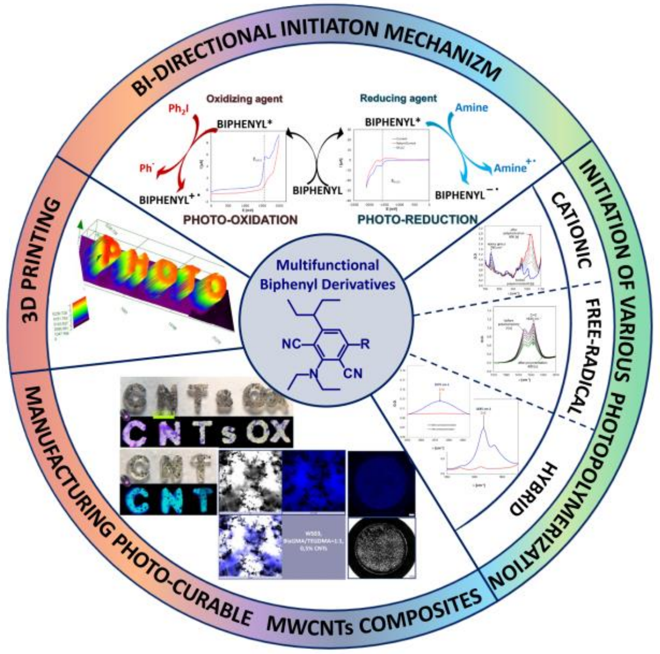
CRACOW UNIVERSITY OF TECHNOLOGY
Department of Chemical Engineering and Technology
Laboratory of Photochemistry and Optical Spectroscopy

Photocurable polymer resins for the fabrication of polymer nanocomposites using 3D-VAT printing technology



Joanna Ortyl
PhD DSc. Prof.

Our vision

The key advantage is to enable the implementation of a functional nanoscale additive into known 3D printing processes, using standard monomers, where printing would take place using commercially available SLA/DLP printers.

