THE INFLUENCE OF FILLER COMBINATION ON THE REFRACTIVE INDEX OF POLYIMIDES USED IN PHOTOVOLTAICS

Andreea Irina BARZIC[1], Raluca Marinica ALBU[1], Maria Andreea LUNGAN[2], Iuliana STOICA[1]

[1] *"Petru Poni" Institute of Macromolecular Chemistry, Iasi, 700487, Romania, e-mail: irina_cosutchi@yahoo.com*
[2] *Sara Pharm Solutions, Calea Rahovei, no.266-268, Electromagnetica Buisness Park, 050912, Bucuresti, Romania, e-mail: mariaandreea.lungan@gmail.com*

Abstract: *This work is focused on investigation of a set of multiphase polyimide composites that can be used in photovoltaic applications as shielding layers. The polyimide is reinforced with two sorts of nanoparticles known for their high refractive index, namely TiO_2 with either ZnS, Se, Te or ZrO_2. The loading level is maintained low (1-8%) in order to preserve the optical clarity of the coatings. The main goal is to attain hybrid materials that match their refractive properties to those of the transparent conductive oxide, namely SnO_2. The effect of the reinforcement degree and the combination of the fillers on the refractive index of the samples is discussed. The optical losses caused by the mismatch of the refraction properties of the layers composing the solar cell are evaluated. These aspects are affecting the percent of radiations that are propagating towards the junction and therefore the conversion efficiency is influenced by this. The presented results are of paramount significance for preparation of the shielding layers used in future photovoltaics with greater performance.*

.

Keywords: *polyimide, composites, reflection losses, photovoltaics.*

1. Introduction

Numerous modern technologies are relying on the use of transparent thermoplastic polymers, namely liquid crystal displays, optical lens, light emitting diodes, optical waveguides and photovoltaic systems [Lin,2020; Hulubei,2019]. In the latter application, polymers are ideal for replacing the rigid glass cover. Under long-term sunlight exposure, the material is subjected to various temperatures, which must not affect its optical and mechanical properties. Moreover, in a solar cell, the polymer layer is joined with a transparent conductive oxide (TCO), so optical phenomena are taking place at the interface and need close investigation. Hence, besides good interfacial adhesion, proper matching of the light dispersion characteristics in each medium must be achieved. This is essential for avoiding reflection losses at the interface, which may cause dramatic decrease of the conversion efficiency of the solar cell.

Polyimides (PIs) are highly distinguished among the engineering plastics for their remarkable balance of thermal, mechanical, adhesion and optical properties. Transmittance of the radiations from visible domain is highly improved when introducing cycloaliphatic sequences in the PI structure, along with flexible bonds and/or bulky side groups [Hulubei,2007]. Such molecular design strategy is aiming to reduce the charge transfer complex (CTC), which affects the PI coloration and transparency [Fe,2012]. A recent approach to increase the refractive index of the PIs consists in inserting of atoms or substituents with elevated atomic polarizability or molar refraction and low atomic/molar volumes [Nam,2019]. The presence of sulfur, phosphorus, heavy and aromatic and π-conjugated structures are ideal candidates for attaining this goal [Nam,2019]. In addition to this, reinforcement of PIs with inorganic and highly polarizable fillers (e.g. ZrO_2, ZnS, TiO_2, ZnO, Se, Te) is further enhancing the refractive index [Kim,2019].

In this paper, a set of multiphase PI composites are analyzed for use as protective covers for solar cells, operating in superstrate configuration. For this purpose, a semi-aliphatic PI matrix is loaded with several types of filler combinations. The group contribution theory is employed for refractive index evaluation of both PI matrix and corresponding composites. Reflection losses of the samples in regard to *SnO_2* TCO layer, are assessed. The data are investigated in relation to the conversion efficiency of the photovoltaic device.

2. Materials

The PI matrix is prepared by polycondensation reaction of 4-(2,5-dioxotetrahydrofuran-3-yl)- tetralin -1,2-dicarboxylic anhydride tetralin dianhydride (TDA) and 3,3'-sulfonyldianiline (S-DAN) in 1-methyl-2-pyrrolidinone solvent. The preparation scheme of this imide polymer structure is depicted in Figure 1.

