World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:4, No:8, 2010

Electrically Conducting Lubricants: Esterified Carbon Nanotubes

Wei Chin, Wen-Kuang Hsu*

***Abstract*—**Fats and oils are made of esterified hydrocarbons (RCOOR') and this work demonstrates the substitution of R by multi-walled CNTs (MWNTs). The resultant materials are fluidic, oily, electrically conducting and excellent lubricants. Esterified MWNTs can also respond to magnetic field when tubules contain long segments of Fe.

***Keywords*—**Liquids Nanomaterials Electric conductors

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I. Introduction

CARBON nanotubes (CNTs) may be regarded as giant cylindrical hydrocarbons and can be functionalized to meet various purposes of engineering and chemistry, for example, single-walled carbon nanotubes (SWNTs) suspended in diazonium solution show chemoselective property,[1] addition of octadecylamine groups to open ended SWNTs enables the band property study,[2] and carboxylic group attached nanotubes nucleate the surface metallization.[3] Oils and fats are made of esterified hydrocarbons (RCOOR') and this work demonstrates the substitution of R by multi-walled CNTs (MWNTs), i.e. esterified carbon nanotubes. We find that resultant materials are fluidic, oily, electrically conducting and excellent lubricants. Esterified MWNTs can also respond to magnetic field when tubules contain long segments of Fe. Reaction of esterified MWNTs with NaOH leads to saponification and solution is foamy with aromatic smell, similar to dishwashing liquid and capable of removing oily stains from plates and clothes.

TEM investigations confirm that esterified product mainly consists of MWNTs and average tube length is shortened by ca. 10% of initial owing to acid treatment (Fig 1a).[4] FT-IR spectrum has verified various functional groups as follows; absorption at 2918 cm^{-1} is ester bonded to carbon rings (1210 cm^{-1} and 1580 cm^{-1}) and 1720 cm^{-1} peak corresponds to carboxylic acid (Fig 1b).[5] Esterified nanotubes are water insoluble and their density and boiling point are 1.39 g/cm^3 and 145-155 ^oC, similar to heavy oils (Fig 2a-b). For ordinary esterified compounds (e.g. estradiol) long carbon chains are saturated by hydrogen and structure cannot transport carriers. Here long chain hydrocarbon is replaced by MWNTs and electron conduction may take place via networked nanotubes, resemblance to polymer composites (Fig. 1a).[6]

Wei Chin and Wen-Kuang Hsu are with Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan
Fax: (+) 00886-3-5722366, E-mail: wkhsu@mx.nthu.edu.tw

