Minu Gupta Bhowon
Sabina Jhaumeer-Laulloo
Henri Li Kam Wah
Ponnadurai Ramasami *Editors*

Chemistry: The Key to our Sustainable Future

Springer

Chemistry: The Key to our Sustainable Future

Minu Gupta Bhowon • Sabina Jhaumeer-Laulloo
Henri Li Kam Wah • Ponnadurai Ramasami
Editors

Chemistry: The Key to our Sustainable Future

Springer

Editors
Minu Gupta Bhowon
Department of Chemistry,
Faculty of Science
University of Mauritius
Réduit, Mauritius

Sabina Jhaumeer-Laulloo
Department of Chemistry,
Faculty of Science
University of Mauritius
Réduit, Mauritius

Henri Li Kam Wah
Department of Chemistry,
Faculty of Science
University of Mauritius
Réduit, Mauritius

Ponnadurai Ramasami
Department of Chemistry,
Faculty of Science
University of Mauritius
Réduit, Mauritius

ISBN 978-94-007-7388-2 ISBN 978-94-007-7389-9 (eBook)
DOI 10.1007/978-94-007-7389-9
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2013953577

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

The second International Conference on Pure and Applied Chemistry (ICPAC 2012) was held from 2 to 6 July 2012 at Hilton Mauritius Resort and Spa, Wolmar, Flic en Flac, in Mauritius. The theme of the conference was "Chemistry: The Key for our Future". ICPAC 2012 was attended by 150 participants from 25 countries. The conference featured 80 oral and 80 poster presentations. The keynote address was given by Prof. Robert Huber, the 1988 Chemistry Nobel Prize winner.

The participants of ICPAC 2012 were invited to submit full papers. This book is a collection of the papers selected during a subsequent peer review.

The book consists of 25 chapters covering a wide range of topics from fundamental to applied chemistry.

We would like to thank all those who submitted full manuscripts for consideration and the reviewers for their timely help in assessing these manuscripts for publication.

We would also like to pay a special tribute to all the sponsors of ICPAC 2012.

We hope that this collection of papers will serve as a useful resource for researchers.

Department of Chemistry
University of Mauritius, Réduit, Mauritius
June 2013

M. Gupta Bhowon
S. Jhaumeer-Laulloo
H. Li Kam Wah
P. Ramasami

Contents

Contributors

Ahlam J. Abdulghani Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

Muhammad B. Abubakar National Centre for Petroleum Research and Development (Energy Commission of Nigeria), Abubakar Tafawa Balewa University, Bauchi, Nigeria

Adeleke Adeniyi Department of Chemistry, Lagos State University, Lagos, Nigeria

Mansoor Ahmad Research Institute of Pharmaceutical Sciences, Department of Pharmacognosy, University of Karachi, Karachi, Pakistan

Nessar Ahmed School of Healthcare Science, Manchester Metropolitan University, Manchester, UK

Zainab Z. Ahmed Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

Ummeh W. Ahsun Aleemiah College (Girls), Phoenix, Mauritius

Khalil H.A. AL-Bayati Department of Physics, College of Science for Women, Baghdad University, Baghdad, Iraq

Safeenaz B. Alladin Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius

Nada I.I. AL-Zubaidi Department of Physics, College of Science, Diyala University, Diyala, Iraq

A. Bialecki Laboratoire de Chimie des Substances Naturelles et des Sciences des Aliments, Faculté des Sciences et Technologies, Université de La Réunion, La Réunion, France

Raheemot Balogun Department of Chemistry, Lagos State University, Lagos, Nigeria

Jamal Benjilali National Institute of Medicinal and Aromatic Plants, Taounate, PAMSN, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Dalila Bousta National Institute of Medicinal and Aromatic Plants, Taounate, PAMSN, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Marie Chan Sun Department of Medicine, Faculty of Science, University of Mauritius, Réduit, Mauritius

Dušan Chorvát Jr. International Laser Center, Bratislava, Slovakia

Klaudia Czaniková Department of Composite Materials, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia

Hanane El-Hajaji Faculty of Sciences Dhar el Mehraz, LIMOM, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Latifa El Mansouri National Institute of Medicinal and Aromatic Plants, Taounate, PAMSN, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Amal El Youbi-Hamsas National Institute of Medicinal and Aromatic Plants, Taounate, PAMSN, University Sidi Mohamed Ben Abdellah, Fez, Morocco

A. Emelia Department of Chemistry, Lagos State University, Lagos, Nigeria

Jevisha Erriah Department of Medicine, Faculty of Science, University of Mauritius, Réduit, Mauritius

Abdellah Farah National Institute of Medicinal and Aromatic Plants, Taounate, PAMSN, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Thimme A. Gowda Haranahalli Ramaswamy Institute of Higher Education, Hassan, Karnataka, India

Said O.S. Hassane Faculty of Sciences and Technology, University of Comoros, Moroni, Comoros

Brian Horsfield Organic Geochemistry Section, GeoForschungsZentrum, Telegrafenberg, Potsdam, Germany

Aminah Ibrahim Department of Chemistry, Lagos State University, Lagos, Nigeria

William K. Isharaza Department of Biochemistry, Mbarara University of Science and Technology, Mbarara, Uganda

Noor Jahan Dow College of Pharmacy, Dow University of Health Sciences, Karachi, Pakistan

Gautam Jaiswar Department of Chemistry, Dr. B. R. Ambedkar University, Agra, India

Aliyu Jauro National Centre for Petroleum Research and Development (Energy Commission of Nigeria), Abubakar Tafawa Balewa University, Bauchi, Nigeria

Peter Kasák Department of Composite Materials, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia

Igor Krupa Center of Advanced Materials, Qatar University, Doha, Qatar

Mohammed Lachkar Faculty of Sciences Dhar el Mehraz, LIMOM, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Hiteyeshi Lallbeeharry Sugar Industry Labour Welfare Fund, Port-Louis, Mauritius

Henri Li Kam Wah Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius

Mohamad F. Mahomoodally Department of Health Sciences, Faculty of Science, University of Mauritius, Réduit, Mauritius

Roman Marsalek Department of Chemistry, Faculty of Science, University of Ostrava, Ostrava, Czech Republic

Ishmael B. Masesane Department of Chemistry, University of Botswana, Gaborone, Botswana

Ofentse Mazimba Department of Chemistry, University of Botswana, Gaborone, Botswana

Mehjabeen Department of Pharmacology, Federal Urdu University of Arts, Science and Technology, Karachi, Pakistan

Riyadh M. Mungur Department of Physics, Faculty of Science, University of Mauritius, Réduit, Mauritius

Fawzia B. Narod Department of Science Education, Mauritius Institute of Education, Réduit, Mauritius

Jared C. Ogunde Scientific Advisory and Information Network (SAIN) and Chemistry Aid Kenya, Nairobi, Kenya

Mária Omastová Department of Composite Materials, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia

Aggrey Omolo Scientific Advisory and Information Network (SAIN) and Chemistry Aid Kenya, Nairobi, Kenya

Yusuf Omotayo Department of Chemistry, Lagos State University, Lagos, Nigeria

Olawale Osifeko Department of Chemistry, Lagos State University, Lagos, Nigeria

Olabisi Owoade Department of Chemistry, Lagos State University, Lagos, Nigeria

Ewa Pavlová Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Atar S. Pipal Department of Chemistry, Dr. B. R. Ambedkar University, Agra, India

Deerajen Ramasawmy Department of Management, Faculty of Law and Management, University of Mauritius, Réduit, Mauritius

Kanisha Ramchurn Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius

Jugjeet S. Ramkissoon Department of Health Sciences, Faculty of Science, University of Mauritius, Réduit, Mauritius

Shahram Ranjbar Department of Physical Chemistry, Razi University, Kermanshah, Iran

Antony J. Rest Chemistry Video Consortium, Educational Techniques Group Trust of the Royal Society of Chemistry (UK) and Chemistry Aid, University of Southampton, Southampton, UK

Soonil D.D.V Rughooputh Department of Physics, Faculty of Science, University of Mauritius, La Réduit, Mauritius

Jacqueline Smadja Laboratoire de Chimie des Substances Naturelles et des Sciences des Aliments, Faculté des Sciences et Technologies, Université de La Réunion, La Réunion, France

Said H. Soidrou National Institute of Medicinal and Aromatic Plants, Taounate, PAMSN, University Sidi Mohamed Ben Abdellah, Fez, Morocco

Anwar H. Subratty Department of Health Sciences, Faculty of Science, University of Mauritius, Réduit, Mauritius

Farid Taherkhani Department of Physical Chemistry, Razi University, Kermanshah, Iran

Ajay Taneja Department of Chemistry, Dr. B. R. Ambedkar University, Agra, India

Sukarma Thareja Department of Chemistry, Christ Church College, CSJM Kanpur University, Kanpur, Uttar Pradesh, India

Raymond G. Wallace Educational Techniques Group Trust of the Royal Society of Chemistry (UK), Chemistry Aid, and School of Science and Technology, Nottingham Trent University, Nottingham, UK

Milton A. Wesuta Department of Biochemistry, Mbarara University of Science and Technology, Mbarara, Uganda

Heinz Wilkes Organic Geochemistry Section, GeoForschungsZentrum, Telegrafenberg, Potsdam, Germany

Asieh Yahyazadeh Department of Chemistry, University of Guilan, Rasht, Iran

Chapter 1
Elastomeric Actuators Based on Ethylene-Vinyl Acetate and Carbon Nanotubes

Klaudia Czaniková, Mária Omastová, Igor Krupa, Peter Kasák, Ewa Pavlová, and Dušan Chorvát Jr.

