

State-of-the-Art and Future Challenges of UV Curable Polymer-Based Smart Materials for Printing Technologies

Cristian Mendes-Felipe, Juliana Oliveira, Ikerne Etxebarria, José Luis Vilas-Vilela, and Senentxu Lanceros-Mendez*

The one-step printing of fully functional electronic devices is one of the main goals of additive manufacturing. In general, this approach is increasingly growing, being one of the key developments additive manufacturing processes based on ultraviolet curing. The main reasons for this increasing interest in UV curing based technologies are its advantages, such as fast curing at room temperature, space and energy efficiency, high-resolution patterns, and solvent-free formulations. Despite the important developments, some challenges remain with respect to improving UV curing process and, in particular, to obtain smart UV curable materials, many times based on the inclusion of specific nanoparticles in a UV curable polymer matrix. Thus, this paper reviews the recent developments in UV curable smart materials for printing technologies focusing on both materials and processes. The curing mechanisms and the main materials used in UV photocurable resins are reviewed as well as the main smart and multifunctional materials obtained based on them. Finally, a summary of the main achievement and the future needs are indicated. This review represents therefore a landmark for the development of a new generation of UV curable smart and multifunctional materials and solutions.

1. Introduction

Over the past years, important efforts have been applied to expand the application of nanomaterials through the development of smart and multifunctional composites for their applications in areas ranging from micro devices, to sensor and actuators, as well as energy and biomedical applications.^[1–3] “Smart” materials are defined as a material in which one of its key properties can be altered in a controlled manner in response to an external stimulus.^[2–4] These stimulus-responsive materials can undergo, for example, variations in shape, mechanical properties, transparency, porosity, electrical or magnetic characteristics in response to thermal, mechanical or chemical external stimuli, among others.^[1]

One of the key implementation areas of smart materials are sensors and actuators, allowing to improve, monitoring, feedback, and safety, key issues of the Internet of Things and Industry 4.0 paradigms.^[5]

In this way, smart materials are an intense research area in which new materials, technologies, and applications will emerge in the near future.^[2,3] Application areas of smart and multifunctional materials expand from consumer electronics, civil engineering, aerospace, and automobile to health care and wearables applications.^[6,7] The potential application of smart materials would allow solving engineering problems with improved efficiency and provide an opportunity for the development of new solutions and products.^[1,8]

On the other hand, strategic and technological problems are still hindering the implementation potential of smart materials, despite their important advantages and specificities.^[3,9]

Namely, silicon-based smart materials are manufactured using the time-consuming, expensive, and complicated fabrication processes of traditional semiconductor devices. Further, those manufacturing methods are often based on subtractive processes. In contrast, several of the recently developed smart materials can be implemented by additive manufacturing (AM).^[1,10]

Additive manufacturing is rapidly expanding and modifying the way in which products are designed and manufactured. This technology allows to create complex geometries with customizable material properties, with design freedom and environmental advantage,^[11] by transforming designed files into

C. Mendes-Felipe, Dr. I. Etxebarria, Prof. J. L. Vilas-Vilela, Prof. S. Lanceros-Mendez
BCMaterials—Basque Center for Materials
Applications and Nanostructures
UPV/EHU Science Park
Leioa 48940, Spain
E-mail: senentxu.lanceros@bcmaterials.net

C. Mendes-Felipe, Prof. J. L. Vilas-Vilela
Macromolecular Chemistry Group (LABQUIMAC)
University of the Basque Country (UPV/EHU)
Leioa 48940, Spain

Dr. J. Oliveira, Prof. S. Lanceros-Mendez
Center/Department of Physics
University of Minho
Braga 4710-057, Portugal

Dr. J. Oliveira
Algoritmi Research Centre
University of Minho
Guimarães 4800-058, Portugal

Prof. S. Lanceros-Mendez
IKERBASQUE
Basque Foundation for Science
Bilbao 48013, Spain

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admt.201800618>.

DOI: 10.1002/admt.201800618

fully functional products. On the other hand, the rapid spread of a wide variety of technologies associated with AM, leads to an absence of a comprehensive set of materials, design principles and manufacturing guidelines.

In this scope, UV curable polymer formulations are distinctively suitable for being implemented by AM technologies due to their rapid cure, wide range of properties, and dimensional accuracy, being inks based on UV curable polymers increasingly used to fabricate smart materials.^[12]

Since its onset, the UV curing industry has become one of the most rapidly developing ones within the coatings industry.^[12,13] With the introduction of photocuring of coatings as a viable industrial process well over a decade ago, the UV curing industry has followed a line of steady growth.^[13]

Among the various curing processes, UV-triggered radical polymerization represents an economic, fast and nontoxic method,^[14] especially for coatings.

