific conditions—at 70 °C during 96 h and 15 L/h velocity air flow. The effectiveness of the inhibitors in base oil environment was rated based on the changes of the oxidative resistance and lubricating properties.

Lubricating properties of the developed base oil and greases and the effectiveness of activity as well as the influence of the modifiers on these properties were assessed using the normalised four-ball test with turns of a movable ball equal to 1,500 rpm. Based on the executed experiments the values of limiting wear load G_{oz}, were assigned. They were assessed based on the one-hour tests with the load of 392.4 N.

Assessment of physical–chemical properties of the greases was carried out based on the measurement of parameters concerning structural and colloidal durability, grease oxidation flexibility, and rheological properties. The penetration of the greases was measured according to the ASTM D 217 method. The greases were than classified into NLGI class. The dropping points of the greases were determined according to the ASTM D 566 method.

Results and discussion

Evaluation of vegetable oil compositions

In the results of conducted research of the oxidative properties of the lubricating compositions based on vegetable oil, the DSC curves were drawn, from which the OOT values were established.

The results of the DSC trials for chosen lubricated composition are shown in Fig. 2.

For all developed lubricating compositions the OOT values were established from DSC curves. The results are presented in Fig. 3.

Based on the results obtained it was found that resistance to oxidation, determined from DSC, of both ETH and BCH, oil additives is higher than that designated for vegetable oil. OC additives have an improving influence on resistance to rapeseed oil oxidation while the additives concentrations were high. Additive OC has a positive effect on the inhibition of oxidation of rapeseed oil for higher concentrations of the additive.

Effectiveness, in the oil environment, of the used inhibitors was assessed based on the change of oxidation onset temperature after thermo-oxidation conducted under controlled conditions. The additive influence was assessed after a thermo-oxidation process that lasted 96 h. The results are presented in Fig. 4.

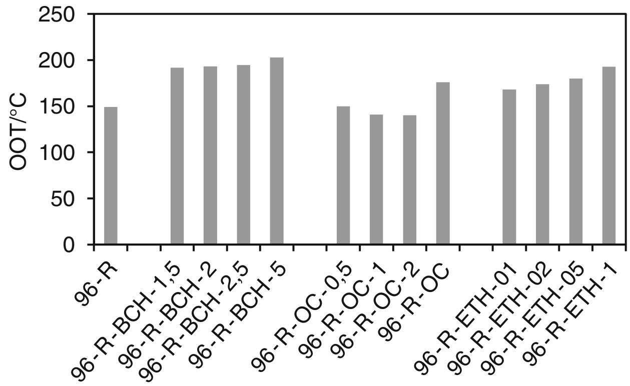

Fig. 4 The antioxidant concentration influence on an OOT of the lubricating compositions after accelerated oxidation test

Determined resistance to the oxidation of the oil compositions, that underwent a process of accelerated oxidation for 96 h under controlled conditions, confirmed the effectiveness of both additives: ETH and BCH for all concentrations tested. The oils from the endosperm milk thistle (OC) effectively prevented oxidation of the oil only if the composition contained the maximum concentrations of OC additive (96-R-OC). Therefore, these results have shown that OC preparation can be used as an element of base oil but not as an additive.

In the scope of research concerning lubricant development, the tribological tests of developed lubricants were carried out. Lubricating properties of the compositions-based vegetable oil were determined both before and after thermo-oxidation. They were assessed based on the 1-h test under a 392.4 N load (Fig. 5).

Comparisons of wear diameters indicate higher values of wear for the samples lubricated with the use of oil compositions after thermo-oxidation. This directly influenced the changes of G_{oz} a limiting wear load, which are presented in Fig. 5. In the case of rapeseed oil without additives (R), after controlled oxidation the value of G_{oz}