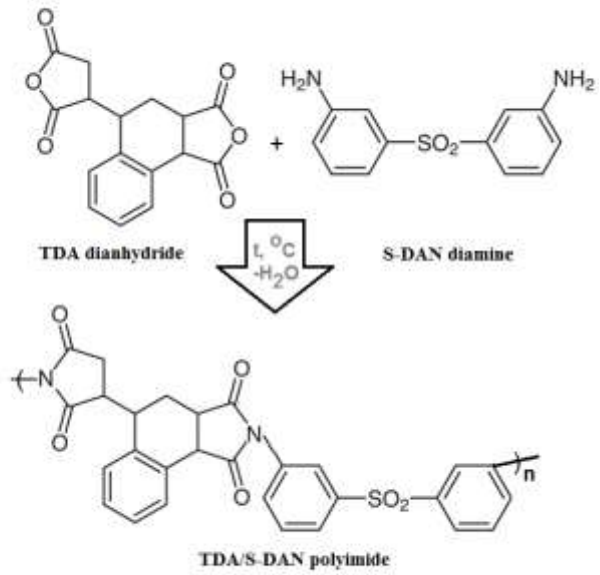

Figure 1: *The preparation of the analyzed TDA/S-DAN polyimide structure.*

TDA/S-DAN matrix is further filled with several combinations of inorganic particles, namely: TiO_2/ZnS, TiO_2/Se, TiO_2/ZrO_2, and TiO_2/Te. The reinforcements agents are added in equal amounts for each case (50/50) and the cumulative amount in the mixture of fillers ranges from 1 to 8%.

Molecular modeling of the TDA/S-DAN structure is performed with Chem 3D Ultra 8 (demo version) software. For obtaining the conformation of the PI five structural units (SUs) in minimized energy conditions, the MM2 force field is used.

3. Results and discussion

3.1 Molecular modeling of PI

The conformational properties of the polymer are greatly influencing their optical, thermal and mechanical properties. The PI chain flexibility is arising from the peculiarities of its chemical structure. The degree of freedom, which depicts the general shape of the macromolecule, is given by torsion angle made by linkages among imide rings and phenyls or among the aromatic rings connected through the sulfone group. The TDA dianhydride presents a carbon-carbon single bond, which enables a high degree of freedom. All these aspects are expressing the flexibility of the TDA/S-DAN chain (modeled for 5 SUs), as seen in Figure 2. This favors good dimensional stability of the PI films.

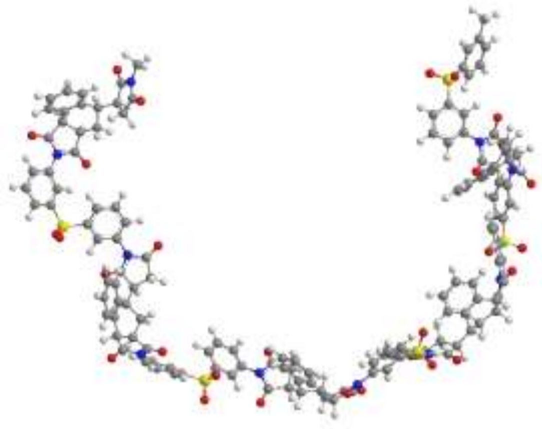

Figure 2: *The molecular modeling image of five SUs corresponding to TDA/S-DAN polyimide.*

3.2 Refraction properties

The refractive index (noted n) is an optical constant that contains information on the speed of the radiations in free space in regard to the studied medium. Also, when discussing the propagation of the radiations in media with distinct refraction properties, n parameter shows the degree of bending of a ray of light when entering from the first medium into the second one.

The refractive index of the PI and its corresponding composites is estimated based on Lorentz-Lorenz relation:

$$R_u = V_u\left(n^2 - 1\right)/\left(n^2 + 2\right) \quad (1)$$

where molar refraction (R_u) and molar volume (V_u) are determined using the group contribution theory [Groh,1991]. The required increments of the substructures forming the PI sample are selected from literature [Groh,1991].

By utilizing the group contribution method, we obtain a molar refraction of 130.89 cm^3/g and molar volume of 337.97 cm^3 for the structural unit of the semi-aliphatic TDA/S-DAN matrix. Inserting these data in the Lorentz-Lorenz relation, a refractive index of 1.702 is attained. The high value of the n parameter could be attributed to the presence of phenyl and imide rings, combined with sulfone groups - all increasing the molecular polarizability.

For the composite samples, the refractive index is considered to be additive function of the inserted fillers and PI matrix compositions, as displayed in equation (2):

$$n_{compos} = n_{PI} w_{PI} + n_{f1} w_{f1} + n_{f2} w_{f2} \quad (2)$$

where w_{PI} is the weight fraction of the TDA/S-DAN polymer, while w_{f1} and w_{f2} are the weight fractions of the first and second filler, respectively.