The advantages of UV curing compared to traditional drying techniques which rely whole or partly on the evaporation of solvents are the “rapid solidification,” high solvent resistance of the cured films, reduced VOC (volatile organic compounds) emissions, high flash points of the ink and overall improved “environmental friendliness,” among others. Further, for the electronics industry, in allows as improved pattern definition.

The current review presents the recent development in UV curable printing technologies with respect to technologies, materials and applications. This paper reports on photoinitiators, monomers and oligomers characteristic of photocurable materials as well as with the corresponding UV curable smart materials obtained from them. Some final comments and future challenges allow to indicate the way for future developments in this scientifically and technologically interesting field.

2. UV Curing Technology and Materials

2.1. Mechanism and Formulations

The use of UV-curable formulations is increasing at a fast rate.^[15] The main reasons for this rapid growth are their fast curing method—in the range of seconds or minutes, the room temperature processing reducing thus the overall energy consumption, space and energy efficiency—smaller curing units as compared with ovens for baking in thermal cure, high-resolution patterns can be obtained, and the use of solvent-free formulations.^[16] In this way, UV-curing is very attractive for the development of engineering applications.

The basic principle that occurs when using UV light is photopolymerization or photocuring (**Figure 1**). Photocuring is commonly defined as a process of rapid conversion of specially formulated, usually liquid solventless compositions into solid films by irradiation with ultraviolet or visible light.^[17] Photopolymerization (**Figure 1**) is defined as a synthesis of polymers by chain reactions that are initiated upon the absorption of light by a polymerizable system, light serving only as an initiating tool and it does not interfere with the propagation and termination stages of the chain process.^[18]

The materials to be used in this polymerization process strongly depend on the fabrication process, which is the scope



C. Mendes-Felipe is a researcher at the BCMaterials, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain. He graduated in chemistry and obtained his master in new materials at the Macromolecular Chemistry Group (LABQUIMAC) at the University of the Basque Country, Leioa, Spain.

His research interest is focused in the area UV curable polymer-based smart and multifunctional materials for printing technologies.



J.L. Vilas-Vilela is currently an associate professor in physical chemistry at the University of the Basque Country, where he is the head of the Macromolecular Chemistry Group. His current research interest includes synthesis and characterization of polymeric and composites materials with smart properties, the synthesis of

biocompatible polymers, and polymers from renewable sources; and the 3D printing of all these materials. He has been working in different companies related with the synthesis and processing of polymeric materials.



S. Lanceros-Mendez is the Ikerbasque Professor at and Scientific Director of the Basque Center for Materials, Applications and Nanostructures, Leioa, Spain. He graduated in physics from the University of the Basque Country, Leioa, Spain and obtained his Ph.D. from the Julius-Maximilians-Universität Würzburg, Germany. He

conducted research at Montana State University, USA, the Pennsylvania State University, USA, and University of Potsdam, Germany. He is an associate professor of the University of Minho, Portugal (on leave) and was an associate researcher at the International Iberian Nanotechnology Laboratory 2012–2014. His work is focused on smart and multifunctional materials for sensors and actuators, energy and biomedical applications.

of the present paper and the inks must be formulated in agreement with the specific printing processes requirements, including, as a relevant parameter, rheological properties.^[1]

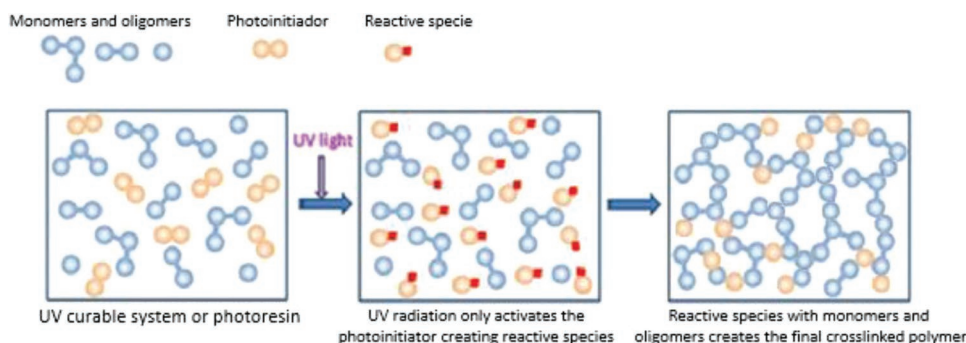


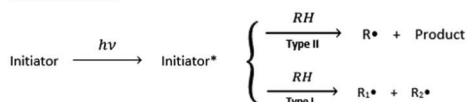
Figure 1. Schematic representation of the photopolymerization process.