Report have indicated that networked nanotubes within polymers can be expressed as combination of resistive and capacitive phases, and corresponding AC circuit elements are $Z = R - j/\omega C$, where $j = -1^{1/2}$ and, Z, R, ω, and C are impedance, resistance, angular frequency and capacitance respectively.[7-8] R and C are dependent of nanotube content and total composite resistance above threshold value is equivalent to resistors connected in parallel, i.e. $1/R_{total} = \sum 1/R_n + 1/R_{contact}$, where R_n and $R_{contact}$ represent individual nanotube resistance and tube-tube contact resistance respectively.[7] At low frequency (<5 kHz), the Z is equal to R and $j/\omega C = 0$ so materials essentially behave as a pure resistive phase. At higher frequency domains (> 100 kHz), the capacitive reactance emerges owing to local tube-polymer-tube structures (M-I-M, similar to plate-to-plate capacitor) and capacitive phase dominates.[8] Here dielectric polymer is absent in our samples and localized M-I-M capacitive structures do not exist, therefore, both resistive and capacitive reactance mainly arise from nanotubes. Fig 2a-b shows experimental set up for AC impedance and capacitance measurements of esterified nanotube fluid contained within a cell and values decrease rapidly from 2000 Ω to 120 Ω at 100 kHz (Fig 3a) and from 35 $\mu F/cm^3$ to 2.5 $\mu F/cm^3$ at 25 kHz (Fig 3b). Note that unchanged impedance at high frequency (>100 kHz) is an indicative of zero capacitive reactance (i.e. $j/\omega C = 0$), which again verifies origin of C from esterified nanotubes, not from localized capacitive phase. We have also measured the pristine solid nanotubes pressurized (20 kg/cm^2) in the same cell and, R and C are 22 Ω and 2.7×10^4 $\mu F/cm^3$ at low frequency. At high frequency (>100 kHz) both decrease to 1 Ω and to few hundreds $\mu F/cm^3$ respectively (Fig 3c-d). Low resistance from solid sample is understandable because $R_{contact}$ is minimized in a compacted sample and total resistance is therefore dominated by $\sum 1/R_n$. In contrast, tube-tube contact is expected to be loose in fluidic material so $R_{contact}$ prevails over R_n. As mentioned above length of esterified nanotubes has been shortened by 10 % so specific surface area for charge storage, hence capacitance, is expected to be lower in esterified nanotubes compared with solid materials, which is consistent with Fig 3b and d. Fig 2c demonstrates a LED circuit connected to nanotube fluid which further verifies the electrical conductivity of esterified sample. In next experiments, we compare tribological parameters of nanotube fluid with commercial product (CPC, super duty motor oil, CD/SF) and testing conditions were set as follows. A cylindrical medium carbon steel (0.5 ×3 cm) is forced (3 kg) onto a rotating stainless steel disc (0.5 m/s) for 5 min and esterified MWNTs

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are then injected into contacting metal surfaces for friction coefficient evaluation; similar procedure is also applied for motor oil tests. Fig 4 shows variation of friction coefficient between metal surfaces before and after addition of esterified nanotubes (a), and motor oil (b). Clearly, values rapidly drop as lubricants are added (arrow), and resultant coefficient is 0.03 for esterified MWNTs and 0.02 for motor oil. Chen et al have measured the friction coefficient of solid CNT coated-metals and values ranged at 0.064-0.16.[9] They also claimed that tribological effect from coated surfaces is due to (a) tube-tube sliding, and (b) nanotubes as spacer between rough surfaces. Here we believe that points (a) and (b) are truly responsible for low friction obtained here but they cannot account for coated metal surfaces. Firstly, friction generates heat (> 600°C) which converts CNT-coated metal into carbide, in other words, the resultant coefficient is actually from carbide surfaces. Secondly, carbide formation explains as to why surface hardness increased from 520 HV to 1035 HV and friction coefficient varied between 0.16-0.064 in Chen et al's experiments.[9] In our study, friction coefficient maintains a constant after nanotube fluid addition, which is indicative of tube sliding and spacer effects, similar to motor oil. We find that nanotube fluid can strongly respond to magnetic field if samples were made by ferrocene pyrolysis known as a production for Fe-nanowires.[10]; Fig 5a-e shows snapshots of fluid attraction by an external magnetic field. Encapsulation of long Fe segments within MWNTs does not influence tribological property and friction coefficient is also 0.03. Reaction of esterified MWNTs with NaOH solution leads to saponification and product is foamy with aromatic smell (Fig 5f), similar to dishwashing liquid and capable of removing oily stains from plates and clothes. In summary, we have demonstrated the conversion of carbon nanotubes into electrically conducting lubricants via esterification. Analyses show that ester groups are bonded to carbon rings and carrier transport is achieved via networked nanotubes. Esterified MWNTs show an excellent tribological effect and can be further saponified to form washing liquid-like solution.

II. Experimental

MWNTs (50 mg) made by catalytic pyrolysis of acetylene are treated by 3:1 mixture of concentrated H_2SO_4/HNO_3 to form carboxylic groups on tube surfaces.[4] MWNT-COOH are then diluted with deionized water to remove residual acid, followed by baking at 50 °C for 10 h. For fischer esterificaiton, the MWNT-COOH, C_2H_5OH and concentrated H_2SO_4 are mixed in a test tube heated with boiling water and dark-oily paste is obtained after 80 min reaction. Product is again heated at 100 °C for 5 h to remove excess of ethyl alcohol and acid.

