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UV-crosslinked polymeric materials for encapsulation of ZnO nanowires in piezoelectric fingerprint sensors

A. Bouvet-Marchand[a], M. Loubat[a], A. Graillot[a,*], J. Volk[b], R. Dauksevicius[c], E. Saoutieff[d], A. Viana[d], B. Christian[e], V. Lebedev[e], C. Sturm[f], C. Loubat[a]

[a]SPECIFIC POLYMERS, Castries, France
[b]MTA EK MFA, Budapest, Hungary
[c]Institute of Mechatronics, Kaunas, Lithuania
[d]Université Grenoble Alpes, CEA, LETI, MINATEC Campus, F-38054 Grenoble, France
[e]Fraunhofer IAF, Freiburg, Germany
[f]Institut für Experimentelle Physik II, Leipzig, Germany

Abstract

The work presented here describes new UV-crosslinkable thin layer polymeric materials for the encapsulation of ZnO nanowires (NWs) in multi-NWs pressure based fingerprint sensors. Such innovative sensor is a novel technology for fingerprint capture developed within the PiezoMAT FP7 European project. The sensing principle is based on the piezoelectric property of ZnO NWs, on which a potential difference is generated when they undergo compression and/or bending forces. Since the pressure induced by the finger cannot be directly applied on the NWs, the deformation is applied through a polymeric material that aims at transferring forces from the finger onto the array of NWs without altering their integrity. Besides, since it is dedicated to be in direct contact with human finger or oil pollutants, the encapsulation layer must also exhibit chemical inertness, as well as hydrophobicity and oleophobicity.

*Keywords:*Piezoelectric sensors, Fingerprint, Encapsulation, Polymer material, Thin layer, Acrylates, UV-crosslinking;

*Alain GRAILLOT. Tel.: +33-499-74-91-35; fax: +33-499-74-91-52.
*E-mail address:*alain.graillot@specificpolymers.fr

1. Introduction

In the scope of the PIEZOMAT FP7 European project, a multi-NWs pressure based fingerprint sensor is currently developed by a consortium of European partners (Fig. 1). The sensor is made of an array of individually contacted piezoelectric ZnO NWs grown by Wet Chemical Growth (WCG) through nucleation windows on Gallium doped Zinc oxide (GZO) seed layer (Chemical Vapor Deposition) [1]. Under mechanical deformations, ZnO NWs generate piezo-potentials and the charges induced by each NW are then collected, which enables to reconstruct a 3D deformation field corresponding to the fingerprint.
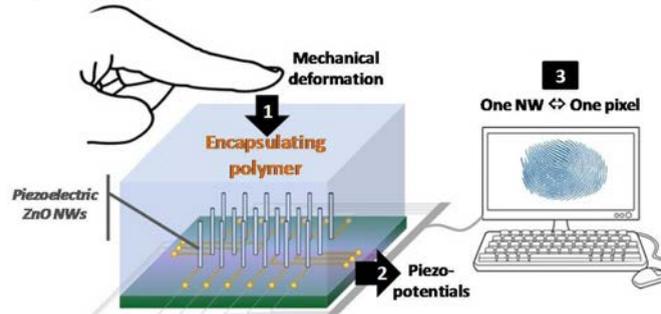

Fig. 1. Schematic representation of polymer-encapsulated multi-NWs pressure based fingerprint sensor

Since the finger pressure cannot be applied directly on the brittle NWs, a polymeric encapsulation material was needed to act as the interface between the finger and the piezoelectric NWs. Selected dielectric polymeric material must be tough enough to protect the NWs from breaking but soft enough to allow NWs deformation and production of electric charges. The optimal mechanical properties and thickness of the polymer layer were determined via parametric simulations, which were performed in COMSOL Multiphysics [2]. Numerical studies were performed to determine whether there is an optimal value of polymer Young's modulus and polymer cap height h_{pol} (the thickness of the polymer layer above the NWs) to maximize the average voltage output. The results revealed that near-optimal values for Young's modulus E^* are located between 0.2 and 0.5 GPa whereas excessively soft polymer ($E^* < 0.1$ GPa) may lead to the penetration of the NWs into the polymer. Besides, the model revealed that h_{pol} would have more impact on the voltage output with respect to E^* and optimal values of h_{pol} are expected to be between 2 and 4µm.

Taking these requirements into consideration, the research work was oriented toward the development of multi-component, solvent-free, spin-coating processable, and UV-crosslinkable materials. The spin coating process was selected since (i) a liquid deposition system must ensure the encapsulation material to be well-spread on the seed layer and in the NWs vicinity and (ii) because it enables the control of the encapsulation layer thickness by varying the spin-coating rotation speed. The UV-curing process, which is an efficient and time saving process commonly used in industry [3], was selected because it leads to crosslinked and thus chemically inert material. Here, 1,6-hexanediol diacrylate (HdA) and poly(propylene glycol) diacrylate (PPGdA) were chosen to be the main two components of the crosslinkable formulation. Influence of both these components content on (i) the formulation viscosity and spin-coating processability and (ii) the final mechanical properties of the encapsulation layer are presented here. Addition of fluorinated acrylates in the previous formulations was also studied since fluorinated additives are known to favor both hydrophobicity and oleophobicity.