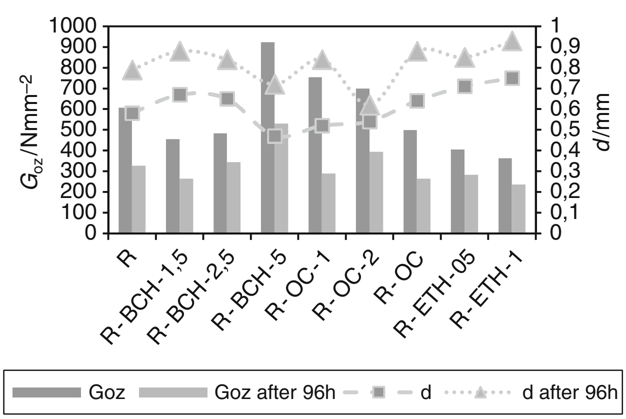

Fig. 5 Tribological characteristics of the modified rapeseed oil, before and after oxidation test namely: G_{oz} limiting wear load, and wear scar diameter of the ball—*d*

decreased about 46%. The largest drop was observed for rapeseed oil with 1% concentration of OC additive—about 60%, however, if OC concentrations were 2% the drop was 42%. Beside BCH (R-BCH-5), it was one of the smallest declines of G_{oz}, which have been noticed, for all analysed compositions. The best lubricating properties characterised the oil compositions with 5% concentration of BCH. In addition, the oxidation onset temperature for this composition was the highest.

Analysis of research results of developed lubricating compositions has shown that thermo-oxidation influenced the lubricating possibilities and there are relation between resistance to oxidation and lubricating properties.

Evaluation of greases

The ecological greases developed based on mineral or synthetic oils were tested to evaluate their properties both physical–chemical and lubricating. Physical–chemical properties were evaluated using the measurement of parameters describing structure (penetration) and resistance to high temperature (dropping point). The results of the trials are shown in Figs. 6 and 7.

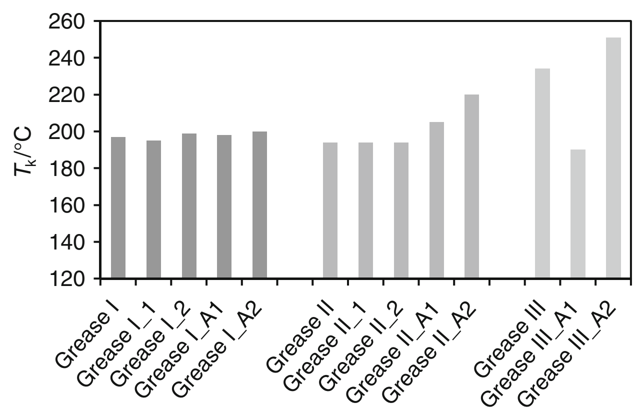

Fig. 6 Dropping point of the greases

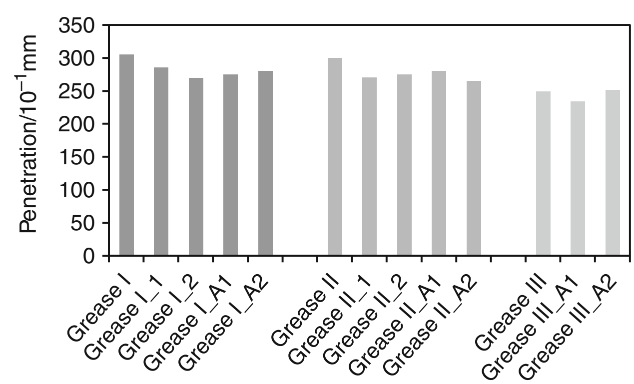

Fig. 7 Penetration of the greases

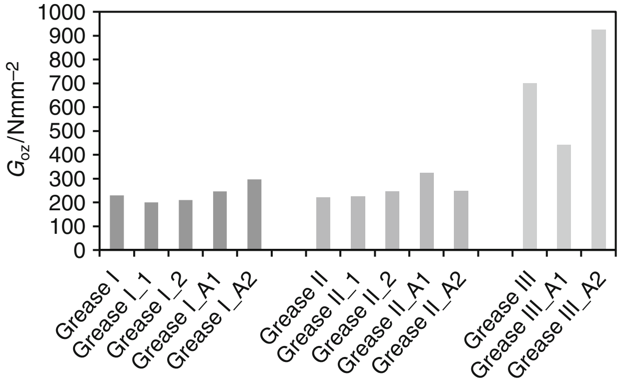

Fig. 8 Anti-wear properties of the greases, after the 1-h wear test, were executed according to the standard four-ball method

