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► To cite this version:

Aude Heloise Bonardi, Fabrice Bonardi, Frederic Dumur, Didier Gigmes, Jean Pierre Fouassier, et al.. Fillers as Heaters for Photothermal Polymerization upon NIR Light. *Macromolecular Rapid Communications*, 2019, pp.1900495. 10.1002/marc.201900495 . hal-02491523

HAL Id: hal-02491523

<https://hal.science/hal-02491523>

Submitted on 2 Jul 2020

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Fillers as Heaters for Photothermal Polymerization Upon NIR Light

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Abstract:

Photoinduced thermal polymerization upon Near-Infrared light (NIR) has been reported in the literature. In this latter approach, a component able to convert the NIR light into heat must be used in combination with a thermal initiator to initiate the free-radical polymerization of (meth)acrylates. In previous recent studies, some dyes have been presented as very efficient heat generators (called heaters). In the present work, different fillers are investigated as heaters and compared to organic NIR dyes. An alkoxyamine (e.g. BlocBuilder-MA) is used as thermal initiator and will be dissociated by the heat generated by the NIR photoexcitation of the fillers. In the present work, several fillers are examined: graphene oxide, graphene nanoplatelets, multi-walled carbon nanotubes and silicon carbide. Due to the energy of the photon delivered, NIR light curing is challenging but offers several advantages compared to visible light. Notably, the most interesting feature is the deeper penetration of the light inside the photocurable resin, enabling the polymerization of thick samples. Parallel to this, incorporation of fillers in resins allows a unique access to composites through photothermal polymerization of (meth)acrylates. Three different wavelengths of irradiation have been studied: 785 nm, 940 nm and 1064 nm.

Most of the photopolymerization processes involves a photoinitiator, which is a compound capable to generate polymerization initiating species (e.g. cations, anions or free radicals) after absorption of a certain wavelength of light. Thus, it is possible to transform a liquid or viscous monomer or resin into a highly crosslinked solid polymer. It allows the fabrication of a large range of materials e.g. coatings, inks, paints, adhesives, composites, 3D printed objects... However, a strong limitation of the photopolymerization technology is the low UV light penetration for the curing of filled samples and in particularly for the access to composites.[1][2] In a recent paper, we have proposed the photothermal polymerization as a first answer to overcome the problem of composites polymerization.[3] In this work, the use of a Near-Infrared light rather than a UV light was proposed, even if UV light remains extensively used in industrial photopolymerization. As a specificity of the NIR light, this wavelength range allows a deeper light penetration inside the reaction media and especially for resins containing high contents of fillers. Initiation of the polymerization process was proposed thanks to a unique combination of a thermal initiator and an organic molecule. The dyes proposed in this work were mostly based on the cyanine scaffold and could act as a light-to-heat convertor (NIR heater).

The mechanisms of light-to-heat conversion is extensively described in the literature for phototherapy applications.[4] Various organic dyes are known in the literature to be efficient for light-to-heat conversion. However, light-to-heat conversion is not restricted to organic dyes and metal components or mineral fillers can also be used. As metal components, gold nanoparticles are often used.[5] But graphene oxide is also described in the literature.[6] In recent and elegant works, free-radical polymerization initiated by carbon black nanoparticles as NIR heaters has been reported.[7] However, with carbon black particles the photothermal polymerization was much less efficient than with organic NIR dyes e.g. IR-780 borate [3]. In this communication, we propose the use of different other fillers as heaters for the polymerization of methacrylate upon NIR light exposure and compare their ability to an organic dye. The different fillers used in this work are presented in the Scheme 1: multi-walled carbon Nanotube, Graphene Nanoplatelets, Graphene oxide and Silicon Carbide. These fillers are already commonly used for composites manufacturing in industry.

