Paweł AKSAMIT, Dariusz ZMARZŁY, Violetta BEDNARSKA
POLITECHNIKA OPOLSKA, INSTYTUT ELEKTROENERGETYKI

Influence of nanostructure additives on dielectric properties of chosen hydrocarbons

Mgr inż. Paweł AKSAMIT

Absolwent Wydziału Elektrotechniki, Automatyki i Informatyki Politechniki Opolskiej kierunek Informatyka (2007). Obecnie jest doktorantem w Instytucie Elektroenergetyki Politechniki Opolskiej. Jego praca naukowa koncentruje się na diagnostyce olejów elektroizolacyjnych. Jest autorem i współautorem ponad 20 publikacji.

e-mail: pawelaksamit@gmail.com

Dr Violetta A. BEDNARSKA

Absolwentka Wyższej Szkoły Pedagogicznej w Opolu (1995). Tytuł doktora nauk fizycznych uzyskała w 1999 na Uniwersytecie Warszawskim. Od roku 2000 pracuje na Wydziale Elektrotechniki, Automatyki i Informatyki Politechniki Opolskiej w Instytucie Elektroenergetyki. Aktualnie bierze udział w pracach nad badaniem wpływu dodatku fullerenów do cieczy dielektrycznych na ich właściwości elektryczne.

e-mail: v.bednarska@po.opole.pl

Dr hab. inż. Dariusz ZMARZŁY

Absolwent Wydziału Elektrotechniki i Automatyki Politechniki Opolskiej (2000). Stopnie doktora nauk technicznych (2002) oraz doktora habilitowanego (2006) uzyskał na Wydziale Elektrotechniki, Automatyki i Informatyki Politechniki Opolskiej. Zajmuje się zagadnieniami dotyczącymi elektryzacji strumieniowej. Jest autorem ponad 100 publikacji. Jest stypendystą Fundacji na rzecz Nauki Polskiej (2007).

e-mail: dariusz@zmarzly.com

Abstract

The paper presents the concept of modifying dielectric properties of hydrocarbons by the addition of C_{60} buckminsterfullerene. Three liquids – toluene (C_7H_8), hexane (C_6H_{14}) and cyclohexane (C_6H_{12}) were examined. The measurements of capacity, dielectric loss tangent, resistivity and tendency to electrification were performed on pure and doped liquids. The influence of C_{60} additives on measured properties were determined.

Keywords: dielectric liquids, nonotechnology, nanoscience, nanoparticles, fullerenes.

Wpływ domieszkowania nanostrukturami na właściwości dielektryczne wybranych węglowodorów

Streszczenie

Praca przedstawia koncepcję modyfikacji elektrycznych właściwości węglowodorów poprzez domieszkowanie fullerenem C_{60}. Przebadano trzy ciecze (toluen, heksan oraz cykloheksan) pod kątem podstawowych własności dielektrycznych oraz tendencji do elektryzacji. Określony został wpływ domieszkowania fullerenem C_{60} na przebadane własności.

Słowa kluczowe: Ciecze dielektryczne, nanotechnologia, nanonauka, nanostruktury, fullereny.

1. Introduction

Hydrocarbons are organic compounds consisting only of hydrogen and carbon. Their general molecular formula is C_xH_x. As they are main compounds of crude oil they are widely used not only in the industry but also in everyday life.

Some hydrocarbons and hydrocarbon mixtures are used in electrical applications as dielectric liquids. A widely used transformer oil is a refined by-product in the distillation of petroleum. It is composed of many types of hydrocarbons – mainly alkanes and cyclic parafines but also significant amount of aromatic hydrocarbons [1]. Due to the wide usage of hydrocarbons as dielectric liquids, their electrical properties are of a very important matter.

The research presented in this paper, shows that it is possible to significantly improve some crucial dielectric characteristics of hydrocarbon dielectric liquids by the addition of C_{60} fullerene.