2. Results and discussion

2.1. Infuence of PPGdA content on formulation viscosity and material mechanical properties.

In order to evaluate the influence of HdA/PPGdA proportions on both the formulation viscosity and UV-crosslinked material mechanical properties, various formulations were prepared and cured. Viscosity of each formulation was evaluated with a Brookfield viscosimeter (Fig. 2 (a)). Mechanical properties (Tg; Tα, E*) of corresponding UV-cured materials were measured respectively by DSC and DMA analysis (Fig. 2 (b)).

Results presented in Fig. 2 (a) clearly show that an increase of PPGdA in the formulation comes with a significant increase of the viscosity. Formulations with low PPGdA content correspond to low viscosity and thus low maximal reachable thicknesses, whereas high PPGdA content lead to thicker layers. Since it was impossible to efficiently spread the formulation on the wafers by spin coating for PPGdA content higher than 80 wt%, the optimum PPGdA content was between 20 wt% and 60 wt%.
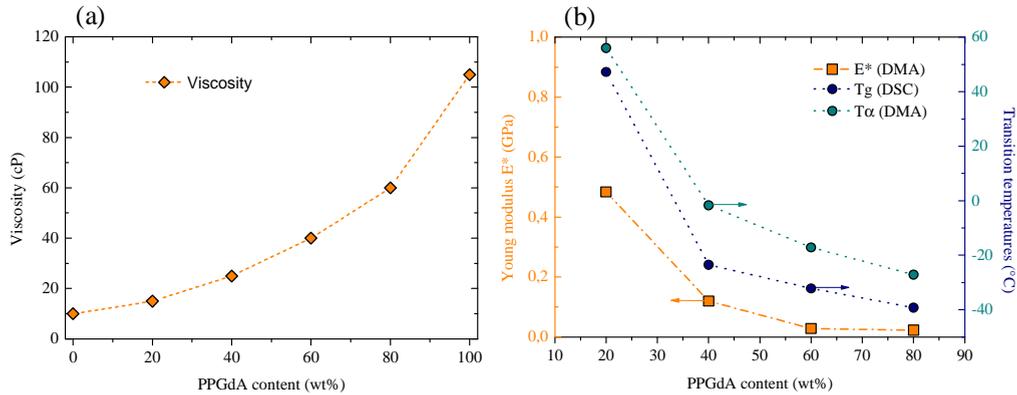

Fig. 2. Influence of PPGdA content on (a) viscosity and on (b) Young modulus (E*), Glass transition (Tg) and α-transition temperatures (Tα)

As it can be seen in Fig. 2 (b), an increase of the PPGdA content (from 20 wt% to 80 wt%) imply a clear decrease of the Young modulus E* (from 0.5 to 0.02 GPa) and both transition temperatures. Such trends were expected since the PPGdA is a high molecular weight diacrylate molecule (average 800 g.mol^{-1}) which acts as a crosslinked points spacer in the UV-cured materials. Comparing these results with the model predictions, it was first concluded that formulations containing 60 wt% and 80 wt% of PPGdA led to too soft polymer materials. More, the mechanical properties of the UV-cured materials containing 20 wt% and 40 wt% of PPGdA appeared to be close enough to the optimal values predicted by the model. The formulation containing 40%wt of PPGdA was then retained for the rest of the study as the best compromise between promising mechanical properties (E* = 0.12 GPa, Tg = -23°C) and formulation viscosity (25 cP).

2.2. NWs encapsulation – compatibility with NWs and polymer cap height

Various samples were encapsulated with the previously selected formulation at different spin-coating rotation speeds, varying from 2000 to 8000 rpm. After encapsulation, the influence of spin-coating rotation speed on encapsulation layer thickness was evaluated (Fig. 3 (a)) and scanning electron microscopy (SEM) was performed on every samples (Fig. 3 (b)).
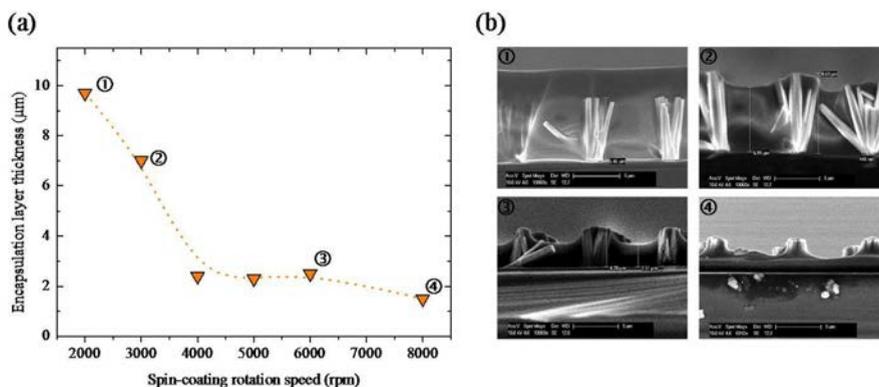