Abstract The development of new types of visual-aid tablet for visually impaired people requires the development of cheap, but still very effective photoactuating materials. This requirement can be satisfied by the use of new kind of elastomers filled by nanofillers, such as carbon nanotubes. Nanocomposites based on commercial ethylene vinyl-acetate (EVA) copolymer and multiwalled carbon nanotubes (MWCNT) were prepared by casting from solution. The non-covalent surface modification of MWCNT was carried out by special, newly synthesized compatibilizer cholesteryl 1-pyrenecarboxylate (PyChol). In order to mimic Braille character, special home-built silicone punch and die moulds were used. The Braille element based on EVA/MWCNT-PyChol composite displays reversible, multiple changes of dimension in the direction of the irradiation during/upon illumination by red and blue light-emitted diode (LED). Transmission electron microscopy (TEM) showed a good dispersion of the MWCNT-PyChol within the matrix. The Braille element behaviour under illumination was analysed by atomic force microscopy

K. Czaniková (✉) • M. Omastová • P. Kasák
Department of Composite Materials, Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
e-mail: upolklcz@savba.sk; Klaudia.Czanikova@savba.sk; Maria.Omastova@savba.sk; upolmaom@savba.sk; peter.kasak@savba.sk

I. Krupa
Center of Advanced Materials, QAPCO Polymer Chair, Qatar University, P.O. Box 2713, Doha, Qatar
e-mail: igor.krupa@savba.sk

E. Pavlová
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
e-mail: pavlova@imc.cas.cz

D. Chorvát Jr.
International Laser Center, Ilkovičova 3, 812 19 Bratislava, Slovakia
e-mail: chorvat@ilc.sk

M. Gupta Bhowon et al. (eds.), *Chemistry: The Key to our Sustainable Future*, DOI 10.1007/978-94-007-7389-9_1, © Springer Science+Business Media Dordrecht 2014

(AFM) and by nanoindentor. Nanoindentor, even if the purpose of its original use is different, can be effectively applied for the determination of the actuation stroke, the sample dimensional changes in the direction of irradiation.

1.1 Introduction

Revolutionary technologies are needed to improve the lives of visually impaired and blind people. Current haptic representation in refreshable displays is technically inadequate and very expensive, thus limiting their use in daily life [1]. Resolution, scalability to larger displays, and portability are deficient [2–4]. Mechanical actuation by optical excitation is a much-sought after technology [5]. The devices which utilise an effective photoactuating material are able to convey information in the form of Braille text, maps and graphics to the visually impaired to improve their mobility and quality of life [1, 6]. Part of the 7 RP Nano-Optical Mechanical Systems (NOMS) project was to prepare photo-actuators which must not display fast actuation response during illumination, but have to provide fully reversible actuation. The main disadvantage of available electronic Braille devices is that they show only a single line of text and cannot display graphical images, mathematical equations, maps, music, and so on [7]. The typical Braille cell is illustrated in Fig. 1.1. It has to be pointed out that in the proposed design not only embossed points are displayed, as it is in the cases of printed Braille characters. In this case, all six points are potentially displayable. The required Braille character is then formed by moving the individual Braille elements up.

So far various prototype electronic Braille cells have been constructed using conjugated polymers such as polypyrrole [8], ionic polymer-metal composite bending type actuators [9], or electrostrictive elastomers [10]. However, according to the best of our knowledge, commercially available devices work on the basis of

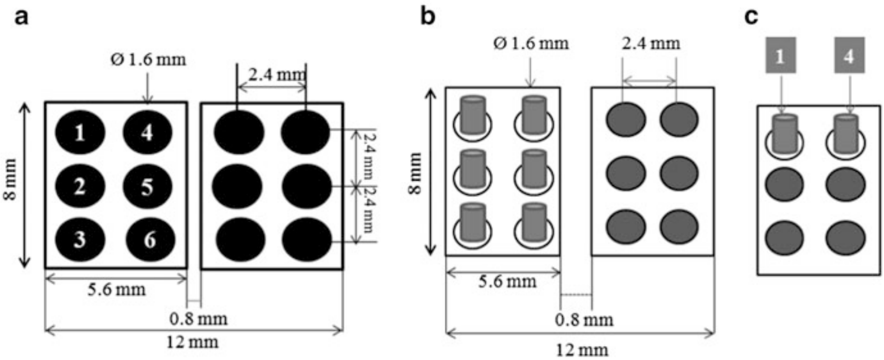


Fig. 1.1 (**a**) Two Braille characters, each one consisting of six raised dots arranged in two columns containing three elements, (**b**) cross-section of the two Braille characters and (**c**) example of Braille symbol – Braille glyph for letter C (raised elements at positions 1–4)

piezoelectric phenomenon. The following parameters have been reported for standardization of Braille devices – the pin matrix density should be up to 1 cell/mm^2, actuating speed have to be more than 50 Hz, and energy density about 10 W/cm^2 [11, 12]. New type of Braille display was presented based on dielectric elastomer. The tactile display is organized with a dual-layer array of tactile cells which generates vertical motion of the Braille pins. The elastomer actuator is compressed in the thickness direction while it is expanded in the lateral direction when a voltage is applied [13–20]. In another study the Braille tablet made by two adjacent Braille cells (consisting of six stimulating pins arranged in a 3×2 array format) were read by the visually impaired persons. The data for two types of recognition rates were obtained as Hit Recognition Rate (HRR) and Number Recognition Rate (NRR). The HRR corresponds to the rate movement of the Braille dots and NRR correctly reading of the Braille dots. The results represented at actuating frequency of the Braille pins was 15 Hz and HRR increases up to about 80 % and the NRR indicates a maximum of 41 %. The obtained results are much better than originally expected [21]. Carpi et al. [22] described the developing push–pull hydrostatically coupled dielectric elastomer actuators. Silicone elastomers membranes filled with oil created bubbles with diameter of 6 mm and were driven up to a voltage of 2.25 kV, applied across a silicone film with a thickness of 42 μm. Specific interest to miniaturize such kind of actuators was motivated by an intention to develop a novel tactile display.

Commercially available refreshable tactile display providing access to high-resolution graphics (pictures, graphs, tables, diagrams etc.) and more than two lines Braille texts are still missing. Only Braille displays using piezoelectric elements work very reliably but on the other hand these displays are still very expensive and noisy [7, 23]. Revolutionary technologies are needed to improve the lives of blind and partially sighted people in order to increase the change of obtaining more information. The nanotubes-polymeric materials are potential candidates for creating new type of actuator because of expected decreased manufacturing costs and true photo-actuation which can be used for construction of haptic display for visually impaired people. The photomechanical actuation is preferred to electromechanical transduction due to the following reasons: wireless actuation, low noise, easy scaling up and down.

The main aim of NOMS project was to develop the prototype of a high resolution, refreshable, tactile visual-aid tablet and demonstrate its capability to depict Braille text and basic graphical information. This tablet have several features, such as full text and graphical capability, fully integrated electronic circuitry, capability to connect to a PC, rapid refresh rate, portability, manufacturability and low cost. Two fundamental requirements are height raise and force output. The minimum stroke height is 0.25 mm and force/pressure about 0.2 N [24]. The promising solution is the use of actuators based on carbon nanotubes-polymeric materials that can be activated by light.

Smart materials can react to a stimulus such as light, temperature, pH, mechanical stress, etc. Dimensional changes in polymers can happen reversibly, dependently on intensity and time of illumination with light [25]. The reversible shape change can be achieved by conformation changes in the case of photochromic molecules, for example, azobenzene undergoes a trans–cis isomerization controlled by the polarization of the light [26].