Contact us

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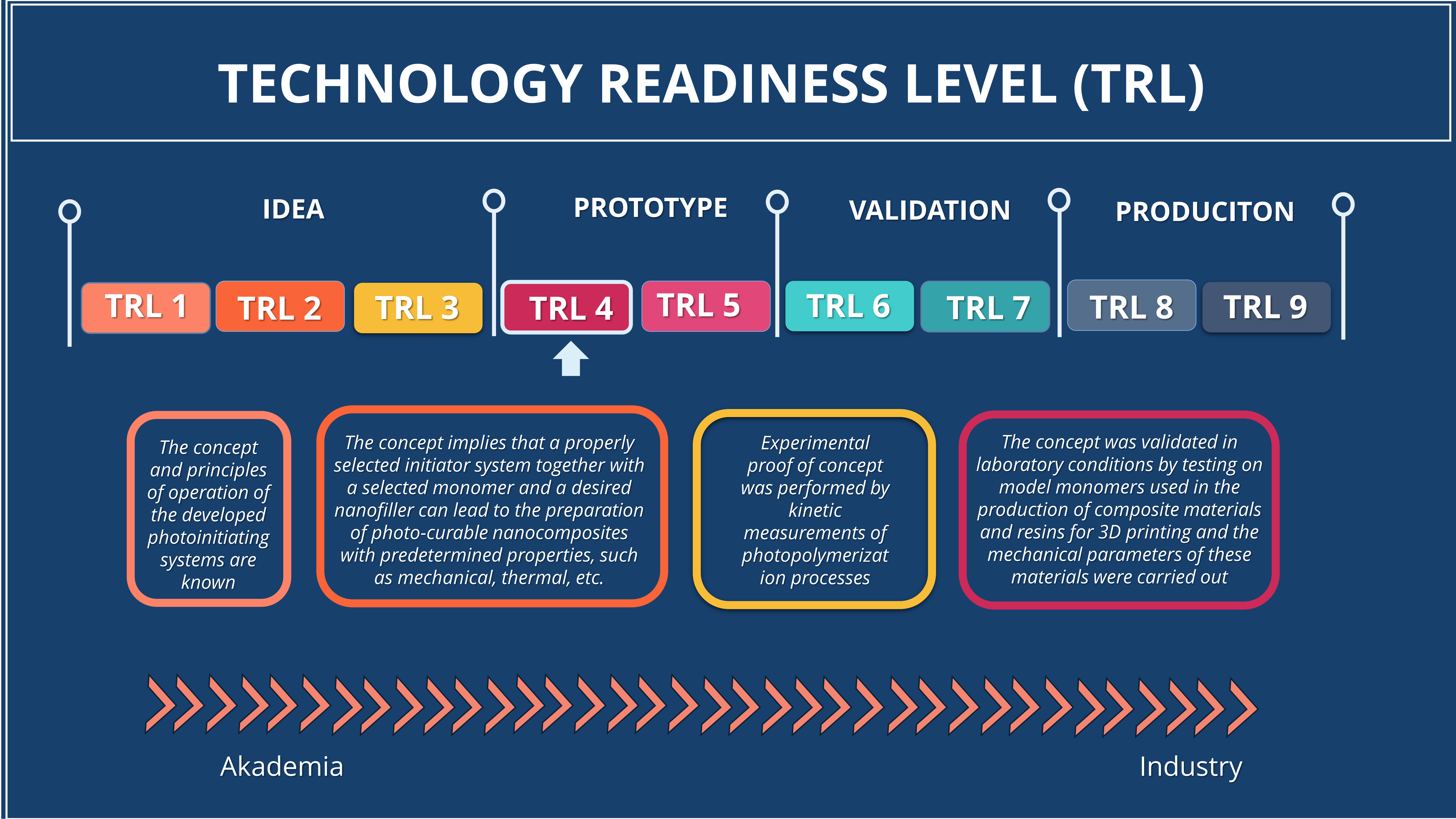
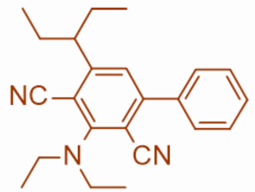


TECHNOLOGY READINESS LEVEL (TRL)
IDEA
PROTOTYPE
VALIDATION
PRODUCITON
TRL 1
TRL 2
TRL 3
TRL 4
TRL 5
TRL 6
TRL 7
TRL 8
TRL 9
The concept and principles of operation of the developed photoinitiating systems are known
The concept implies that a properly selected initiator system together with a selected monomer and a desired nanofiller can lead to the preparation of photo-curable nanocomposites with predetermined properties, such as mechanical, thermal, etc.
Experimental proof of concept was performed by kinetic measurements of photopolymerizat ion processes
The concept was validated in laboratory conditions by testing on model monomers used in the production of composite materials and resins for 3D printing and the mechanical parameters of these materials were carried out
Akademia
Industry