2. Nanostructures and fullerenes

Nanostructures are structures which size in at least one dimension is less than 100nm. The nanosize is not the only criteria though, as great majority of common particles would easily meet it. Nanostructures are also characterized by properties that differs significantly from the analogous structures known from the macro world.

Definitely the biggest breakthrough in the field of nanotechnology and nanoscience was the discovery of fullerenes. They were discovered by Robert Curl, Richard Smalley and Harold Kroto in 1985. For this discovery the scientists got the Nobel Prize in Chemistry in 1996 [2, 3, 4].

Fullerenes are aromatic compounds of carbon. The most common and the most stable fullerene structure is C_{60} called also a buckminsterfullerene. It consists of 60 atoms of carbon connected by 90 covalent bonds. The shape of the C_{60} fullerene is often compared to football ball because of the 20 hexagons and 12 pentagons that builds the closed sphere of fullerene (fig. 1) [5].

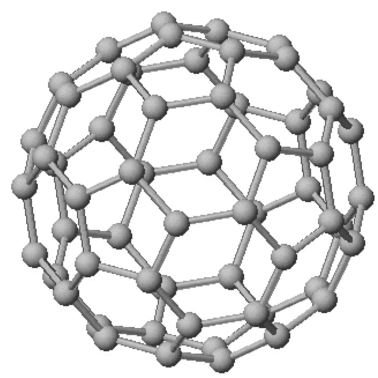

Fig. 1. Fullerene C_{60} shape visualization; nodes represents the carbon atoms, edges are the covalent bonds (source: images.google.com)
Rys. 1. Wizualizacja kształtu fullerenu C_{60}; węzły reprezentują atomy węgla, krawędzie odpowiadają wiązaniom kowalencyjnym (źródło: images.google.com)

Since their discovery fullerenes have been widely researched for their physical and chemical properties.

The shape of the C_{60} fullerene was explained by the Euler's theorem. It comes from this theorem that C_{60} is the smallest possible cluster of carbon, that can form a closed structure. This is also the reason why C_{60} is the smallest stable fullerene [6].

Some of physical properties of C_{60} fullerene presented in table 1 [7, 8].

Tab. 1. Physical properties of C_{60} fullerene [7, 8]
Tab. 1. Fizyczne własności fullerenu C_{60} [7, 8]

Mass density	1,72 g/cm^3
Molecular density	1,44 x 10^{21}/cm^3
Outer diameter	1 nm
Bulk modulus	14 x 10^9 Pa
Debye temperature	185 K
Thermal conductivity (300K)	0,4W/mK
Boiling point	Sublimes at 800K
Static dielectric constant	4,0 – 4,5
Resistivity	1014 Ωm

In C_{60} fullerene each atom of carbon is bonded with 3 other atoms by sp^2 hybridised covalent bonds. C_{60} is electronegative and due to pure electron delocalization it is not a superaromatic compound [9]. Electronegativity and a lack of 12 π-electrons needed for closed shell configuration are the reasons for a C_{60} tendency to acquire foreign electrons [10]. Various researches shown the π-acceptor properties of C_{60} fullerene [10, 11]. Other suggests the ability of C_{60} to act as an universal acceptor of electronically excited states energy [12].

Apart from the pure fullerenes characterized shortly above, two other classes of fullerenes are distinguished. Fullerenes with other compounds bonded to the outside of the fullerene cage are called exohedral. On the other side, the spherical shape of fullerene gives the possibility to trap other molecules inside the cage. Such structures are called endohedral fullerenes. One of the most significant applications of endohedral fullerenes is probably the superconductivity of fullerenes which was achieved at the relatively high temperature of 117 K using $C_{60}/CHBr_3$ molecule [13].

3. Fullerene-doped dielectrics

Although the subject of using pure fullerenes for synthesis of ultra thin dielectric films is well known and researched [14, 15, 16, 17], one could hardly find any researches analyzing the influence of fullerenes on dielectrics. One of those few works are Subocz's researches on the influence of C_{60} and C_{70} fullerenes additives on the dielectric properties of polyimide films [18]. The subject of dielectric liquids nano-modifications is even less researched.