Acknowlegment

We thank the National Science Council of Taiwan for financial support (NSC-95-2112-M-007-047-MY2037).

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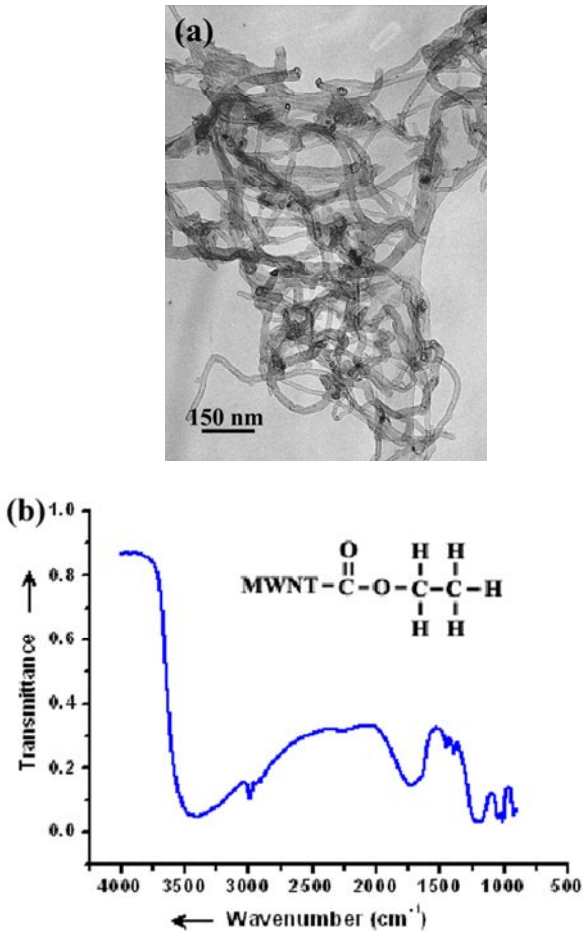
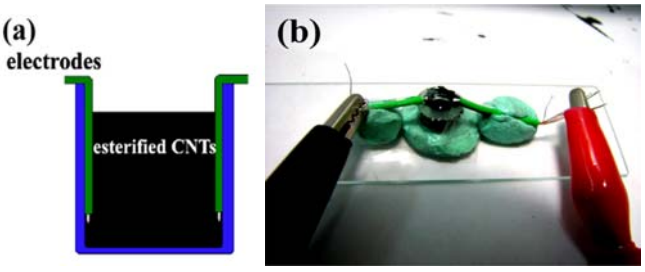


Fig. 1. (a)TEM image of esterified MWNTs. (b) FT-IR spectrum of esterified MWNTs.