The majority of the compositions of photocrosslinkable materials in commercial use consist of mixtures of prepolymers or oligomers combined with di- or polyfunctional monomers and photoinitiators.^[19] Such compositions can be divided into two groups: (1) the ones that cure by free-radical mechanism and (2) the ones that cure by an ionic one.

2.1.1. Free Radical Curing Mechanism

The synthesis of macromolecules by free radical chain polymerization of monomers begins with the generation of free radicals, which are conveniently performed through photo-reactions of the initiator molecules. The simplified overall mechanism is described in **Figure 2**. The most widely used UV-curable resins are based on acrylate, which show high reactivity, i.e., short reaction times in the order of fractions of a second, and offer a large choice of monomers and oligomers. Acrylate-based resin systems typically consist of three basic components: photoinitiator (which generates free radicals when exposed to UV light), functionalized oligomers or prepolymers (which forms the backbone of the polymer network), and monomers (which acts as a reactive diluent to adjust the system viscosity).^[16]

Photoinitiation



Propagation



Chain-Transfer



Termination



Figure 2. Schematic representation of a free radical polymerization reaction of monomer M, a commonly compound with a C=C bond with photoinitiator R.

There are two types of compounds that are commonly used as photoinitiators of free radical polymerizations, which differ in their mechanism for the generation of reactive free radicals: type I or unimolecular photoinitiators and type II or bimolecular photoinitiators. Type I photoinitiators are organic molecules that undergo rapid bond cleavage after absorption of a photon, generating two free radicals that start the polymerization. Type II photoinitiators, including organic molecules, form relatively long lived excited triplet states capable of undergoing hydrogen-absorption or electro-transfer reactions with co-initiator molecules that are deliberately added to the monomer containing system.^[16] Typical type I and type II photoinitiators are listed in **Table 1**. In general, the used monomers, oligomers or prepolymers are the same for both types of photoinitiators.

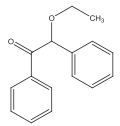
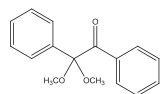
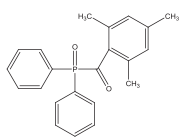
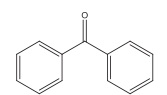
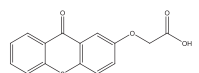
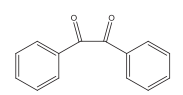
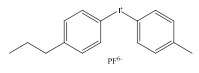
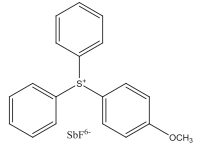
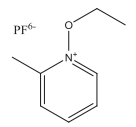
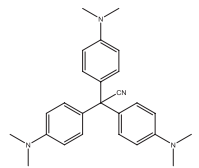
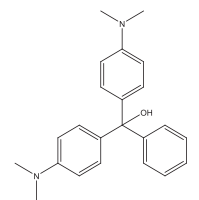
Most of type I photoinitiators contain aromatic carbonyl groups since these compounds undergo rapid bond cleavage resulting in the formation of a pair of radicals. Benzoin ethers, like benzoin ethyl ether, were the first commercially used class of unimolecular photoinitiators and they cleave into benzoyl radical and benzyl ether radical by UV absorption.^[20] Benzil ketals, such as 2, 2-dimethoxy-2-phenylacetophenone, is another effective photoinitiator with good package stability and which photo-cleavage produces benzoyl and dimethoxybenzyl radicals.^[21] Acyl phosphine oxides, such as 2,4,6-trimethylbenzoyl)diphenylphosphine oxide, produces radicals that are much more reactive towards olefinic compounds than carbon-centered radicals.^[22,23]

Type II photoinitiators are organic compound that can form long-lived triplet states after absorbing a photon. These triplet species can abstract a hydrogen or an electron from coinitiator species to produce free radicals. Benzophenone, thioxanthone derivatives or other ketones like 1,2-diketones are typical bimolecular photoinitiators that abstract hydrogen atoms from hydrogen donors to yield excited complexes that initiate polymerization.^[24] Those compounds show the advantage of reducing the oxygen inhibition.^[25]

In spite of the number of available photoinitiators, the search for new initiators is ongoing with the main objective of improving their efficiency.^[26] For example, S-(4-benzoyl)phenylthiobenzoate, BpSBz, has been found to be a type I photoinitiator. Upon exposure to UV light it is cleaved into free radicals which initiate the polymerization of methyl methacrylate.^[27] The most relevant free-radical photoinitiator structures can be found in the references provided in Table 1.

In the case of monomers, also called reactive diluents, used in photopolymerization by free radical mechanism, a large number of them are commercially available. **Table 2** presents

Table 1. Chemical structures of typical photoinitiators used in photopolymerization by free radical and ionic mechanisms.