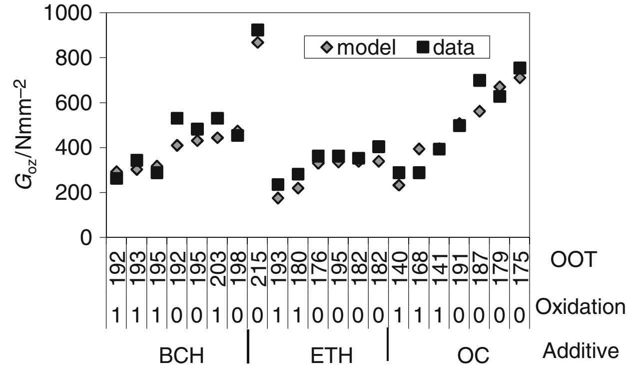

Fig. 9 Comparison of limiting wear load: data and model calculation for lubricating composition

Comparison of lubricating properties of the greases developed on the mineral or synthetic bases indicate that using synthetic oil can be created greases that are characterised by better resistance to deformation and oxidative resistance.

Significant influences on analysed properties have a type and a concentration of additives. The presented results show that for the greases stability, which was assessed-based penetration, the differences were small—the biggest one was about 10%. While the differences of the dropping point were even above 25%. The percentage of lithium thickener had virtually no influenced on the oxidative resistance, however, its increase improves the stability of grease structure. The percentage concentration of analysed additives for the lubricants based on synthetic oils significantly affected the resistance to oxidation of greases.

Lubricating properties of developed greases and effectiveness of activity as well as influence of the modifiers on these properties were assessed based on the normalised four-ball test. Based on executed experiments the value of G_{oz} limiting wear load, were assigned (Fig. 8).

Greases developed based on synthetic oil have better lubricating properties compare to greases-based mineral oils. The change in the concentrations of the thickener in mineral greases has no impact on lubricating properties. However, a polymer additive can influence the improvement or deterioration of the lubricating properties of greases as a dependence of additive concentrations.

Development of predictive models for lubricants

In the next step of the investigation, the modelling of lubricating properties based on research results was conducted. In terms of modelling, the regression models and artificial neural network were analysed. The possibility of including in the model the quality variables was one of the advantages of using neural networks. It was especially important in the case of the vegetable oil compositions that were made in two different ways and with the use of different kind of additives. The neural network models were created with the use of STATISTICA Neural Networks software.

Modelling of lubricating properties of the composition of vegetable oil

Based on the findings of investigation of the vegetable oils with additives, the possibility of predicting the lubricating characteristics as a dependence on oxidative resistance properties, which was determined from calorimetric studies, was examined.

The correlation ratio between the limiting wear load (G_{oz}) and the oxidation onset temperature (OOT) amounted to 0.37. Therefore, there were no sufficient grounds for building a linear regression model for these variables.

In the next step of research in addition to the quantitative, the qualitative variables were also included into the model. The following were taken into consideration: the limiting wear load, the way of composition performing (with or without thermo-oxidation), and the type of

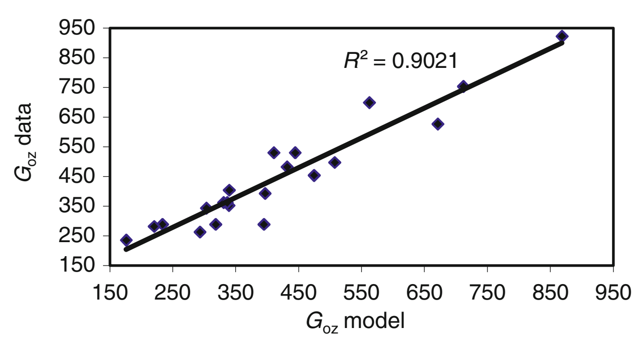

Fig. 10 Presentation of the fit of model to the measured data for lubricating composition

Table 3 Regression characteristics for MLP (5,3,1)

	Training G_{oz}	Verification G_{oz}	Test G_{oz}
Data Mean	485	376	392
Error Mean	−55	−11	36
Abs E. Mean	59	28	52
S.D. Ratio	0.22	0.38	0.35
Correlation	0.98	0.96	0.94

Data Mean average value of input value, *Error Mean* average error of input value calculation by model, *SD Ratio* ratio of the standard deviations of the error of output calculation and the standard deviation of output (it is assumed that the value of the ratio of standard deviations above 0.7 almost disqualifies utility model), *Correlation* Pearson-*R* correlation coefficient of data and model calculation

additive. In this case of modelling the artificial neural networks were applied. The modelling results are presented in Fig. 9. The points on the chart can be used in order to compare the G_{oz} data and the G_{oz} calculated by the neural network model.