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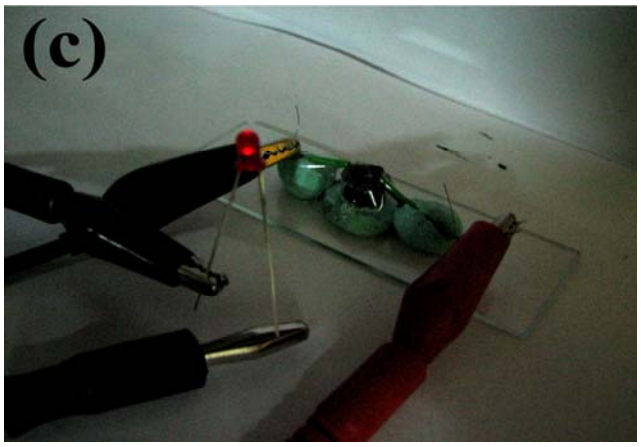
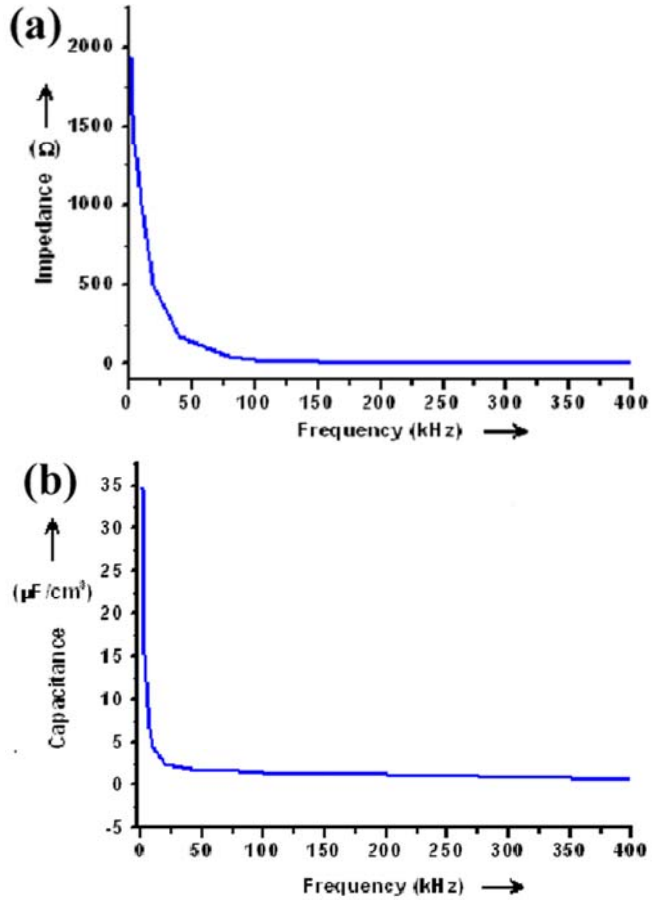
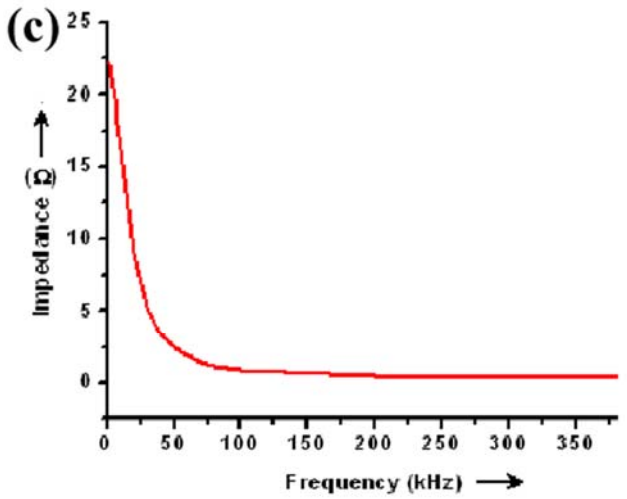


Fig. 2 (a) Experimental set up for two terminal AC impedance and capacitance measurements. (b) Esterified MWNT fluid contained in a cell. (c) A LED circuit connected to MWNT fluid, and light-on verifies the electrical conductivity of esterified nanotubes.