The clue matter in doping liquids with fullerenes is the solubility. As researches show, there is not any single physicochemical characteristics that could easily determine the solubility of fullerenes in organic liquids [19, 20]. It is proven, that the solubility of C_{60} fullerene increases with increasing solvent polarizability and decreases with increasing solvent polarity and cohesive energy density [19]. Table 2 presents the solubility of C_{60} in several common organic solvents [21].

It is important to mention that the solubilities determined by different researchers and published in different sources might differ a lot [22]. The reason might be the difference in purity of C_{60} or a solvent. However, the data from table should be treated only as a rough guide.

The research presented in this paper consisted of determining the influence of C_{60} additives on several electrical properties of three groups of common hydrocarbons being the components of mineral transformer oil – alkanes, cycloalkanes and aromatic hydrocarbons. Hydrocarbons examined were respectively hexane (C_6H_{14}), cyclohexane (C_6H_{12}) and toluene (C_7H_8). Their 3D structural models are presented in figure 2.

Tab. 2. Solubility of C_{60} fullerene in common solvents [19]
Tab. 2. Rozpuszczalność fullerenu C_{60} w typowych rozpuszczalnikach [19]

1-chloronaphthalene	51 mg/ml
1-methylnaphthalene	33 mg/ml
Chlorobenzene	27 mg/ml
1,2-dichlorobenzene	8,5 mg/ml
carbon disulfide	7,9 mg/ml
Toluene	2,8 mg/ml
Benzene	2,8 mg/ml
carbon tetrachloride	0,32 mg/ml
n-hexane	0,043 mg/ml
Cyclohexane	0,036 mg/ml
Ethanol	0,001 mg/ml
Methanol	0 mg/ml

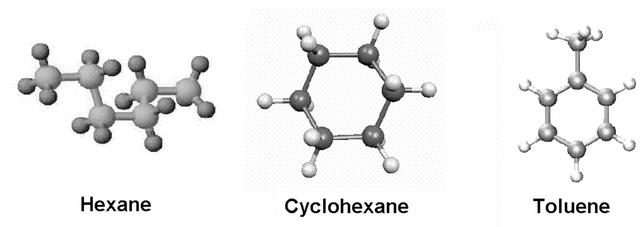

Fig. 2. 3D structural models of examined hydrocarbons
Rys. 2. Trójwymiarowe modele strukturalne badanych węglowodorów

4. Measurement setup

All electrical properties except tendency to electrification were measured using three-electrode liquid measurement cell with nominal capacity of 150pF. Capacity and dielectric loss tangent were measured using integrated, automatic RLC measurement bridge ECL-3131D and sine wave generator. For resistivity measurements specialized MR0-4c meter was used.

Tendency to electrification was measured using rotating electrometer constructed by D. Zmarzły in Faculty of Electrical Engineering, Automatic Control and Computer Science of Opole University of Technology where authors of this paper work. The simplified schematic of this setup is presented in figure 3.

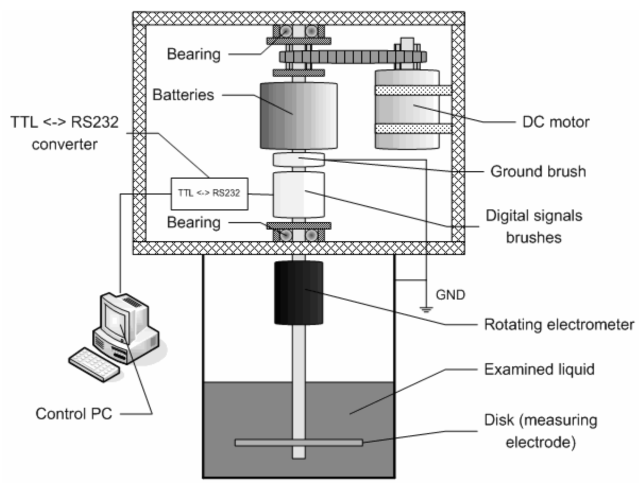

Fig. 3. Setup for tendency to electrification measurements
Rys. 3. Układ do pomiaru tendencji do elektryzacji

The setup consists of disc rotating in the examined liquid, connected electrically by axle with hot electrode of electrometer.

