ONE-COMPONENT CATIONIC PHOTOINITIATORS BASED ION COUMARIN SCAFFOLD IODONIUM SALTS AS HIGHLY SENSITIVE PHOTOACID GENERA 3D-VAT PRINTING NANOCOMPOSITE PHOTOPOLYMERS

Joanna Ortyl[1,2], Mariusz Galek[2], Filip Petko[1,2], Andrzej Swieży[1,2]

[1]Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland;
[2] Photo HiTech Ltd., Life Science Park, Bobrzyńskiego 14, 30-348 Cracow, Poland.

Coumarin and its derivatives gain great interest in the field of photochemistry, due to their properties such as polarized structure, desirable spectral properties, and high photoactivity. The outstanding photoreactivity has allowed coumarin to find wide photopolymerization applications. Coumarin derivatives are used as photosensitizers in cationic and radical polymerization.[1] However, coumarins are particularly important because they are perfect for one-component photoinitiating systems.

The use of the coumarin chromophore in the structure of iodonium salts was a breakthrough in the design of iodonium salts. Until then, one-component iodonium photoinitiators were simple diaryliodonium salts proposed in the 1970s by Prof. Crivello.[2] These salts have the significant disadvantage of poor absorption above 300 nm, which limits their applications. The new iodonium salts solve this problem with their efficient absorbing coumarin chromophore and the push-pull effect in their structure.[3]

The influence of the arrangement of electron-donating substituents in the coumarin chromophore on their photophysical properties and photoinitiating activity is analyzed. Five new coumarin-based iodonium salts exhibit two patterns of D–π-A structure – longer and shorter. They differ in the strength of the push–pull effect, which determines all properties of such compounds. Due to the intense ICT absorption band, new photoinitiators a reactive at 365 nm, 405 nm, and 415 nm. They exhibit excellent photoinitiating activity toward monomers such as vinyl ethers, epoxides, oxetanes, and glycidyl ethers at room temperature.[4] Coumarin-based iodonium salts proved to be excellent photoinitiators for nanocomposite DLP 3D-VAT printing.

Acknowledgments: The presented work was funded by the OPUS LAP project contract number 2020/39/I/ST5/03556 “Advanced photopolymerized nanocomposite materials processed by additive manufacturing”.

References

1. F. Dumur, Recent Advances on Coumarin-Based Photoinitiators of Polymerization, Eur. Polym. J., 2022, 163, 110962.
2. Crivello, J. V.; Lam, J. H. W., Macromolecules 1977, 10 (6), 1307–1315.
3. M. Topa, E. Hola, M. Galek, F. Petko, M. Pilch, R. Popielarz, F. Morlet-Savary, B. Graff, J. Laleveé and J. Ortyl, One- Component Cationic Photoinitiators Based on Coumarin Scaffold Iodonium Salts as Highly Sensitive Photoacid Generators for 3D Printing IPN Photopolymers under Visible LED Sources, Polym. Chem., 2020, 11(32), 5261– 5278.

4. F. Petko, A. Świeży, M. Jankowska, P. Stalmacha, J. Ortyl, Push–pull coumarin-based one-component iodonium photoinitiators for cationic nanocomposite 3D-VAT printing, Polym. Chem., 2023, 14, 3018