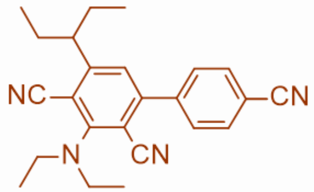
Basic information of the invention

MATERIALS

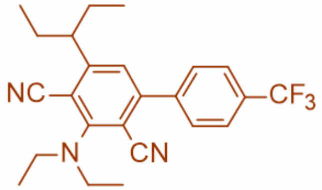
BIPHENYL DERIVATIVES



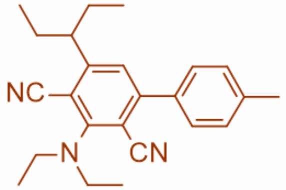
BI-PH



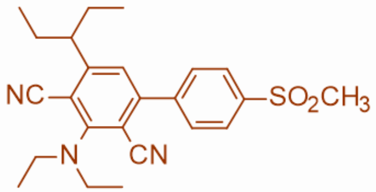
BI-PH-CN



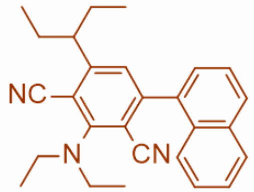
BI-PH-CF_3



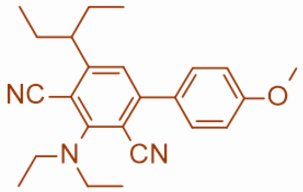
BI-PH-CH_3



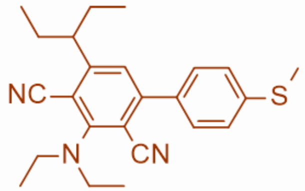
BI-PH-SO_2-CH_3



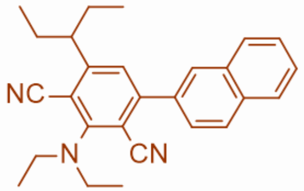
BI-1-NPH



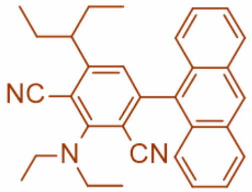
BI-PH-O-CH_3



BI-PH-S-CH_3

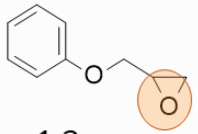


BI-2-NPH

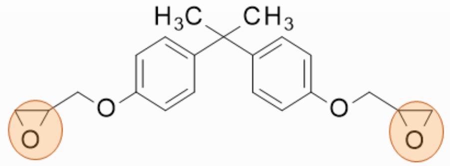


BI-1-AN

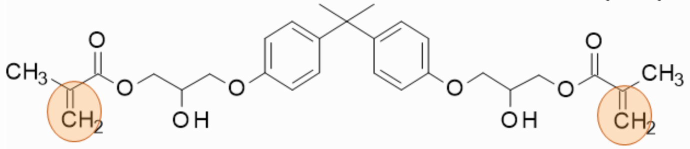
MONOMERS



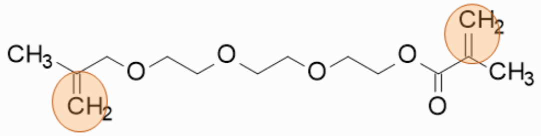
1,2-epoxy-3-phenoxypropane (**EPXPROP**)



2,2-bis[4-(glycidyloxy)phenyl] propane (**DGEBA**)

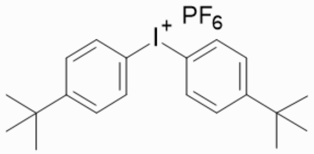


bisphenol A-glycidyl methacrylate (**BisGMA**)



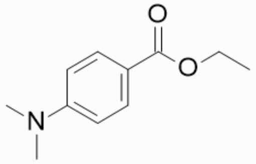
triethylene glycol dimethacrylate (**TEGDMA**)

PHOTOINITIATOR



bis-(4-t-butylphenyl)iodonium hexafluorophosphate (**Speedcure 938**)