The electrometer is attached to the axle and rotates together with disc during measurements. The main part of electrometer is the supersensitive current/voltage converter, connected to A/D converter and microcontroller communicating with a PC that controls the whole measurement process. Electrometer and connected electronics is powered from batteries that also rotates together with the disc. Electrical signals are transferred to the steady part of the setup through electrical brushes. Some of the signals transfers the digital measurement data. Two parallel brushes consist on the reliable connection of the electrometer ground with the liquid tank and the chassis of the entire device.

5. Results

The results of dielectric loss tangent measurements are shown on figures 4 to 6.

For n-hexane the dependency between the C_{60} amount and the dielectric loss tangent is complex and depends much on the frequency. There is although the easily identifiable tendency to increase of dielectric losses for higher concentrations of fullerenes. For the lowest concentration examined (0,5mg/100ml) dielectric losses remain roughly the same increasing slightly for low frequencies and decreasing for high frequency ranges.

Most interesting results were observed for cyclohexane and toluene. For cyclohexane the dielectric loss factor was reduced about 100 times with a C_{60} concentration of 1mg/100ml and bigger in the whole frequency range. For toluene reduction of dielectric loss tangent of 10 times was achieved.

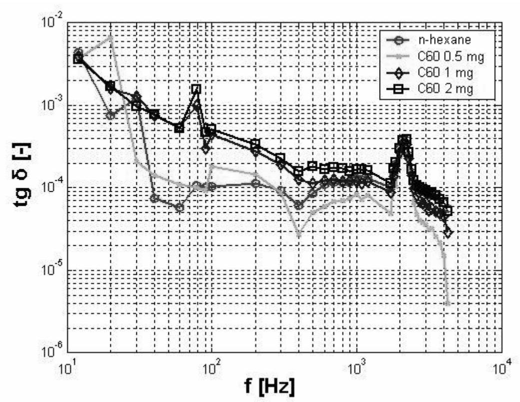

Fig. 4. Dielectric loss tangent of pure and C_{60}-doped n-hexane as a function of frequency; liquid sample capacity – 100ml

Rys. 4. Tangens kąta stratności czystego i domieszkowanego C_{60} n-heksanu w funkcji częstotliwości; objętość próbki – 100ml

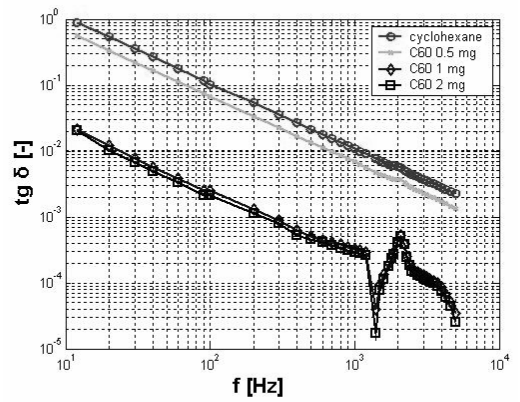

Fig. 5. Dielectric loss tangent of pure and C_{60}-doped cyclohexane as a function of frequency; liquid sample capacity – 100ml

Rys. 5. Tangens kąta stratności czystego i domieszkowanego C_{60} cykloheksanu w funkcji częstotliwości; objętość próbki – 100ml