The refractive index of each filler is taken from literature [Kim,2019; Ciesielski,2018]. These data are subsequently introduced in the equation (2) together with n value of the TDA/S-DAN matrix for assessment of the refraction properties of the multiphase PI composites. As illustrated in the Figure 3, the magnitude of the refractive index is influenced by the type of filler combinations. Since TiO_2 in rutile phase has a refractive index of 2.7, this type of inorganic particles is mixed with other ones (ZnS, Se, ZrO_2, or Te) and embedded in the PI. Regardless the level of loading, the system containing TiO_2 and Se has the lowest n values, whereas the composite filled with TiO_2 and Te has the highest refractive index values. This is the result of differences in polarizability and implicitly of the refractive index of the secondary filler.

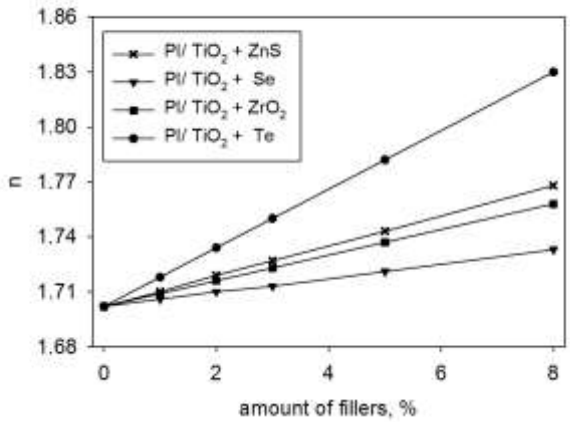

Figure 3: *The refractive index variation with the introduced filler amount in the TDA/S-DAN polyimide.*

On the other hand, it can be observed that as the reinforcement degree of the PI matrix is increasing from 1% to 8%, the refractive index is enhanced. The loading level is maintained low in order to preserve the transparency of the multiphase composites in the visible domain. The latter aspect, combined with high refraction properties lie at the basis of the requirements for shielding covers for solar cells since they interfere in the conversion efficiency.

3.3 Optical losses

When light is passing from the protective cover to the TCO layer, a part of the incident rays are reflected in the incident medium. This is taking place when there is a large discrepancy between the refractive indices of each medium. The TCO considered in this study is tin oxide (SnO_2), known to have a wide band gap energy (3.6 eV) and refractive index of 1.925 at 589 nm [Gong,2019]. At normal incidence, the reflection losses are evaluated and displayed in the Figure 4. The presence of the filler in higher amounts seems to diminish the optical losses at sample/TCO interface, thus a higher percent of radiations are passing towards the active zone of the photovoltaic cell, increasing its efficiency.

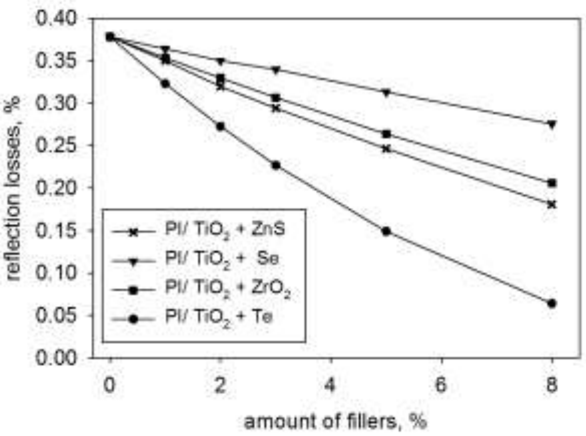

Figure 4: *The reflection losses dependence on the introduced filler amount in the TDA/S-DAN polyimide.*

As the refractive index of the studied PI composites is closer to that of the tin oxide, the optical losses become smaller. The system made from TDA/S-DAN filled with TiO_2 and Te lead to the best results, given the lowest reflection losses attained in this case. In other words, the incident rays are transmitted in a bigger percent and converted into electricity by the junction of the solar cell. This idea is supported by other researchers that highlight the importance of the light management in solar cells [Enrichi,2020; Jäger,2020; Jacobs,2019]. The future of these applications is still relying on improving the propagation of the radiations in such layered devices and specific strategies are formulated to diminish the optical losses [Krc,2006; Wang,2016].

4. Conclusions

This work is analyzing some multiphase polyimide systems reinforced with two kinds of fillers. The purpose of these materials was to reduce the optical losses when they are used for solar cell shielding. A semi-aliphatic polyimide containing chalcogen atoms is used as matrix. Molecular modeling data indicate that the used polymer structure displays high chain flexibility, enabling good dimensional stability of the films. The level of filler loading is kept low to avoid light scattering and thus to maintain good optical clarity of the samples The combination of the inserted particles is influencing the magnitude of the refractive index. As the refraction properties of tin oxide and the composite samples are closer, the optical losses at their interface are reduced. This is observed particularly for the TDA/S-DAN filled with TiO_2 and Te. For this system, an upgraded conversion efficiency of the solar cell could be achieved.