Liquid-crystal elastomers inherently possess photo-actuating behaviour due to the photoisomerization conformational changes of rod-like dye molecules when small amounts of nanofillers-carbon nanotubes were incorporated into the matrix. The photo-actuation mechanism in the case of liquid-crystal elastomers filled with multiwalled carbon nanotubes (MWCNT) composites containing very low content of MWCNT was explained by the absorption of light in the UV-vis or near IR region, and the light was rapidly converted into local heat. The local heat is then efficiently transferred to the stretched polymer chains near the MWCNT. Subsequent contraction of the stretched polymer chains leads to the photo-mechanical actuation [27, 28].

Ethylene vinyl acetate (EVA) is a commercial elastomer whose properties depend on the ethylene/vinyl acetate ratio [29]. The domain structure of EVA copolymers consists of partially crystalline polyethylene blocks and flexible vinyl acetate blocks [30]. This is mainly focused on EVA containing non-covalently modified multiwalled carbon nanotubes by newly prepared surfactant, arbitrarily here called PyChol and on their photo-actuation response. The composites were prepared by casting from solution due to better dispersion of MWCNT-PyChol within the dissolved polymeric matrix against the mixing with molten polymer [31]. The cast composite foil was used to prepare Braille element using specially designed moulds. The height of the Braille element temporarily increases after illumination and this process is fully reversible. After switching off the light, the Braille element returns to its original shape and height. New developed methods, namely the method using the atomic force microscopy (AFM) and nanoindentor were used to investigate the photo-actuation behaviour of the prepared composites. As far as we know, these methods for characterisation of photoactuation were not reported in literature till now. Here it must be mentioned, that almost all the reported results which can be found in literature are based on the characterisation of photoactuating behaviour of materials in the form of strips. For this characterisation, various setups, usually home-made ones were created, utilising the measurements of the force change at the fixed length during illumination [32–36]. The reports on the testing of photoactuation of Braille characters are very rare, the newest papers in this field have been presented by Camargo et al. [37].

1.2 Methodology

1.2.1 Materials

Tetrahydrofuran (THF, POCH S.A. 99.5 %, Poland) was dried and freshly distilled from sodium/benzophenone. A commercial ethylene-vinyl acetate copolymer (EVA, Levapren 500, Lanxess, Germany) containing 50 wt% of vinyl acetate was

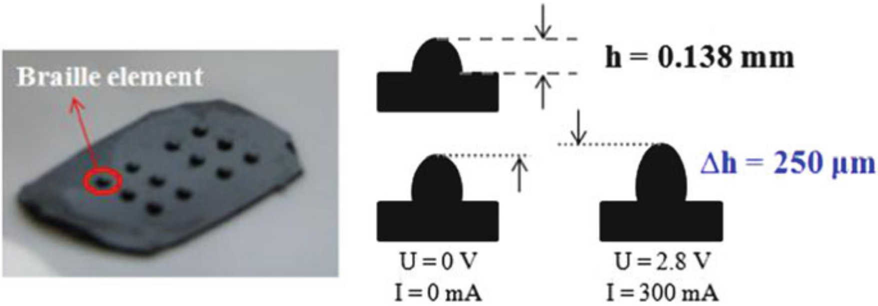


Fig. 1.2 The prepared two Braille characters and detail of the Braille element based on an EVA composite filled with non-covalent modified carbon nanotubes

used as a matrix. MWCNT (Nanostructured & Amorphous Materials, Inc.; Houston, TX 77084, USA) were used as the filler. The purity of the MWCNT was 95 %, the outside diameters were in the range of 60–100 nm, the lengths were in the range of 5–15 μm and the surface area was 64 m^2/g.

1.2.2 Preparation of Composites

The EVA/MWCNT nanocomposites were prepared by casting from solution. Non-covalent surface modification of MWCNT was done using special compatibilizer cholesteryl 1-pyrenecarboxylate (PyChol). The weight ratio MWCNT/Py-Chol was chosen as 1/5 after first testing with lower amount of modifier. The used amount of the carbon nanotubes was selected according to the published results [5]. The solution was sonicated for 2 h at amplitude of 20 % (~35 μm, ~60 W/cm^2, Hielscher 400 S) and a duty cycle of 100 %. After sonication, 10 g of EVA was added and the final solution was stirred and subsequently poured into a Teflon-coated Petri dish and allowed to dry. The sample was dried in the oven and additional drying was performed in a vacuum oven for 6 h at 70 °C. The EVA/MWCNT-PyChol composite foil was prepared by compression moulding (Fontijne SRA-100, The Netherlands) for 15 min at a pressure of 2.4 MPa and temperature of 60 °C. Special custom-made punch/die moulds were applied to the EVA/MWCNT-PyChol nanocomposite to achieve the shape of a Braille element [38].

The composite material was placed between punch/die moulds and loaded by 200 g weight in the oven at 60 °C and subsequently cooled down in ice water in order to freeze the structure. The final shape of the two Braille characters and also one Braille element are shown in Fig. 1.2.

1.2.3 Transmission Electron Microscopy (TEM)

TEM was performed with a Tecnai G2 Spirit Twin 12, FEI, and thin samples were prepared by ultramicrotome (Ultracut UCT, Leica) under cryo-conditions (the sample and knife temperatures were −70 °C and −45 °C, respectively). The ultrathin sections were transferred to a microscopic grid, covered with a thin carbon layer to improve their stability under the electron beam and observed in a TEM microscope. All micrographs are bright field images taken at an accelerating voltage of 120 kV that show dark carbon nanotubes in the light polymer matrix.

1.2.4 Photo-Actuation Study of Prepared Braille Element by Atomic Force Microscopy and by Nanoindentation

In this paper we present two newly developed methods for characterisation of the photoactuation behaviour of nanocomposites. Despite the fact that both utilised equipment are commonly used for totally different types of material characterisation, they can be also adapted for the characterisation of the photoactuating behaviour.

The first of these methods, the Atomic Force Microscopy (AFM), is a well-established tool for the study of structural and physical properties of macromolecules at the surface, as well as high-precision 3D topography. It allows characterization of the surface both in dry and wet conditions with nm resolution, depending on the size of tip. Here, we applied AFM in contact mode (Smena Solver P47H, NT-MDT, Russia) to study the deformation changes of Braille element under illumination using light-emitted diodes (LEDs). However, it must be pointed out that this method enables only the qualitative characterisation of the photoactuation process. Simply said, we can obtain only the information whether the material is photoactuating or not. This fact is caused by the restricted amplitude of the cantilever movement, as can be seen later.

Two types of LEDs were used - red LED (Philip Luxeon, $\lambda = 627$ nm) and blue LED (Philip Luxeon, $\lambda = 470$ nm) at applied current of 150 mA or 300 mA. A Si cantilever (length 100 μm and width 35 μm) with a force constant of 11 $N{\cdot}m^{-1}$ and a tip curvature of 10 nm (NT-MTD, Russia) was used. The changes in the position of the AFM tip in the vertical direction were recorded and plotted against time. The hole in alumina foil is used for focusing the light to the Braille element illumination, where the CNT are aligned in order to achieve the actuation. Scheme of a AFM setup is shown in Fig. 1.3.

Nanoindentor Hysitron TriboLab® Nanomechanical Test Instrument equipped with a Scanning Probe Microscope (SPM) and a Berkovich probe was used for the characterisation of the photoactuating behaviour of materials. The actual use of nanoindentor is the characterisation of mechanical properties of the surfaces. However, similarly as in the case of AFM, it can be adapted for the photoactuation measurements. The TI 750 Ubi nanomechanical test instrument is a dedicated scanning nanoindentor. The principal components in a nanoindentation experiment are the sensors and actuators used to apply and measure the mechanical load and indentor displacement, and the indentor tip. The latter component is conventionally made of diamond, formed into a symmetric shape. The force and displacement are recorded as the indentor tip is pressed into the test material’s surface (in our case on

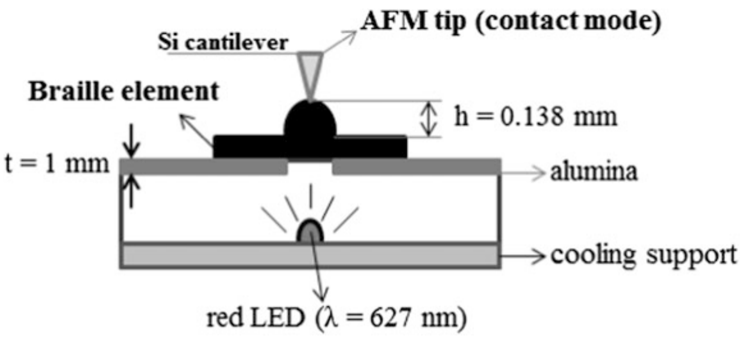


Fig. 1.3 Sketch of the setup for AFM measuring height changes for Braille element during illumination by *red LED*

the Braille element) with a prescribed loading and unloading profile. For our purpose, we only used the fact that it is possible to determine accurately the height of the Braille element on the top before and after illumination. This gives us the information about total actuation deformation of the material, and, what time is needed to reach that maximum. In this case we do not obtain the whole dependence deformation versus time, as it was possible in the case of AFM measurement.