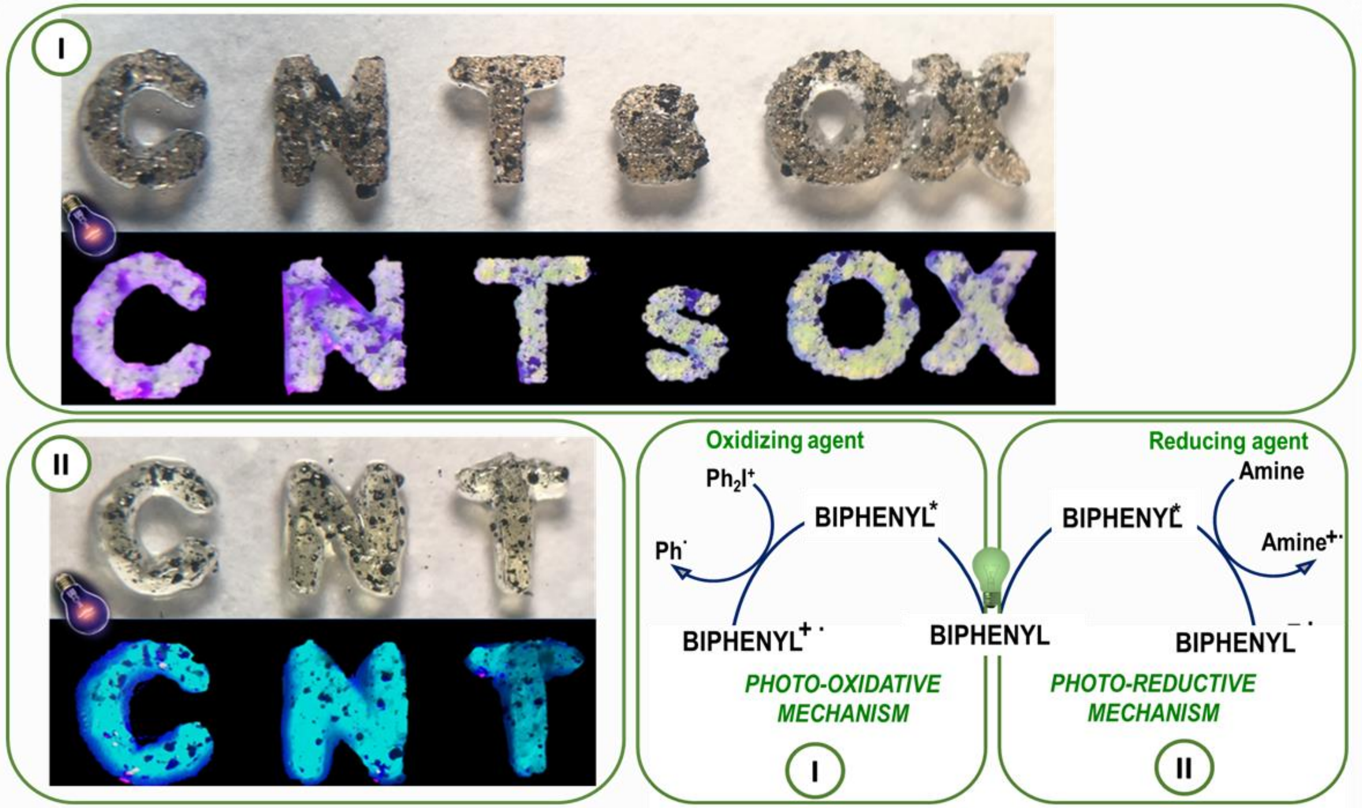
CO-INITIATOR



Ethyl 4-(dimethylamino) benzoate (**EDB**)