SCHEME 1. FILLERS USED AS HEATERS IN THIS WORK

Multi-walled Carbon Nanotubes are fillers which exhibit unique electronic and mechanical properties. More precisely, these compounds are characterized by their low density, high elastic modulus, strengths 10 to 100 times higher than that of the strongest steel at a fraction of the weight.[8] One application of composites with carbon nanotubes is electromagnetic shielding or antistatic.[9] Graphene Nanoplatelets are also already used for the design of nanocomposites.[10] Notably, an enhanced thermal conductivity of the corresponding epoxy composites was demonstrated upon incorporation of Graphene Nanoplatelets. As a consequence, these fillers have thus a huge potential for applications in electrical insulation with enhanced thermal conductivity.[11] Composites prepared are also lightweight and easily processed. Graphene oxide has been widely used for the design of graphene-based functional materials.[12] A graphene oxide sheet is a single graphite layer bearing various oxygenated functional groups. Graphene oxide as fillers are used to produce conducting polymers with applications in drug releasing and energy storage for example. These composites exhibit good electrochemical activity, large specific surface areas, high conductivity and biocompatibility.[12] To finish, we have also chosen silicon carbide (SiC) as fillers. It has been used for a wide variety of industrial purposes due to its high hardness and high resistivity to extremely high temperature.[13-14] SiC is used for cutting tools, refractory components and high-power electrical systems. SiC ceramics are already well described in the literature due to their remarkable resistance to radioactivity: these ceramics are notably used in nuclear plants.[15]

Light-to-heat conversion abilities of these different fillers have been estimated upon irradiation to a laser diode@1064 nm. Temperature profiles associated with the photoexcitation at 1064 nm of the different fillers dispersed in Mix-MA (Scheme 2) are reported in the Figure 1. However, due to their filler characters, they are not soluble in the monomer and precipitate **within few hours after preparation**. Therefore, their use as photothermal initiators can only be carried out just after mixing. We observed that with the four tested fillers, it was possible to reach a temperature higher than 60°C, temperature which is necessary for the homolysis of the thermal initiator (BlocBuilder-MA in Scheme 2) and its initiation of the benchmark methacrylate blend (Mix-MA - Scheme 2).[3] However, **from the** temperature profiles, the best heaters are Graphene Nanoplatelets > Multi-walled Carbon Nanotubes ~ Graphene oxide >> SiC (Figure 1). Indeed, after 30s of irradiation, only the first three fillers are able to generate more than 60°C in Mix-MA i.e. SiC is associated with a slower temperature increase (Figure 1, curve 4).

Scheme 2. Chemical structure of the monomers in the benchmark methacrylate blend (Mix-MA) and the thermal initiator **BlocBuilder-MA**.

FIGURE 1. TEMPERATURE PROFILES OF MIX-MA UNDER AIR (TEMPERATURE OF THE SAMPLE VS. IRRADIATION TIME) IN THE PRESENCE OF 0.1 W% (1) MULTI-WALLED CARBON NANOTUBES, (2) GRAPHENE OXIDE, (3) GRAPHENE NANOPATELETS, (4) SILICONE CARBIDE, IRRADIATION WITH A LASER DIODE@1064 NM AT 2W/CM²; THICKNESS=10MM; THE IRRADIATION STARTS AT T = 17S.

The formulations with graphene oxide visually exhibiting a better homogeneity of the dispersions than with the other fillers (Graphene Nanoplatelets, Multi-walled Carbon Nanotubes and silicon carbide) for which a rapid precipitation of fillers could be observed, this filler was selected for the photothermal polymerization experiments (i.e. using 0.1 wt%) in combination with 2 wt% of BlocBuilder-MA as the thermal initiator in the Mix-MA resin. Three wavelengths of irradiation have been tested: @785 nm, @940 nm and @1064 nm. As shown in the Figure 2, the photopolymerization is particularly successful using the Laser Diode at 1064 nm: the polymerization starts very rapidly when the Laser Diode is turned on. However, the two other NIR wavelengths (785 and 940 nm) of irradiation were also efficient with high final methacrylate function conversions (>75%) for multifunctional monomers.

FIGURE 2. POLYMERIZATION PROFILES OF MIX-MA UNDER AIR (METHACRYLATES FUNCTION CONVERSION VS. IRRADIATION TIME) IN THE PRESENCE OF GRAPHENE OXIDE (0.1WT%) AND BLOCBUILDER-MA (2WT%) UPON IRRADIATION TO (1) LASER DIODE@785 NM, (2) LASER DIODE@940 NM, (3) LASER DIODE@1064 NM, THICKNESS=1.4MM; THE IRRADIATION STARTS AT T = 17S.