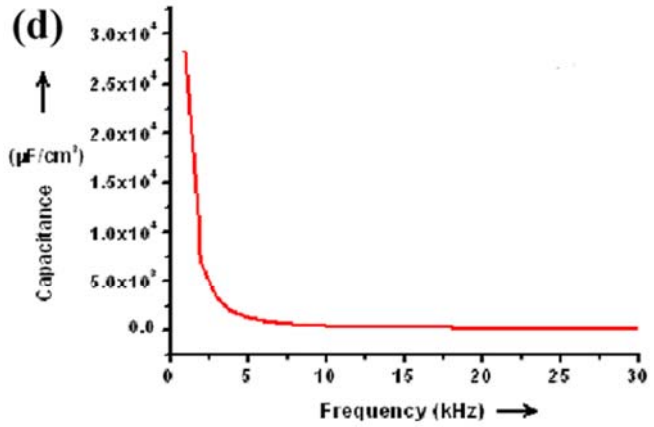
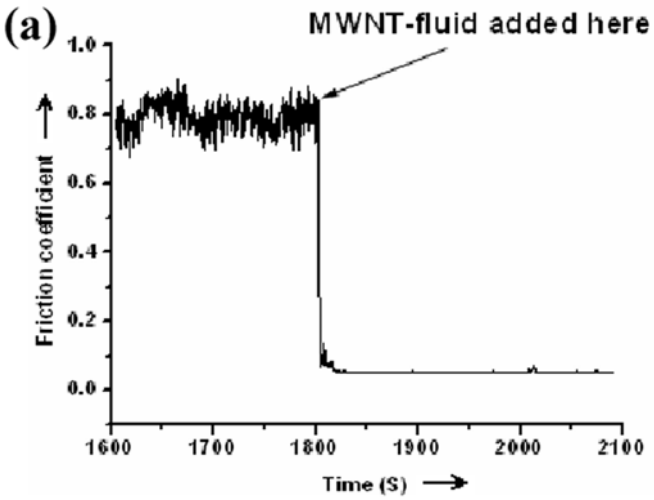


Fig. 3 Frequency dependent impedance (a) and capacitance (b) of esterified nanotubes, and frequency dependent impedance (c) and capacitance (d) of pristine solid SWNTs pressurized in a same volume cell.



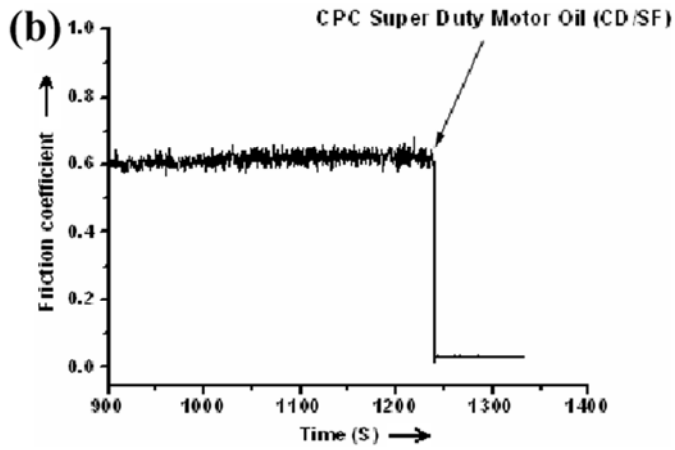


Fig. 4 Time dependent friction coefficient profiles of esterified nanotubes (a) and commercial product (CPC, super duty motor oil, CD/SF) (b).

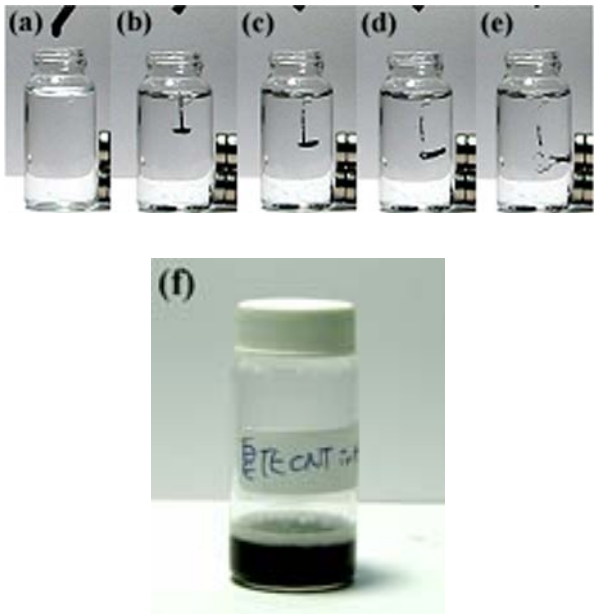


Fig. 5 Snapshots of SWNT fluid attraction by external magnetic field (a-e), and saponified SWNT solution (f).

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