1.3 Results and Discussion

1.3.1 A Dispersion Study of Carbon Nanotubes Within Polymeric Matrix

The proposed non-covalent surface modification of carbon nanotubes (CNT) is based on the van der Waals interaction between the nanotubes and various molecules that consist of aromatic rings through π-π stacking. The main advantage of this procedure is that CNT are not broken during treatment as well as it does not disturb delocalized π electrons and thus, it does not change the inherent electrical conductivity of CNT. Moreover, this kind of non-aggressive treatment does not lead to the breaking of nanotubes, as it usually happens during modification by strong acids [39].

Specially developed surfactant, based on pyrene molecules and long alkyl or cholesteryl groups, was used for CNT surface modification to ensure affinity and good compatibility of the CNT surface with polymeric matrix and good filler dispergation. For better dispergation of CNT we modified the carbon nanotubes non-covalently using PyChol surfactant.

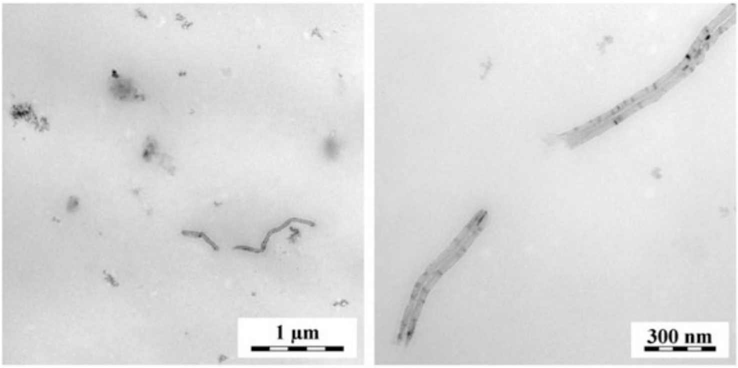


Fig. 1.4 TEM images of the Braille element based on an EVA composite containing 0.1 wt% MWCNT

Table 1.1 The power of the red LED, illumination and relaxation times (T_{illum} and T_{relax}) height changes of the Braille element based on an EVA/0.1 wt% MWCNT-PyChol composite at two different applied currents

Applied current (mA)	Power of LED (mW)	T_{illum}^{*} (s)	T_{relax}^{*} (s)	Height changes (µm)
150	3.5	35	65	2.52
300	6.6	6	30	2.54

The extent of MWCNT dispersion within the EVA polymeric matrix was characterized using TEM. Figure 1.4 depicts a good dispersion of carbon nanotubes due to cholesteryl 1-pyrenecarboxylate compatibilizer used for CNT non-covalent surface modification. Single carbon nanotubes and a minimal amount of their agglomerates were observed, but also a small amount of amorphous carbon nanotube impurities were detected within EVA matrix. The dispersion study of the nanocomposite with unmodified MWCNT was also done by TEM (not shown here), in this case worse dispersion was obtained compared to nanocomposite prepared with compatibilizer.

1.3.2 The Photo-Actuation Study of Braille Element by AFM and Nanoindentation

The photo-actuation response during/after illumination of the Braille element was investigated by AFM method. Two Braille characters were prepared using special titanium punch and die moulds, as depicted in Fig. 1.2. The Braille characters were cut to individual Braille elements for characterization of photo-actuation response.

Using red LED diode when the applied current was set to 150 mA (power 3.5 mW) the original height of Braille element (BE) was increased about 2.52 µm after 35 s of illumination. After switching off the light, the time for the BE relaxation to original shape was 65 s (Table 1.1). A faster response was obtained when the power of the red LED was increased to 6.6 mW (300 mA). In this case, the

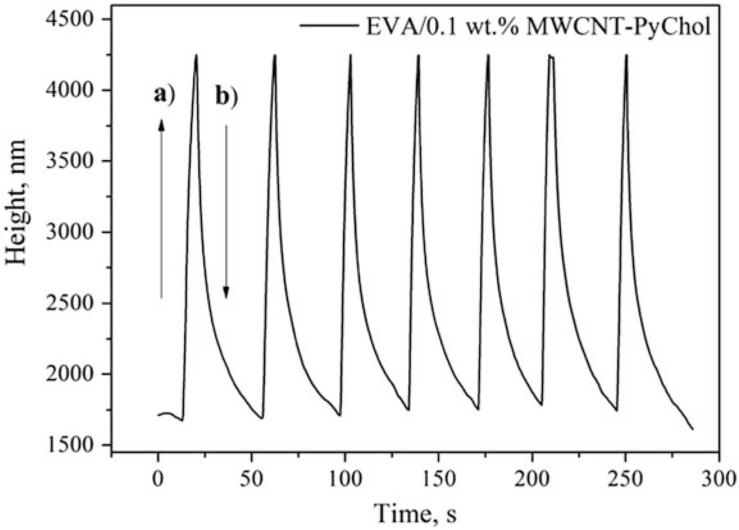


Fig. 1.5 An AFM recording of the height changes over time for a Braille element based on an EVA/0.1 wt% MWCNT-PyChol composite (**a**) upon illumination (*red LED*, at an applied current of 300 mA) and (**b**) after switching off the *red LED*

Braille element grew to 2.54 μm within 6 s and then BE returned back to its original position after 30 s. Figure 1.5 depicts the actuation during illumination with red LED at applied current of 300 mA (a) within 6 s, and after switching off the light-emitting source (b) the Braille element relaxed to the original height.

Table 1.1 summarized the results obtained during AFM study of BE illumination by red LED at 150 mA and 300 mA applied currents, illumination and relaxation times, measured height changes (μm) of the Braille element based on an EVA/0.1 wt% MWCNT-PyChol composite. The original height of the Braille element was 0.138 mm.

In the next study, the photo-actuation response of the Braille element was measured using a blue diode ($\lambda = 470$ nm) at applied current of 300 mA, see Fig. 1.6.

In the case of blue LED at 300 mA applied current the power of this LED is 9.6 mW. Figure 1.6 depicts the measured photo-actuation response of Braille element during illumination by blue LED. The results show high reproducibility of photo-actuation. Figure 1.6 represents 19 cycles of reversible actuation of the characterized BE as an example of BE behaviour during illumination. The maximum deformation of BE observable by AFM due to cantilever movement upon illumination was obtained after 6 s of illumination in both cases when the applied currents were set 150 mA or 300 mA. As can be seen in Fig. 1.6, the Braille element returned to its original position after 15 s (b), which means that the relaxation time was approximately half of that measured after illumination using red LED at the same set current of 300 mA. The main advantage of using blue LED with high

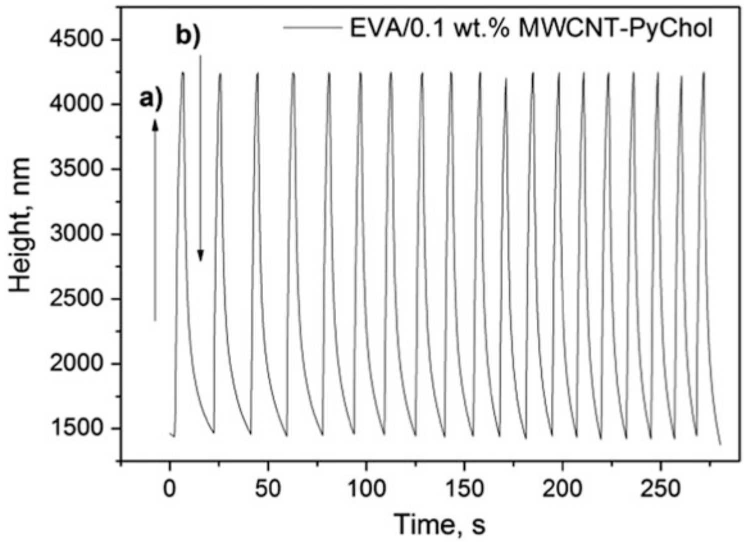


Fig. 1.6 An AFM recording of the height changes over time for a Braille element based on an EVA/0.1 wt% MWCNT-PyChol composite (**a**) upon illumination (*blue LED*, at an applied current of 300 mA) and (**b**) after switching off the *blue LED*

power was faster actuation and relaxation responses. The photo-actuation measurement by AFM was realizable only over a range of −3.0 μm to +3.0 μm, which is the maximum amplitude of the cantilever movement. AFM method was used here to observe the photo-actuation responses of new types of prepared composites and to obtain information about the rates of actuation and relaxation for prepared Braille elements. On the other hand, it was not possible to determine the maximum amplitude of the actuation and relaxation for these samples due to the limited amplitude of the cantilever movement.