Multi Layer Perceptron—MLP (5,3,1) has been used as the architecture of Artificial Neural Network. The model structure consists of: five inputs (OOT—quantitative variable, a type of additive—three-valued qualitative variable, thermo oxidation (TO)—qualitative variable), and the hidden layer with three neurons and one output (G_{oz}).

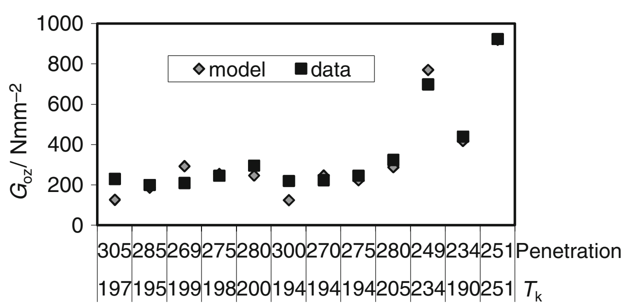

Fig. 11 The calculated by model values of Goz, against experimental data for greases

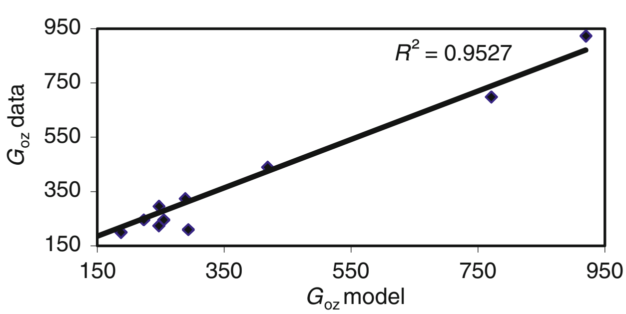

Fig. 12 Presentation of the fit of model to the measured data for greases

The developed model has a high determination coefficient—$R^2 = 0.9$. The linear regression of the data and the network calculations is presented in Fig. 10.

To check if the model has abilities to generalise, regression analyses were performed. The regression characteristics are presented in Table 3. Based on the results both vectors, the verification and the test, has been proved that model based on a neural network has abilities to generalise Table 3.

The modelling results, among them the performed sensitivity analysis of model inputs, show a significant impact on its quality in addition to the quantitative characteristics (OOT variable) the qualitative variables: the type of additive (Additive variable) and if the thermo-oxidation was used (OT variable).

Modelling of lubricating properties of the greases based on synthetic or mineral oils

Based on the research results of the developed greases, the model of wear properties of the greases were developed.

The results were analysed in order to create the computational model for tribological properties prediction (G_{oz}) based on the physical–chemical properties of lubricant (T_k—dropping point, penetration).

The coefficient of determination for model that were developed with the use of conventional approaches of multiple-regression was $R^2 = 0.66$, which means that only 66% of the diversity of outcomes is likely to be predicted by the model.

However, in the result of modelling, the artificial neural network model MLP (2,3,1) was developed, which was characterised by a good ability for outcome prediction. Coefficient of determination was above 0.96.

A comparison of the outcomes of experimental with the predicted by the model is shown in the Fig. 11.

The linear regression of data and model calculations is presented in Fig. 12.

The verification proved that the model has a good ability for prediction and generalisation. The research results showed that the predictive ability of neural network was better than conventional multiple-regression approaches.

Conclusions

The research resulted in the development of new ecological greases that are characterised by both not-toxic and good tribological properties. From an application point of view, the developed greases meets requirements for typical bearing greases use in the food industry.

Analyses have indicated that the thermo-oxidation of the lubricating compositions influenced on their lubricating possibilities and there is a relation between resistance to oxidation and lubricating properties.

The computational model of the limiting wear load prediction, based on the oxidation properties of vegetable oil compositions, was developed. The possibility of the inclusion of qualitative variables, due to the use of artificial neural networks into model allowed the development of a model with good predicting properties.

