VAT PHOTOPOLYMERIZATION OF SWCNT-BASED SOFT COMPOSITES WITH HIGH MIXED ION-ELECTRON CONDUCTIVITY ENABLED BY IONIC LIQUIDS

Sergei Nechausov[1], Aslan Miriyev[1]

[1]Department of Mechanical Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel

Vat photopolymerization (VPP) is a UV-light-assisted additive manufacturing technique capable of producing high-resolution parts with excellent surface finishes and micron-scale features. VPP has been effectively used to fabricate thermoelectric, bioelectronic, energy storage, sensor and actuator devices[1]. One of the next-generation functional materials proposed for the fabrication of these devices is mixed ion-electron conductors (MIECs), capable of efficiently transporting and coupling both ionic and electronic charges[2]. We have recently demonstrated the compatibility of imidazolium-based ionic liquids (ILs) with specific photopolymerizable monomers and cross-linkers. This compatibility allowed us to formulate a photopolymer composition for VPP of ionic conductive gels[3]. The insertion of single-walled carbon nanotubes (SWCNT) into photopolymer compositions for VPP can provide sufficient electronic conductivity for the 3D printed material with a low electrical percolation threshold. However, the VPP of SWCNT composites is a long-standing challenge, as SWCNTs in dispersions typically agglomerate in bundles by van der Waals forces. Moreover, SWCNT dispersions are poorly transparent to UV light and exhibit non-Newtonian behavior due to forming an elastic nanotube network. Considering these aspects is crucial for successful 3D printing of SWCNT dispersions using UV-assisted techniques.

Here, we demonstrate that adding 1-alkyl-3-methylimidazolium tetrafluoroborate [AlkylMIm][BF_4] ILs in photopolymer compositions allowed dispersing SWCNT bundles, provided ionic conductivity in the resulting 3D printed material, and accelerated the photopolymerization. Using polar monofunctional monomers N-vinylpyrrolidone and 2-hydroxyethyl methacrylate with polyethylene glycol methacrylate (M_w ~ 750) as a cross-linker allowed avoiding syneresis of IL from polymer matrix during UV and thermal post-curing process.

We showed that the dispersion stability increased with the increase of alkyl tail length of IL cation and obtained the following stability order: [EthylMIm]<[ButylMIm]<[HexylMIm]~[OctylMIm]. The increase of the conversion after applied thermal post-curing was shown by dynamic-DSC and FTIR. Rheology analyses showed that the photopolymer compositions with SWCNT concentration lower than 0.4 wt.% exhibit shear thinning behaviour with dynamic viscosity (<10 Pa*s) at a shear rate of 10 s^{-1}, appropriate for VPP. The impact of SWCNT on photorheology curves, specifically the gel time and plateau of storage modulus, was also examined.

Equivalent circuits were employed to separate the ionic and electronic conductivity by fitting Nyquist plots obtained through impedance spectroscopy. Analyzing the photorheology and working curves of the photopolymerizable IL-SWCNT dispersions allowed us to successfully 3D print MIECs reinforced with high SWCNT content (up to 0.4 wt%) with enhanced thermal, electronic and ionic conductivity, and mechanical properties.

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2. S. Hazra, A. Banerjee, A. Nandi, ACS Omega, 7, 37, 32849-32862, 2022.
3. S. Nechausov, et al., Additive Manufacturing, 56, 102895, 2022.