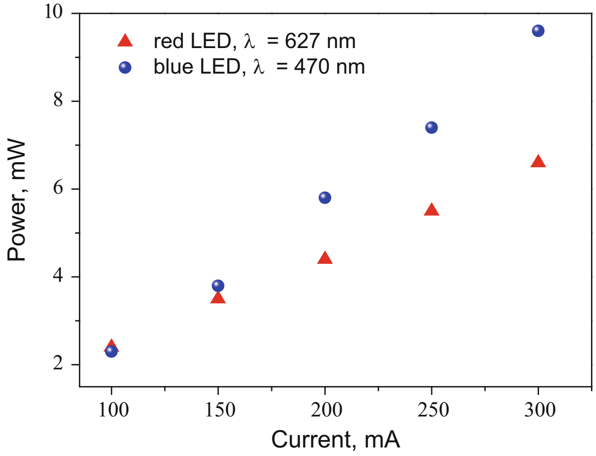
Due to this limitation, the method based on the nanoindentor was introduced to determine the maximal deformation changes under illumination for the Braille element. As mentioned above, this method could not determine the dimensional profiles over time like AFM, but it could give us information about the real height changes of the Braille element before and during illumination. In this case, the Braille element was illuminated from the bottom using (as depicted in Fig. 1.3) a red or blue LED. One Braille element was illuminated and the surrounding area of Braille element was shielded with alumina foil. The photo-actuation response of the Braille element under illumination was measured at various current settings. An appropriate photo-actuation of the composite material was observed. An expansion was obtained during illumination. The results are presented in Table 1.2 for the Braille element measured at 200 and 300 mA following illumination with red or blue LEDs.

A maximum deformation change upon illumination using blue LED about 15.2 μm was obtained at applied current of 300 mA. This deformation was much higher than that following illumination of the Braille element using a red LED.

Table 1.2 The power of the red and blue diodes, height changes of the Braille element based on an EVA/0.1 wt% MWCNT-PyChol composite as measured by nanoindentation at different applied currents

Applied current (mA)	Power of red LED (mW)	Height changes (μm)	Power of blue LED (mW)	Height changes (μm)
200	4.4	6.4	5.8	9.8
300	6.6	9.7	9.6	15.2

Fig. 1.7 Power outputs (mW) against different applied current (mA) for *red LED* (λ = 627 nm) and *blue LED* (λ = 470 nm)



These data were also in good agreement with the faster actuation and relaxation responses previously observed by AFM when using a blue LED instead of a red one. The power (mW) for both diodes was measured at different applied currents (mA) as depicted in Fig. 1.7.

Higher actuation obtained with blue LED diode (Table 1.2) is associated by increased scattering and by higher absorption at lower wavelength [40] compared with red LED diode (at applied current of 300 mA) by nanoindentation technique. The same effect by AFM method was obtained, as faster relaxation speed was investigated when driven by blue LED (9.6 mW) than red LED one (6.6 mW) at applied current of 300 mA. Information about the rates of actuation and relaxation times were investigated by AFM. The precise, actual height changes of Braille element during illumination were obtained by nanoindentation method. The height of the Braille element temporarily increases after illumination and this process is fully reversible as shown by AFM study. After switching off the light, the Braille element returns to its original shape and height. The photo-thermo-mechanical actuation mechanism is explained by presence of carbon nanotubes in elastomeric nanocomposite, which convert light to heat and increase the heat transfer efficiency. It is caused by inherent high conductivity of carbon nanotubes that originates from their delocalized π-bonded skeleton [41]. The accumulated heat from CNT is released to polymeric matrix and triggering the actuation. Even by AFM study it was not possible to determine the maximum amplitude of the actuation and relaxation, but it showed that prepared nanocomposite is perfectly stable, and fully reversible actuation was determined after hundreds of cycles. The new developed nanocomposites based on EVA copolymer and well dispersed carbon nanotubes are promising materials for creation of actuators which are activated by light. Therefore photoactuation study of nanocomposites is in progress in our laboratory and other, more complex methods will be used in the near future for detailed characterization of Braille element prepared from EVA and carbon nanotubes.

1.4 Conclusions

The EVA/0.1 wt% MWCNT-PyChol composites were prepared by casting from solution. The reason for the selection of this filler content was motivated by the works published very recently, where this filler content was reported as sufficient for the evocation of photoactuating effect, maintaining the properties of a neat polymeric matrix. To improve the dispersion of carbon nanotubes within the EVA polymeric matrix, newly synthesized cholesteryl 1-pyrenecarboxylate compatibilizer (PyChol) was used. The ratio CNT/PyChol equal to 1/5 was determined from the optimisation process, testing the dispersibility and the dispersion stability over long time in the low molecular solvents. Very good dispersion of modified fillers within the EVA matrix was demonstrated by TEM. The photo-actuation behaviour of Braille element prepared from nanocomposite was investigated by the newly developed methods, utilising commercial devices such as AFM and nanoindentor, which are originally employed for different types of characterisations. However, after a small adaptation, these methods were able to characterize the photoactuation response of investigated materials upon illumination by red and blue LEDs. An expansion was detected upon illumination of the bottom of the Braille element. AFM method was chosen to determine the actuation and relaxation times, both of which depended on the type and power of the LEDs used. This method is very simple and offers fast information about qualitative behaviour of materials under irradiation. As for the characterisation by nanoindentor, this one provided information about the total deformation amplitude of material.

Acknowledgements This work was supported by project NOMS, which is funded by the European Commission under contract no. 228916. The authors are grateful to Centro Nacional de Microelectrónica (CNM) – Spain for provision of special punch and die silicon moulds. This contribution/publication is also the result of the implementation of the following project: Centre for materials, layers and systems for applications and chemical processes under extreme conditions Stage II, which is supported by the Research & Development Operational Program and funded by the ERDF. This work was also partly financially supported by VEGA 2/0149/14, and VEGA 2/0119/12. IMC in Prague are grateful for the institutional support under RVO: 61389013.