The conducted research shown that the resistance to wear depended on the physical–chemical properties of greases. Based on research results, the artificial neural model for prediction of the limiting wear load based on a dropping point and a penetration was developed.

In the case of the prediction of the wear properties of the lubricants, the research results showed that the predictive ability of neural networks were better than for the models based on conventional regression approaches.

Models based on artificial neural networks have good prediction ability, however, the interpreting the artificial neural networks is very difficult.

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References

1. Lugt MP. Review on grease lubrication in rolling bearings. Tribol Transduct. 2009;52(4):470–80.
2. Cann PM, Hurley S. Friction properties of grease in elastohydrodynamic lubrication. NLGI Spokesm. 2002;66:6–15.
3. Delgado MA, Franco JM, Kuhn E. Effect of rheological behaviour of lithium grease on the friction process. Indus Lubr Tribol. 2008;60(1):37–45.
4. Drabik J., Pawelec E. Oxidation stability and tribological properties of non-toxic grease. In: ECOTRIB'07 European conference on tribology and final conference of COST 532 action. Slovenia: Triboscience and Tribotechnology; 2007. p. 435–442.
5. Ossia CV, Han HG, Kong H. Response surface methodology for eicosanoic acid triboproperties in castor oil. Tribol Int. 2009; 42:50–8.
6. Causseau T, Graca B, Campos A, Seabra J. Friction torque in grease lubricated thrust ball bearings. Tribol Int. 2011;44:523–31.
7. Delgado MA, Valencia C, Sa′nchez MC, Franco JM, Gallegos C. Thermorheological behaviour of a lithium lubricating grease. Tribol Lett. 2006;23:47–54.
8. Bystrzejewski M, Huczko A, Lange H, Drabik J, Pawelec E. Influence of C60 and fullerene soots on the oxidation resistance of vegetable oils. Fullerenes Nanotubes Carbon Nanostructures. 2007;15:427–38.
9. Keating MY, Howell JL. Decomposition of perfluoropolyether lubricants. A study using TGG–MS in the presence of alumina powder. J Therm Anal Calorim. 2011;106:213–20.
10. Ungureşan M-L, Màicàneanu A, Dulf F-V, Dulf E-H, Gligor DM. Application of linear regression analysis for iron and copper removal process using natural zeolites. J Therm Anal Calorim. 2010;99:211–28.
11. Briere L-AK, Brandt J-M, John B, Medley JB. Measurement of protein denaturation in human synovial fluid and its analogs using differential scanning calorimetry. J Therm Anal Calorim. 2010; 102:99–106.
12. Badenhorst H, Brian RandB, Focke WW. Modelling of natural graphite oxidation using thermal analysis techniques. J Therm Anal Calorim. 2010;102:99–106.
13. Chaliampalias D, Vourlias G, Pavlidou E, Chrissafis K. Examination of the oxidation resistance of Cr–Mo–V tool steel by thermal analysis. J Therm Anal Calorim. http://www.springerlink.com/content/qx2066371j06k1u0/fulltext.pdf. Accessed 27 Nov 2011.
14. Konno K, Kamei D, Yokosuka T, Takami S, Kubo M, Miyamoto A. The development of computational chemistry approach to predict the viscosity of lubricants. Tribol Int. 2003;36:455–8.
15. Sinha AN, Mukherjee PS, De A. Assessment of useful life of lubricants using artificial neural network. Ind Lubric Tribol. 2000;52:105–9.
16. Trzos M. Neural models for prediction of lube oils' wear resistance properties. Tribologia. 2004;196:273–84.
17. Korres DM, Anastopoulos G, Lois E, Alexandridis A, Sarimveis H, Bafas G. A neural network approach to the prediction of diesel fuel lubricity. Fuel. 2002;81:1243–50.
18. Olden JD, Jackson DA. Illuminating the ''black box'': a randomization approach for understanding variable contributions in artificial neural networks. Ecol Model. 2002;154:135–50.
19. Gyurova LA, Friedrich K. Artificial neural networks for predicting sliding friction and wear properties of polyphenylene sulfide composites. Tribol Int. 2011;44:603–9.