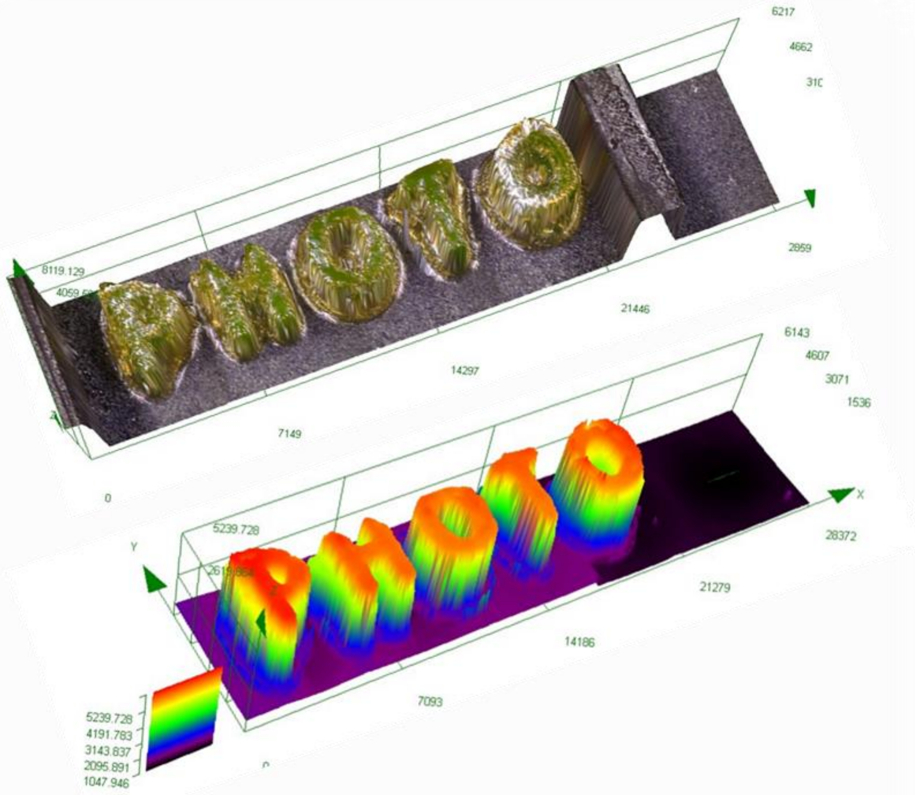
Basic information of the invention

3D PRINTING OF PHOTOCURABLE NANOCOMPOSITES



3D inscriptios made by free-radical photopolymerization of monomer BisGMA/TEGDMA (50 %/50 % w/w) mixtures in the presence of a two-component photoinitiating system based on I) BI-PH-O-CH3 (0.1 wt.%) + iodonium salt (1 wt. %), II) BI-PH-CN (0.1 wt.%) + EDB (1.5 wt. %) at room temperature and under atmospheric conditions. A: photocurable MWCNT nanocomposites seen in sunlight; B: photocurable MWCNT nanocomposites seen under excitation 365 nm UV- LED light source.

3D PRINTING OF CLEAR RESIN



. 3D inscription made by the cationic photopolymerization of monomer mixtures: DEGBA/EPXPROP composition (70%/30% w/w) in the presence of a two-component photoinitiating system based on BI-PH-S-CH3 (0.2 wt. %) and bis-(4-t-butylphenyl)iodonium hexafluorophosphate (2 wt. %).

Basic information of the invention

REAL-TIME MONITORING OF PHTOCURING PROCES OF NANOCOMPOSITES

BIPHENYL DERIVATIVES + **SPEEDCURE 938**

+ **RESIN: BisGMA/TEGDMA (1:1)** + **carbon nanotubes**

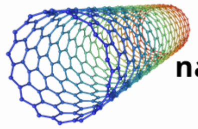


PHOTO-OXIDATION MECHANISM

BIPHENYL DERIVATIVES + **EDB**

+ **RESIN: BisGMA/TEGDMA (1:1)** + **carbon nanotubes**

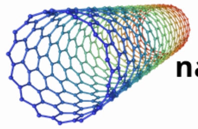


PHOTO-REDUCTION MECHANISM

REAL-TIME FTIR

$$Conversion\ [\%] = \left(1 - \frac{A_{After}}{A_{Before}}\right) * 100\ \%$$

A_{Before} – area of the absorbance peak corresponding to a given group or bond in the investigated monomer prior to photopolymerization, and A_{After} – area of the same absorbance peak, at the given polymerization time.