References

1. Campo EM, Roig J, Roeder B, Wenn D, Mamojka B, Omastov M, Terentjev EM, Esteve J (2011) Nano opto-mechanical systems (NOMS) as a proposal for tactile displays. Proc SPIE 8107, Nano-Opto-Mechanical Systems (NOMS): 81070H. doi:10.1117/12.897529; http://dx.doi.org/10.1117/12.897529
2. Pasquero J (2006) Survey on communication through touch. TR-CIRM, Centre for Intelligent Machines, McGill University, Canada. Technical Report: TR-CIM 06.04
3. Bonet-Borrás C (2004) Braille the pleasure of reading: we blind people want to continue reading with our fingers. UPGRADE, Lect Notes Comput SC 5:77–83
4. Parkes D (1988) Nomad: an audio-tactile tool for the acquisition, use and management of spatially distributed information by partially sighted and blind persons. In: Tatham AF, Dodds AG (eds) Proceedings of the second international symposium on maps and graphics for visually handicapped people, King's College, University of London, pp 24–29
5. Camargo CC, Campanella H, Marshall JE, Torras N, Zinoviev K, Terentjev EM, Esteve J (2011) Localised actuation in composites containing carbon nanotubes and liquid crystalline elastomers. Macromol Rapid Commun 32:1953–1959
6. Mamojka B, Teplický P (2012) Aplications of optically actuated haptic elements. In: Miesenberger K, Karshmer A, Penaz P, Zeglar W (eds) ICCHP 2012, Part II, Springer, Berlin Heidelberg, LNCS 7383, pp 659–663
7. KGS Corporation, http://www.kgs-jpn.co.jp/eindex.html
8. Madden JD, Cush RA, Kanigan TS, Hunter IW (2000) Fast contracting polypyrrole actuators. Synth Met 113:85–92
9. Kato Y, Sekitani T, Takamiya M, Doi M, Asaka K, Sakurai T, Someya T (2007) Sheet-type Braille displays by integrating organic field-effect transistors and polymeric actuators. IEEE Trans Electron Devices 54:202–209
10. Lee S, Jung K, Koo J, Lee S, Choi H, Jeon J, Nam J, Choi H (2004) Braille display device using soft actuator. In: Bar-Cohen Y (ed) Proceedings of SPIE smart structures and materials: electroactive polymer actuators and devices (EAPAD), vol 5385, pp 368–379
11. Jungmann M, Schlaak HF (2002) Taktiles display mit elektrostatischen Polymer-Aktoren. Internationales wissenschaftliches Kolloquium, Tagungsband, p 47
12. Asamura N, Shinohara T, Tojo Y, Koshida N, Shinoda H (2001) Necessary spatial resolution for realistic tactile feeling display, Robotics and Automation. In: Proceedings 2001 ICRA. IEEE international conference on, vol. 2, pp 1851, 1856, 21–26 May 2001. doi:10.1109/ROBOT.2001.932878
13. Choi HR, Lee SW, Jung KM, Koo JC, Lee SI, Choi HG, Jeon JW, Nam JD (2004) Tactile display as a Braille display for the visually disabled, Intelligent Robots and Systems, 2004 (IROS 2004). In: Proceedings 2004 IEEE/RSJ international conference on, vol. 2, pp 1985, 1990, 28 Sept–2 Oct 2004. doi:10.1109/IROS.2004.1389689
14. Koo IM, Jung KM, Koo JC, Nam J, Lee YK, Choi HR (2008) Development of soft actuator based wearable tactile display. IEEE Trans Robot 4:549–559
15. Pelrine R, Kornbluh R, Pei Q, Joseph J (2000) High-speed electrically actuated elastomers with over 300% strain. Science 287:836–839
16. Chakraborti P, Karahan Toprakci HA, Yang P, Di Spigna N, Franzon P, Ghosh T (2012) A compact dielectric elastomer tubular actuator for refreshable Braille displays. Sensor Actuat A-Phys 179:151–157
17. Carpi F, Frediani G, De Rossi D (2011) Hydrostatically coupled dielectric elastomer actuators: new opportunities for haptics. Mater Res Soc Symp Proc 1312:3–12
18. Gorny LJ, Zellers BC, Lin M, Liu S, Zhang QM (2010) The development of compact electroactive polymer actuators suitable for use in full page Braille displays. In: Proceedings of SPIE – the International Society for Optical Engineering Article number 76420B
19. Pei Q, Yu Z, Niu X, Brochu P (2010) Electroactive polymers for rigid-to-rigid actuation and Braille e-books. SPIE Newsroom. doi:10.1117/2.1201002.002632

20. Carpi F, Frediani G, De Rossi D (2010) Hydrostatically coupled dielectric elastomer actuators. IEEE/ASME Trans Mech 15:308–315
21. Choi HR, Koo IM, Jung K, Roh S, Koo JC, Nam J, Lee YK (2009) A Braille display system for the visually disabled using a polymer based soft actuator. In: Carpi F, Smela E (eds) Biomedical applications of electroactive polymer actuators. Wiley, Oxford
22. Carpi F, Frediani G, Tarantino S, De Rossi D (2010) Millimetre-scale bubble-like dielectric elastomer actuators. Polym Int 59:407–414
23. HyperBraille, http://www.hyperbraille.de/?lang=en
24. Fricke J (1997) Substituting friction by weak vibration on a tactile pin array, Developments in Tactile Displays (Digest No. 1997/012). In: IEE Colloquium on, vol., pp 3/1, 3/3, 21 Jan 1997. doi:10.1049/ic:19970082
25. Courty S, Mine J, Tajbakhsh AR, Terentjev EM (2003) Nematic elastomers with aligned carbon nanotubes: new electromechanical actuators. Europhys Lett 64:654–660
26. Yu Y, Nakano M, Ikeda T (2003) Photomechanics: directed bending of a polymer film by light. Nature 425:145
27. Ajayan PM, Terrones M, Guardia A, Huc V, Grobert N, Wei BQ, Lezec H, Ramanath G, Ebbesen TW (2002) Nanotubes in a flash – ignition and reconstruction. Science 296:705
28. Loomis J, King B, Burkhead T, Xu P, Bessler N, Terentjev EM, Panchapakesan B (2012) Graphene-nanoplatelet-based photomechanical actuators. Nanotechnology 23:045501
29. George JJ, Bhowmick AK (2009) Influence of matrix polarity on the properties of ethylene vinyl acetate-carbon nanofiller nanocomposites. Nanoscale Res Lett 4:655–664
30. Martinez-Garcia A, Reche AS, Martin-Martinez JM (2004) Improved adhesion of EVAs with different vinyl acetate contents treated with sulphuric acid. J Adhes Sci Technol 18:967–982
31. Czaniková K, Krupa I, Ilčíková M, Mosnáček J, Kasák P, Mičušík M, Chorvát D Jr, Omastová M (2011) In: Proceedings of SPIE – Bellingham, USA: SPIE – International Society for Optical Engineering, 8107, art. n. 810707
32. Lu S, Panchapakesan B (2007) Photomechanical responses of carbon nanotube/polymer actuators. Nanotechnology 18:305502
33. Hu Y, Chen W, Lu L, Liu J, Chu C (2010) Electromechanical actuation with controllable motion based on a single-walled carbon nanotube and natural biopolymer composite. ACS Nano 4:3498–3502
34. Hu Y, Wang G, Tao X, Chen W (2011) Low-voltage driven sustainable weightlifting actuator based on polymer-nanotube composite. Macromol Chem Phys 212:1671–1676
35. Harvey CLM, Terentjev EM (2007) Role of polarization and alignment in photoactuation of nematic elastomers. Eur Phys J E 23:185–189
36. Ahir SV, Squires M, Tajbakhsh AR, Terentjev EM (2006) Infrared actuation in aligned polymer-nanotube composites. Phys Rev B 73:085420
37. Camargo CJ, Campanella H, Marshall JE, Torras N, Zinoviev K, Terentjev EM, Esteve J (2012) Batch fabrication of optical actuators using nanotube-elastomer composites towards refreshable Braille displays. Micromech Microeng 22:075009
38. Czaniková K, Krupa I, Ilčíková M, Kasák P, Chorvát D Jr, Valentin M, Slouf M, Mosnacek J, Mičušik M, Omastová M (2012) Photo-actuating materials based on elastomers and modified carbon nanotubes. J Nanophotonics 6:063522
39. Spitalsky Z, Krontiras ZA, Georga SN, Galiotis C (2009) Effect of oxidation treatment of multiwalled carbon nanotubes on the mechanical and electrical properties of their epoxy composites. Compos Part A-Appl S 40:778–783
40. Uğur G, Chang J, Xiang S, Lin L, Lu J (2012) A near-infrared mechano responsive polymer system. Adv Mater 24:2685–2690
41. Ahir SV, Huang YY, Terentjev EM (2008) Polymers with aligned carbon nanotubes: active composite materials. Polymer 49:3841–3854

Chapter 2
Identification of Volatile Compounds from Flowers and Aromatic Plants: How and Why?

A. Bialecki and Jacqueline Smadja

Abstract When working on volatile compounds from plants, the objectives are multiples and can be summarized in four points: (1) Research of bioactive molecules, (2) Chemotaxonomic studies, (3) Applications in perfume industry, (4) Plant-insect interactions. Each of these four points will be discussed and illustrated by one or several examples of research projects conducted in the Chemistry Laboratory of Natural Substances and Food Sciences. The first two points exclusively concern volatile compounds generated by essential oils extracted from endemic or indigenous plants of Reunion, Mauritius and Madagascar islands. The two last points are dedicated to volatiles found in the airspace (headspace) surrounding flowers. This paper will also present a selection of sampling methods for volatile compounds that range from conventional, inexpensive, solvent-free, quick sampling methods to innovative methods, as well as an overview of detection and identification methods of volatiles including GC-FID and GC-MS.