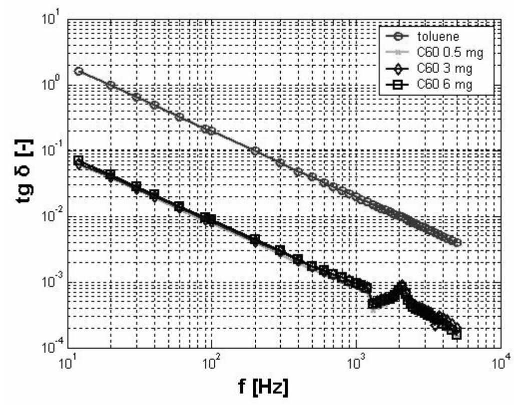

Fig. 6. Dielectric loss tangent of pure and C_{60}-doped toluene as a function of frequency; liquid sample capacity – 100ml

Rys. 6. Tangens kąta stratności czystego i domieszkowanego C_{60} toluenu w funkcji częstotliwości; objętość próbki – 100ml

On all plots, specific extremes appear at the frequency above 1kHz. As they appear and look the same on all measurements, they are most probably connected with some resonant behavior of measurement setup. The reason why they are not visible on curves for pure cyclohexane and toluene is the low relative value of this artifact to the values measured.

For place saving, the figures for capacity and resistivity measures are not presented. Is is enough to say, that the differences observed for all liquids, though repeatable, were negligible. For both capacity and resistivity the differences were at the range of hundredth parts of percent.

Streaming electrification measurements were done only for toluene. The reason why toluene was chosen, not other or all liquids, is that pure toluene has much higher tendency to electrification than other examined liquids. Additionally it is much better fullerene solvent than cyclohexane and n-hexane as shown in table 2.

The measurements were done for the maximal achievable concentration of C_{60} in toluene. The C_{60} was added to the liquid as long as the saturation was observed, that means there was visible that further amounts of C_{60} added to the liquid do not dissolves. Two runs were done for both pure and doped toluene to check the repeatability of the measurement. The results are presented in figure 7.

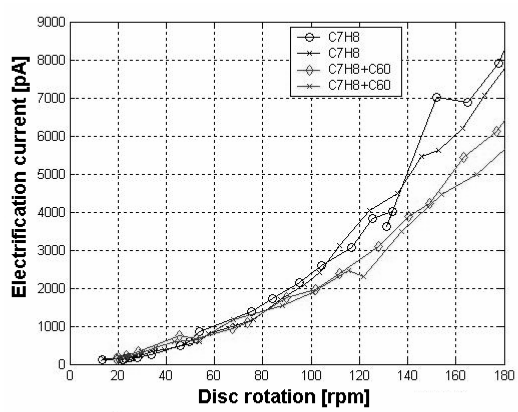

Fig. 7. Streaming electrification current as a function of disc rotation speed for pure and doped toluene

Rys. 7. Prąd elektryzacji w funkcji prędkości obrotowej tarczy dla czystego i domieszkowanego toluenu

The measurements reveled that C_{60} doped toluene characterizes lower electrification current from the pure liquid. The difference for the higher rotations used in measurements achieve 20 – 25%.

6. Summary

The research proven that it is possible to significantly improve dielectric properties of hydrocarbon liquids by the addition of C_{60} fullerenes. The most significant changes were noted for dielectric loss tangent where the difference between pure and doped liquid was at a range of 100 times for cyclohexane and 10 times in case of toluene.

Doping with C_{60} has also positive impact on the harmful phenomenon of streaming electrification, reducing the electrification current by 20 – 25% in case of toluene.

The physicochemical nature of the influence observed is not known. It might be the subject of the further research. However the results obtained are of a great practical significance.

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Artykuł recenzowany

INFORMACJE

Najnowsza książka Wydawnictwa PAK

Na przełomie sierpnia i września ukazała się kolejna książka Wydawnictwa PAK autorstwa Tomasza Boczara pt.: Energia wiatrowa. Aktualne możliwości wykorzystania.

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44-100 Gliwice, ul. Akademicka 10, p. 30b,
tel./fax: 032 237 19 45, e-mail: wydawnictwo@pak.info.pl