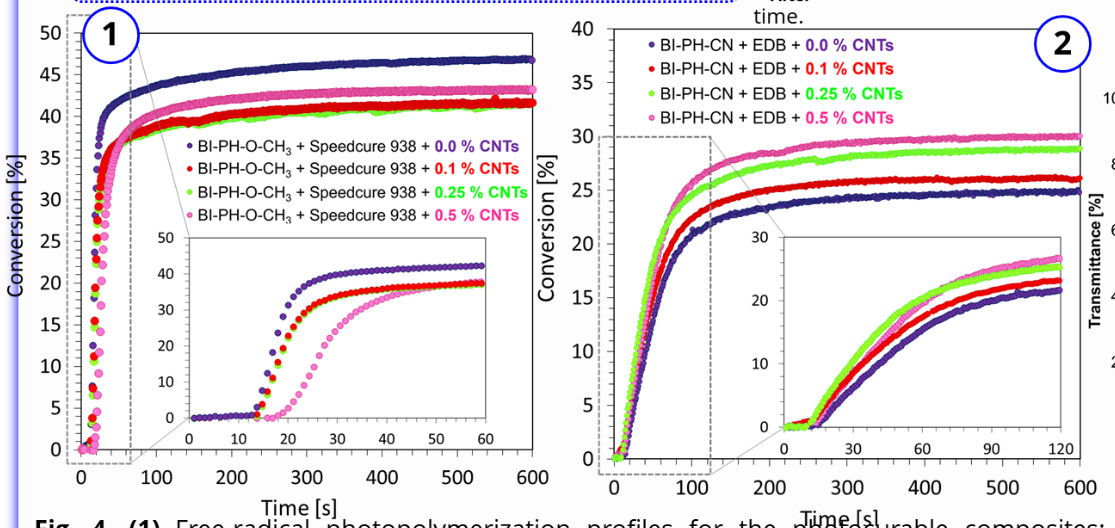


Fig. 4. (1) Free-radical photopolymerization profiles for the photocurable composites: BisGMA/TEGDMA (50 %/50 % w/w) with bis-(4-t-butylphenyl)iodonium hexafluorophosphate (1 % wt.) and BI-PH-O-CH3 (0.1% wt.), (2) Free-radical photopolymerization profiles for the photocurable composites: BisGMA/TEGDMA (50 %/50 % w/w) with EDB (1.5% wt.) and BI-PH-CN (0.1% wt.), polymerized at 365 nm (16.27 mW/cm^2).

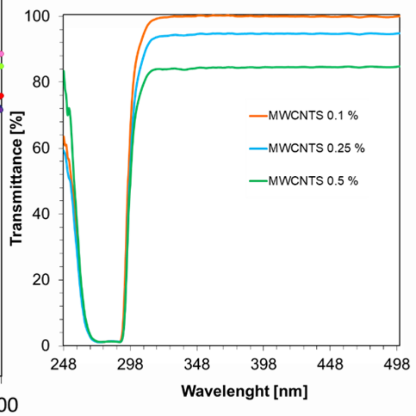


Fig. 5. Transmittance spectrum of thin layer of resin with different content od MWCNTs (0.1; 0.25; 0.5 wt. %), without photoinitiating system