2.1 Introduction

Aromatic plants are often confused with medicinal plants because they secrete chemicals which sometimes have pharmacological effects. But rigorously, aromatic plants are considered as plants which secrete volatiles by, at least, one vegetative or reproductive organ, often leaves but also roots, stems, bark, seeds, fruits and flowers. These volatiles may act as aroma and flavour molecules due to their interactions with human receptors. The primary functions of these compounds released into the atmosphere are to defend plants against herbivores and pathogens or to provide a reproductive

A. Bialecki (✉) • J. Smadja
Laboratoire de Chimie des Substances Naturelles et des Sciences des Aliments, Faculté des Sciences et Technologies, Université de La Réunion, 15 Avenue René Cassin, CS 92003, 97 744 Saint-Denis cedex 9, La Réunion, France
e-mail: anne.bialecki@univ-reunion.fr; jacqueline.smadja@univ-reunion.fr

M. Gupta Bhowon et al. (eds.), *Chemistry: The Key to our Sustainable Future*,
DOI 10.1007/978-94-007-7389-9_2, © Springer Science+Business Media Dordrecht 2014

advantage by attracting pollinators and seed dispersers [1]. Today, a total of 1,700 volatile compounds have been described from more than 90 plant families [2]. These volatiles constitute about 1 % of plant secondary metabolites known to date and are typically classified into four major categories: terpenoids, phenylpropanoids/benzenoids, fatty acid and amino acid derivatives [3]. Knowledge of the identity and relative amounts of the volatile substances released by plants is of great importance to several fields of basic and applied research in biology, chemistry and many other disciplines. Obtaining this knowledge requires overcoming many analytical challenges posed by these complex mixtures, because they present large variations in component amounts, chemical structures and functionalities.

After a short presentation of the functions of plant volatiles, the chemical compounds classes in plant volatiles, and a discussion on Sect. 2.3, this chapter will cover several practical approaches to plant volatiles analysis: isolation techniques, separation and detection techniques, and compound identification procedures. A few examples will be presented next, to highlight some of the research topics focused on plant volatiles and developed by the Chemistry Laboratory of Natural Substances and Food Sciences (LCSNSA).

2.2 Plant Volatiles

2.2.1 Functions of Plant Volatiles

It is recognized that these compounds stored in specialized secretory structures such as glandular trichomes or resin ducts [4, 5] are not only emitted by plants in response to abiotic stress such as light and temperature changes, flooding and drought, ultraviolet radiation and oxidants, but they are also used as a sophisticated "language" by plants to have a dialogue with other organisms: microbes, animals, and even other plants [1, 3, 4, 6–10].

Some compounds may attract beneficial insects such as pollinators, whereas others are involved in different modes of defense: direct defense, indirect defense and inter-plant priming.

Direct defense involves the production of compounds that inhibit microbial growth, also kill or repel herbivores. *Indirect defenses* involve the production of compounds that minimize infestations of herbivores by attracting natural enemies preying upon or parasitizing herbivores according to the proverb "The enemy of my enemy is my friend". Finally, chemical volatile signals released from injured plants not only affect herbivores and pathogens but may also signal alarm to neighbouring plants by triggering defense responses. This is called *inter-plant priming*.

Many of these compounds have been referred to as "secondary metabolites" to distinguish them from the "primary metabolites" required for the growth of plants. These secondary metabolites however, are likely to be essential for successful competition or reproduction.

2.2.2 Chemical Compounds Classes in Plant Volatiles

The volatile compounds emitted by plants are generally lipophilic and belong to several different classes but are united by their low molecular weight (from 30 to 300 amu) and vapour pressure sufficient to be released and dispersed into the air under normal pressure and temperature. In aromatic and scented plants, they originate from four categories of chemicals: terpenes derivatives, aromatic derivatives, fatty acid derivatives and amino-acid derivatives. Other groups seem to be more sporadic [3, 4, 10–13].

Terpenes Derivatives

Terpenes derivatives, also called isoprenoids, are defined as materials derived from the head-to-tail linkage of the isoprene moiety (2-methylbutane). The isopropyl part of 2-methylbutane is defined as the head, and the ethyl residue as the tail. Depending on the number of isoprene subunits one differentiates between hemi- (C_5), mono- (C_{10}), sesqui- (C_{15}), di- (C_{20}), sester- (C_{25}), tri- (C_{30}), tetraterpenes (C_{40}) and polyterpenes $(C_5)_n$ with $n > 8$. In mono-, sesqui-, di- and sesterterpenes, the isoprene units are linked to each other from head-to-tail; tri- and tetraterpenes contain one tail-to-tail connection in the centre (Fig. 2.1).

Sometimes skeletal rearrangements occur and fragmentation or degradation reactions can reduce the number of carbon atoms so that the empirical formula does not contain a simple multiple of five carbons, thus providing irregular terpenes. Nonetheless, the natural product chemist quickly recognizes the characteristic terpene framework of the structure.

Terpenes encountered among the volatile compounds from plants are exclusively mono-, sesqui- and diterpenes, as well as irregular ones.

Monoterpenes. These substances can be further divided into three groups depending on whether they are acyclic (e.g. myrcene), monocyclic (e.g. limonene) or bicyclic (e.g. α-pinene). Within each group, the monoterpenes may be simple unsaturated hydrocarbons (e.g. limonene) or may have functional groups and be alcohols (e.g. α-terpineol), aldehydes (e.g. citronellal), ketones (e.g. carvone), esters (e.g. linalyl acetate) (Fig. 2.2).

Sesquiterpenes. Like monoterpenes, the sesquiterpenes fall chemically into groups according to the basic carbon skeleton; the common ones are either acyclic (e.g. α-farnesene), monocyclic (e.g. γ-bisabolene) or bicyclic (e.g. α-guaiene) (Fig. 2.3). However, within each group there are many different compounds known. Today, several thousands sesquiterpenoids with well-defined structures, belonging to some 200 skeletal types, are listed.

Diterpenes. Very few diterpenes are reported in floral scents; this may be due to their general low volatility (Fig. 2.4).

Irregular terpenes. The irregular terpenes include compounds varying in the number of carbon atoms from 8 to 18. Among these are apocarotenoids, which are biodegradation products of carotenoid compounds (C_{40}) like β-carotene. Ionones

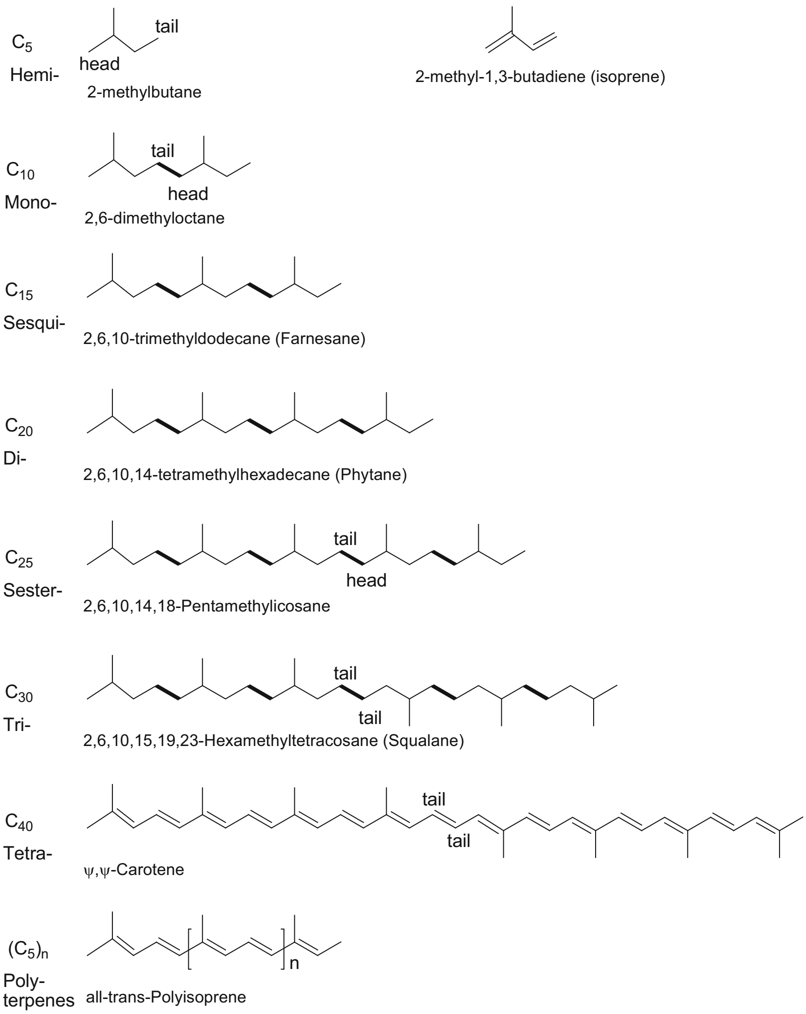


Fig. 2.1 Parent hydrocarbons of terpenes (isoprenoids)

such as dihydro-β-ionone, 6-methyl-5-hepten-2-one and geranyl acetone are the compounds the most often cited (Fig. 2.5).