Acknowledgements: This work was supported by a grant of Romanian Academy Projects "Polymer materials. Correlations of structure, morphology, optical and electrical properties" (P8.3). The financial support of European Social Fund for Regional Development, Competitiveness Operational Programme Axis1 – Project ‘Petru Poni Institute of Macromolecular Chemistry–Interdisciplinary Pol for Smart Specialization through Research and Innovation and Technology Transfer in Bio(nano) polymeric Materials and (Eco)Technology’, InoMat-Pol (ID P_36_570, Contract 142/10.10.2016, cod MySMIS: 107464) is gratefully acknowledged.

5. References

1. [Lin,2020] Lin Y., Bilotti, E., Bastiaansen, C.W.M., Peijs, T., Transparent semi-crystalline polymeric materials and their nanocomposites: A review, Polym. Eng. Sci., 60, 2351, 2020.
2. [Hulubei,2019] Hulubei, C., Albu, R.M., Lisa, G., Nicolescu, A., Hamciuc, E., Hamciuc, C. and Barzic, A.I., Antagonistic effects in structural design of sulfur-based polyimides as shielding layers for solar cells, Sol. Energ. Mater. Sol. Cells, 193, 219, 2019.
3. [Hulubei,2007] Hulubei, C., Hamciuc, E., Bruma, M., New imide type polymers based on epiclon, Rev. Roum. Chim., 52, 891, 2007.
4. [Fe,2012] Ke, F., Song, N., Liang, D., & Xu, H., A method to break charge transfer complex of polyimide: A study on solution

behavior, J. Appl. Poly. Sci., 127, 797, 2012.

5. [Nam,2019] Nam, K.-H., Lee, A., Lee, S.-K., Hur, K., Han, H. (2019). Infrared Transmitting Polyimides Based on Chalcogenide Element-Blocks with Tunable High-refractive Indices and Broad Optical Windows, J. Mater. Chem. C, 7, 10574, 2019.
6. [Kim,2019] Kim, H., Ku, B.C., Goh, M., Ko, H.C., Ando, S., You, N.H., Synergistic Effect of Sulfur and Chalcogen Atoms on the Enhanced Refractive Indices of Polyimides in the Visible and Near-Infrared Regions, Macromolecules, 52, 827, 2019.
7. [Groh,1991] Groh, W. and Zimmermann, A., What is the lowest refractive index of an organic polymer?, Macromolecules, 24, 6660, 1991.
8. [Ciesielski,2018] Ciesielski, A., Skowronski, L., Pacuski, W., Szoplik, T., Permittivity of Ge, Te and Se thin films in the 200–1500 nm spectral range. Predicting the segregation effects in silver, Mat. Sci. Semicond. Process., 81, 64, 2018.
9. [Gong,2019] Gong, J., Wang, X., Fan, X., Dai, R., Wang, Z., Zhang, Z. and Ding, Z., Temperature dependent optical properties of
SnO2 film study by ellipsometry, Opt. Mater. Express, 9, 3691, 2019.
10. [Enrichi,2020] Enrichi, F., Righini, G.C., Solar Cells and Light Management Materials, Strategies and Sustainability, Elsevier, 2020.
11. [Jäger,2020] Jäger, K., Sutter, J., Hammerschmidt, M., Schneider, P.-I., Becker, C., Prospects of light management in perovskite/silicon tandem solar cells. Nanophotonics, 10, 1991, 2020.
12. [Jacobs,2019] Jacobs, D. A., Langenhorst, M., Sahli, F., Richards, B. S., White, T. P., Ballif, C., Catchpole, K.R., Paetzold, U.W., Light Management: A Key Concept in High-Efficiency Perovskite/Silicon Tandem Photovoltaics, The J. Phys. Chem. Lett., 10, 3159, 2019.
13. [Krc,2006] Krc, J., Zeman, M., Campa, A., Smole, F., Topic, M., Novel approaches of light management in thin-film silicon solar cells, MRS Proceedings, 910. doi:10.1557/proc-0910-a25-01, 2006.
14. [Wang,2016] Wang, D.-L., Cui, H.-J., Hou, G.-J., Zhu, Z.-G., Yan, Q.-B., Su, G., Highly efficient light management for perovskite solar cells, Scientific Reports, 6. 18922, 2016.
15. [Bardhan,2021] Bardhan Roy, A., Vinay Kumar, K., Saha, M., Light management studies by using different surface texturing for thin c-Si solar cells. Applied Physics A, 127(2), 2021.