PHOTO-DSC

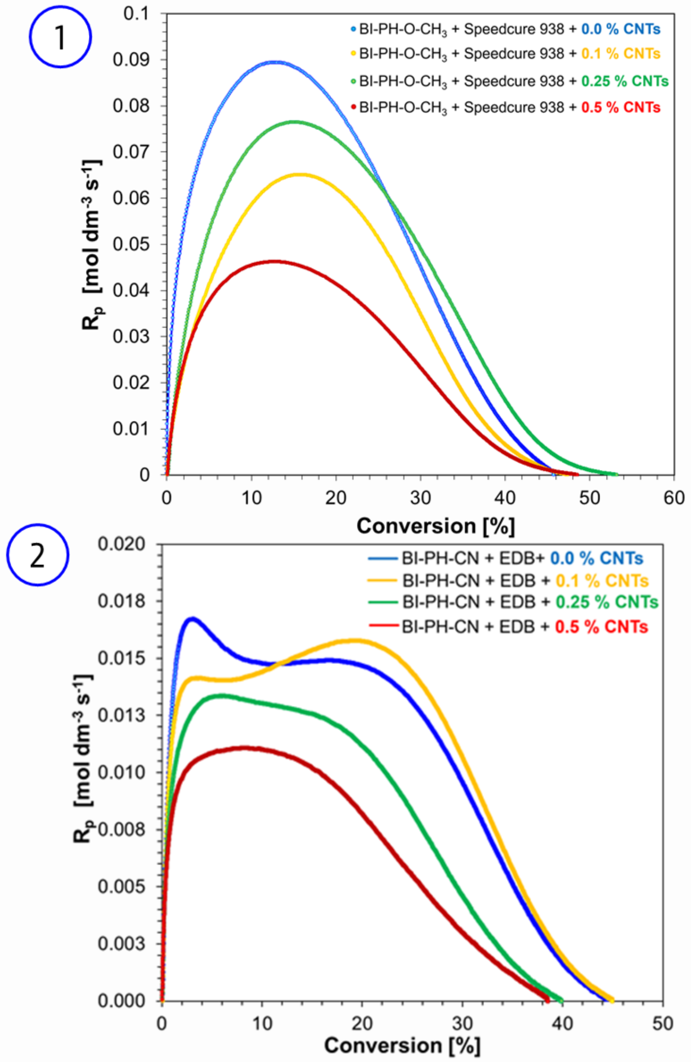


Fig. 6. (1) The effect of double bond conversions in BisGMA/TEGDMA/CNTs composites the on rate of polymerization (Rp) , initiated with BI-PH-O-CH3 (0.1 %wt.)/Speedcure 938 (1 % wt.) system: a) at 25°C, (2) The effect of double bond conversions in BisGMA/TEGDMA/CNTs composites on rate of polymerization (Rp) initiated with BI-PH-CN (0.1 %wt.)/EDB (1.5 % wt.) system: a) at 25°C.

„Our” commercial SLA/DLP 3D Printers

Zortrax Inkspire	Prusa SL1	Moai Peopoly	Formlabs Form 2	ANYCUBIC-mono	Sparkmaker
3D-DLP 405nm DLP-RGB	3D-DLP 405nm	3D-SLA 375nm 3D-SLA 405nm	3D-SLA 405nm	3D-DLP 405nm DLP-MONO	3D-DLP 405nm

Benefits

Research results have demonstrated the feasibility of using well-known 3D-VAT technology to obtain high-precision nanocomposites (polymeric materials containing nanometer-sized filler).

MARKET DEMAND FOR THE PRODUCT

Companies specializing in the manufacture and distribution of photo-curable compositions

Manufacturers of 3D printers

Companies with engineering and technical profile

The growth rate of the global nanocomposites market over the next 8 years will be about 15% per year!

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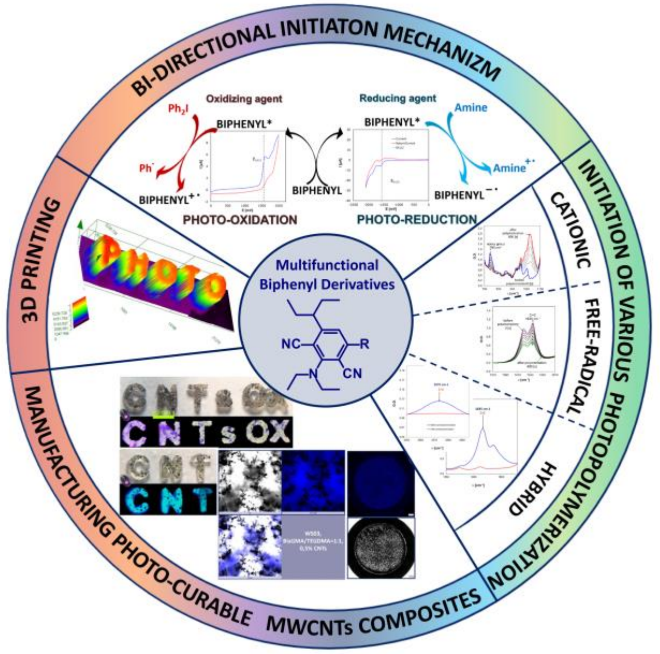

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