The mechanism of polymerization is the same as for the photothermal polymerization previously reported with an organic NIR dye used as a light-to-heat converter (in [3]). The polymerization starts when the temperature reaches 50-60°C corresponding to the activation **temperature of Blocbuilder-MA**. Thus, the initiating radicals are formed, allowing the initiation step of polymerization to occur. The mechanism is presented in the Scheme 3. Here, the filler acts as a light-to-heat converter: through irradiation with a NIR light, the filler releases heat. Remarkably, graphene oxide is a better NIR heater than carbon black nanoparticles reported in [7] to initiate polymerization reaction; **indeed**, the photothermal effect of carbon black particles in Mix-MA was reported low in these conditions in [3].

SCHEME 3. CREATION OF INITIATING RADICALS THROUGH PHOTOTHERMAL EFFECT

Then, the heater behavior of graphene oxide is compared to those of organic NIR dyes that have the huge advantages to be fully soluble and stable in organic monomers [3]. The dye Ir-780 borate (Figure 3) proposed by us in [3] was selected for such a comparison (from its excellent heater behavior). As shown in Figure 3, faster light-to-heat conversion is observed for the organic dye (e.g. 100°C is reached after less than 30s of irradiation for the NIR dye vs. 60s for graphene oxide; Figure 3: curves 2 vs. 1). This is in agreement with the higher final methacrylate function conversion for Ir-780 borate/Blocbuilder-MA vs. graphene-oxide/Blocbuilder-MA (75% vs. 65% after 100 s of irradiation).

FIGURE 3. THERMAL IMAGING PHOTOPOLYMERIZATION FOLLOW-UPS (TEMPERATURE VS. IRRADIATION TIME; 1.4 MM SAMPLE) UNDER AIR IRRADIATION FOR MIX-MA IN THE PRESENCE OF BLOCBUILDER-MA (2W%) AND (1) IR-780 BORATE (0.1W%) UPON IRRADIATION AT 785 NM (2) GRAPHENE OXIDE (0.1W%) UPON IRRADIATION AT 1064 NM; IRRADIATION STARTS AFTER 17s.

In conclusion, these preliminary experiments demonstrate the ability of fillers such as graphene oxide to initiate a photothermal polymerization upon NIR light excitation. Thanks to the temperature measurements, good polymerization efficiencies were anticipated and found experimentally. These initial results are encouraging for composites manufacturing upon NIR light irradiation; however, the organic NIR dyes approach as heaters remains the privileged one with good solubility and stability (without any precipitation) in organic monomers associated with higher photothermal effect. The use of NIR for the curing of carbon or glass fibers composites with high depth of cure will be presented in forthcoming works.

Experimental part:

Compounds: Multi-walled Carbon Nanotube, Graphene Nanoplatelets, Silicon Carbide, Graphene Oxide (Scheme 1) have been purchased from Sigma-Aldrich. Ir-780 (Figure 3) has been purchased from Sigma-Aldrich. The benchmark monomer “Mix-MA” is a mixture of (hydroxypropyl)methacrylate (HPMA, 33w%), 1,4-butanediol dimethacrylate (1,4-BDMA, 33w%) and urethane dimethacrylate monomer (UDMA, 33w%), obtained from Sigma Aldrich and represented in Scheme 2. Ir-780 borate was synthesized as previously reported in the literature, without modification and in similar yield [3].

Thermal imaging experiments: an infrared thermal imaging camera Fluke TiX500 was used for thermal imaging experiments. The thermal images were extracted using a Fluke SmartView4.1 Data and then batch processed using a script written in Python. The procedure has been described more in detail in [16].

RT-FTIR polymerization kinetics: a Real-Time Fourier Transform Infrared (RT-FTIR) spectrometer (Jasco 4600) was used to follow the kinetics of polymerization. The follow of the band located at $6100\text{-}6220\text{cm}^{-1}$ is directly related to the double bond C=C conversion. Polymerization is performed in a mold (1.4 mm thick), under air by irradiation with a laser diode. Laser is turned on 17 seconds after the first spectra measurements in order to have a baseline. Details for each experiment are given in the figures caption of the concerned experiment. The procedure has been described more in details in [17].

Acknowledgements

The authors gratefully acknowledge the financial support from the ANR agency and for the grant “ANR FastPrinting”.

Conflict of interest

The authors declare no conflict of interest.

Keywords

Fillers, photothermal effect, graphene oxide, photopolymerization, NIR light, photoinitiator.

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