Fig. 3. (a) Influence of spin-coating rotation speed on encapsulation layer thickness and (b) corresponding SEM images

SEM pictures first highlighted that the polymer was well-spread on the wafer surface and was well-surrounding the NWs. Furthermore, the encapsulation process did not seem to affect the NWs integrity as their geometry, orientation and location remain the same before and after encapsulation. Besides, the results showed in Fig. 3 (a) pinpoints that it was possible to control the polymer layer thickness between 1.5 µm and 10 µm by applying the proper spin-coating conditions. Thus, it would then be possible to encapsulate NWs with the selected formulation with the proper polymer cap height as long as the NWs height does not exceed 8 µm. For longer NWs, multiple layer deposition might be considered.

2.3. Chemical inertness and surface properties

The chemical inertness of the encapsulation layer was ensured by its crosslinked nature [4]. In order to bring oleophobicity and hydrophobicity, fluorinated acrylate monomer was introduced into the formulation. Several formulations with different ratio of perfluorooctyl acrylate (PFA) were prepared to evaluate the influence of PFA content on the surface properties (Fig. 4 (a)). Thin layers were obtained by spin-coating at two extreme spin-coating rotation speeds (Fig. 4 (a): 8000 rpm; Fig. 4 (b): 2000 rpm). Hydrophobicity and oleophobicity were evaluated by contact angle measurements performed with a device using a simplified experimental setup [5].
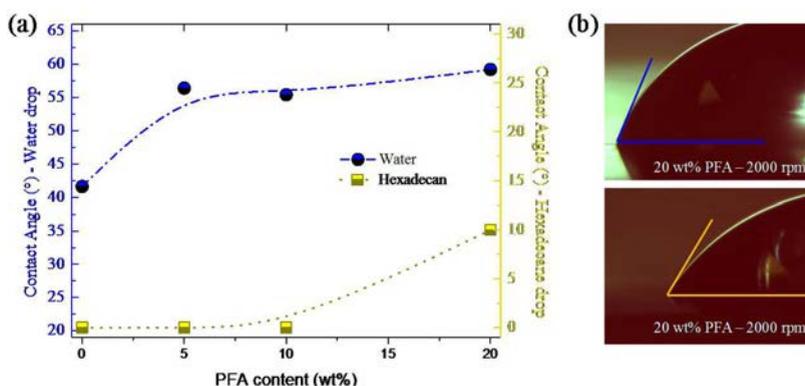

Fig. 4. (a) Influence of PFA content (wt%) on water and hexadecane contact angle (rotation speed: 8000 rpm) (b) Maximal contact angles obtained for thicker polymer layer (spin-coating rotation speed: 2000 rpm) for water (top picture) and oil (bottom picture)

It first appears that the developed encapsulation layer (without PFA) is neither hydrophobic (water contact angle of 42°) nor oleophobic (hexadecane contact angle of 0°). However, increasing the content of PFA came with an increase of both water and hexadecane contact angles. Furthermore, it can be seen in Fig. 4. (b) that increasing the thickness layer enhance hydrophobic and oleophobic surface properties (contact angles of 67° and 53° for water and hexadecane respectively).

3. Conclusions

Within the framework of FP7 European project PiezoMAT, several partners are working to produce a multi-NWs pressure based fingerprint sensor. Chemically inert UV-crosslinkable polymer encapsulation layer have been developed to transfer the mechanical force from the finger to the NWs while protecting their integrity. The work presented here highlighted that it was possible to prepare and to process a crosslinkable formulation based on diacrylate (macro)monomers and to obtain thin polymer encapsulation layers exhibiting Young modulus (E^*) and thickness (h_{pol}) in line with model's recommendations. More, the surface properties (hydrophobicity and oleophobicity) have been improved by incorporating fluorinated acrylate into the formulation which might enhance the external stress resistance and the life-time of the developed sensors.

Acknowledgements

References

[1]   J. Volk, J.Radó, I.E. Lukács, Integrated piezoelectric nanowire arrays for high resolution tactile mapping, Proc. Eng., Submitted (2016).
[2]   R. Dauksevicius, R. Gaidys, E. P. O' Reilly, Numerical study of near-optimal parameters of polymeric encapsulation layer containing a periodic array of piezoelectric nanowires used for force sensing, 17th International Conference EuroSimE, 2016, pp. 1-6.
[3]   C. Decker, The use of UV irradiation in polymerization, Polym. Int.45 (1998) 133-141.
[4]   A. Bhattacharya, R. Paramita, Polymer Grafting and Crosslinking, John Wiley & Sons, Inc., 2008.
[5]   G.Lamour, A. Hamraoui, A. Buvailo, Contact Angle Measurements Using a Simplified Experimental Setup, J. Chem. Educ.87 (2010) 1403-1407.