Aromatic Derivatives

The second category of volatile organic compounds, aromatic derivatives also named as phenolic compounds or benzenoids, are mainly synthesized *via* the shikimate pathway. This pathway got its name from shikimic acid, which is the key step in the formation of the aromatic compounds. Examples of these include: acetophenone, *ortho*-vanillin, cinnamyl alcohol (Fig. 2.6).

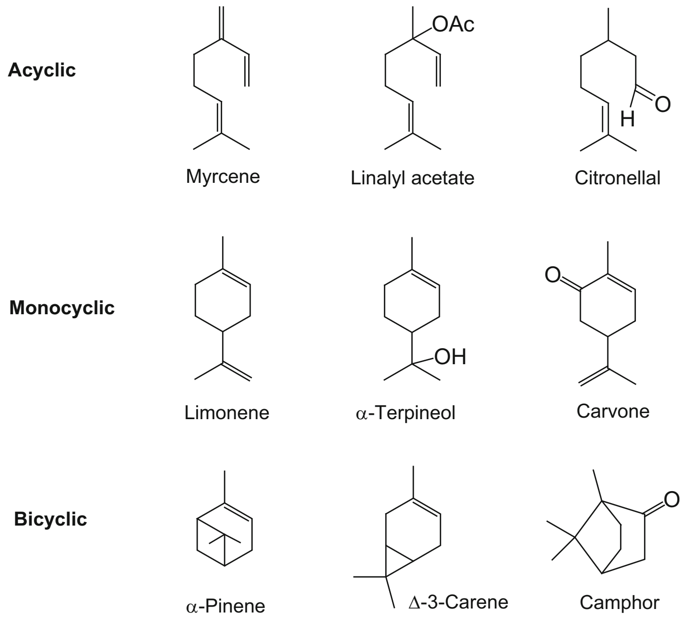


Fig. 2.2 Chemical structures of some monoterpenic compounds

Fatty Acid Derivatives

Fatty acid derivatives are often associated with green leaf odour emitted immediately following the breakdown and lipoxygenation of lipid membranes after mechanical damage. However, these green leaf volatiles are sometimes also produced by flowers. Among the fatty acid derivatives, both saturated and unsaturated hydrocarbons are fairly common, the majority having between 2 and 17 carbon atoms (Fig. 2.7). Aldehydes, alcohols and ketones are also common. Free acids are less common, whereas esters encompass the largest number of different chemical structures. Special mention should be made of the six carbon-compounds known as "green-leaf" volatiles like (*Z*)-3-hexenyl acetate found in vegetative as well as floral scents of numerous plants. This compound probably plays a role in plant defense [1, 7, 8].

Amino Acids Derivatives

Many plant volatiles including aldehydes, alcohols, esters, acids and nitrogen- and sulfur containing compounds are derived from amino acids such as alanine, valine, leucine, isoleucine and methionine, which play an important role in plant defense by recruiting the natural enemies of the attacking herbivore. Amino acids on de-amination form α-keto acid, which in turn forms formaldehyde, acids, alcohols

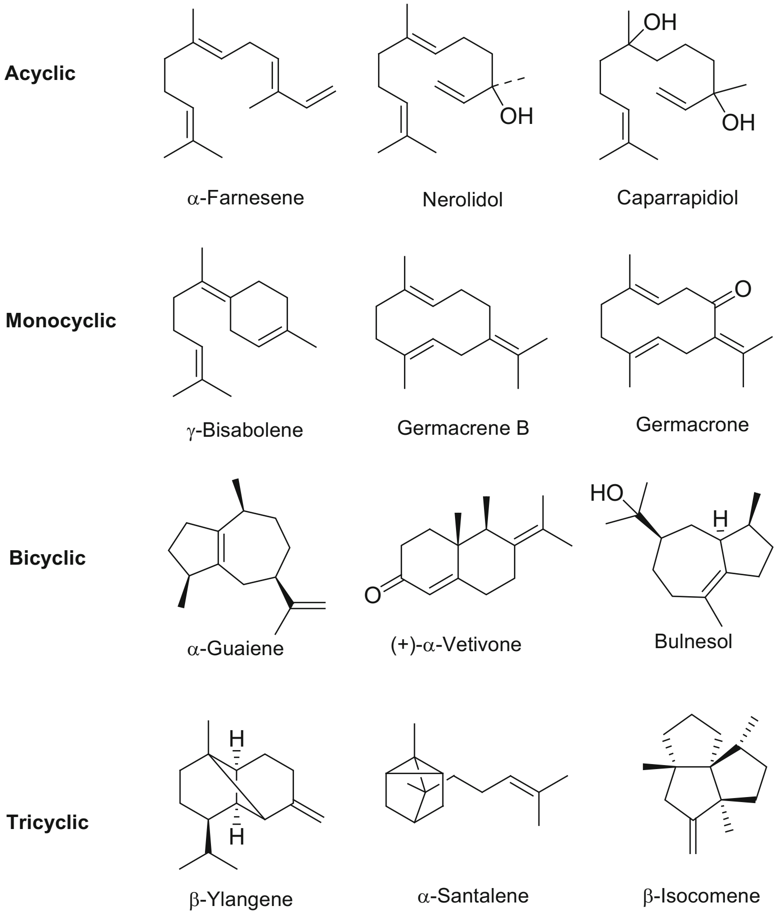


Fig. 2.3 Chemical structures of some sesquiterpenic compounds

and esters on decarboxylation, reduction, oxidation and esterification. Methionine and cysteine have been found to be the precursor of sulfur containing volatiles such as methanethiol, dimethyl disulfide and thioesters responsible for the odour of garlic, onions and boiled potatoes (Fig. 2.8).

2.2.3 Variation in Plant Volatiles

The presence, yield and composition of secondary metabolites in plants, in particular volatile compounds, can be affected in a number of ways, from their formation in the plant to their final isolation. Factors affecting volatile compounds production

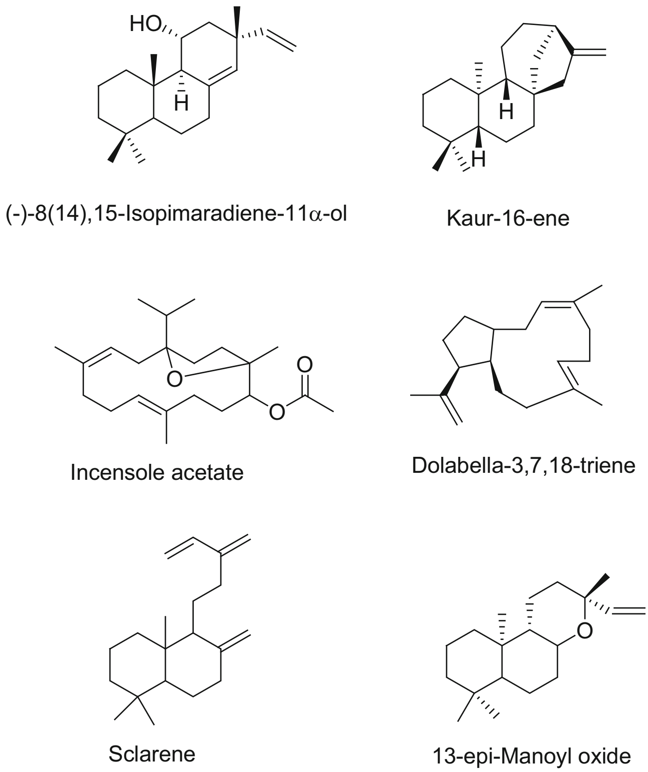


Fig. 2.4 Chemical structures of some diterpenic compounds

include: (1) *physiological variations* such as organ development, pollinator activity cycle, type of plant material (leaves, flowers, etc.), type of secretory structure, seasonal variation, mechanical and chemical injuries; (2) *environmental conditions* like climate, pollution, diseases and pests, edaphic factors; (3) *geographic variation*; (4) *genetic factors and evolution*; (5) *storage* [14].

2.3 Why Investigate Plant Volatiles?

Knowledge of the identity and relative amounts of the volatile substances emitted by plants is of great importance to several fields of basic and applied research mainly in chemistry and biology. So, they are studied for different purposes.

The first one is purely *economic* as plant volatiles can be used in a wide variety of consumer goods such as detergents, soaps, toilet products, cosmetics, pharmaceuticals, perfumes, confectionery food products, soft drinks, distilled alcoholic beverages (hard drinks) and insecticides.