Photopolymerization mechanism	Type	Class	Example	Chemical Structure	Reference
Free radical	I	Benzoin ethers	Benzoin ethyl ether		[20]
Free radical	I	Benzil ketals	2, 2-dimethoxy-2-phenylacetophenone		[21]
Free radical	I	2,4,6-trimethylbenzoyl)diphenyl-phosphine oxide	Acyl phosphine oxides		[22,23]
Free radical	II	Benzophenone derivatives	Benzophenone		[24]
Free radical	II	Thioxanthone derivates	2-((9-oxo-9H-thioxanthen-2-yl)oxy)acetic acid		[24]
Free radical	II	1,2-diketones	Benzil		[24]
Ionic	Cationic	Diarylodonium salt	(4-Methylphenyl) [4-(2-methylpropyl)phenyl] iodonium hexafluorophosphate		[42]
Ionic	Cationic	Triarylsulfonium salt	Diphenyl(4-methoxyphenyl)sulfonium hexafluoroantimonate		[43]
Ionic	Cationic	Ammonim salt	N-ethoxy-2-methylpyridinium hexafluorophosphate		[44]
Ionic	Anionic	-	Crystal violet leuconitrile (CVCN)		[45]
Ionic mechanism	Anionic	-	Malachite green leucohydroxide (MGOH)		[45]

some of the most used monomers. A monomer is selected for a specific application or processing technology based upon its effect on viscosity, curing speed, film properties, shrinkage during polymerization, cost, shelf life, volatility, odor, and toxicity. Acrylates are the most widely used reactive diluents.^[21]

When selecting a monomer, a high functionality (number of double bonds that will be attacked and will lead to polymerization) is pursued for fast reactions. However, this can result in early gelation or vitrification of the cross-linked structure, hindering complete conversion, being mono and

Table 2. Commonly used monomers in photopolymerization by free radical and ionic mechanisms.

Photopolymerization mechanism	Class	Example	Chemical Structure	Merits	Drawbacks	Reference
Free radical	Monoacrylates	2-Ethyl hexyl acrylate (EHA)		Good flexing action	Volatile, slow cure and poor solvent resistance	[28]
Free radical	Monoacrylates	n-butyl acrylates (BA)		Good viscosity reducer and flexing action	Volatile, slow cure and poor solvent resistance	[29]
Free radical	Diacrylates	1,4-butanediol diacrylate (BDDA)		Relatively good viscosity reducer and low volatility	Suspected skin irritation sensitizers	[30]
Free radical	Diacrylates	Diethyleneglycol diacrylate (DEGDA)		Good viscosity reducer	Adverse dermatitic and toxicity properties	[31]
Free radical	Triacrylates	Pentaerythritol triacrylate (PETA)		Rapid cure	Eye irritant and suspect to be carcinogenic	[32]
Free radical	Tetraacrylates	Pentaerythritol tetraacrylate		Low volatility	Eye irritant and suspect to be carcinogenic	[32]
Free radical	Vinyl ethers	Diethyleneglycol divinyl ether (DEGDE)		High diluting power and low toxicity	Eye irritant	[33]
Free radical	Vinyl ethers	1,4-Cyclohexanedimethanol divinyl ether (CHDMDE)		High diluting power and low toxicity	Eye irritant and toxicity properties	[33]
Free radical	Vinyl ethers	Triethylene glycol divinyl ether (TEGDE)		High diluting power and low toxicity	-	[33]
Free radical	-	Styrene		Low cost and high flexibility when cured	Volatile and hazardous	[21]
Free radical	-	N-vinyl pyrrolidone		Low toxicity and high flexibility when cured	-	[21]
Ionic	Vinyl ethers	Diethyleneglycol divinyl ether		Fast photopolymerization	Inconvenient and expensive synthesis	[48]
Ionic	Propenyl ethers	Trimethylolpropane tripropenyl ether		Good reactivity	-	[47]
Ionic	Propenyl ethers	Trimethylolpropane dipropenyl ether		Good reactivity	-	[47]
Ionic	Epoxides	3,4-Epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate		Low shrinkage and chemical and thermal resistance	Fragility and low toughness	[49]
Ionic	Epoxides	Diclycidylether derivative of bisphenol A (ADE)		Low shrinkage and chemical and thermal resistance	Fragility and low toughness	[50]

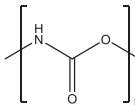
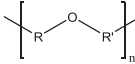
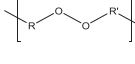
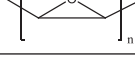
difunctional monomers the most widely used. In addition, the introduction of heterocyclic structures with oxygen causes a substantial acceleration of the polymerization rate.^[17] 2-Ethyl hexyl acrylate (EHA),^[28] n-butyl acrylates (BA),^[29] 1,4-butanediol diacrylate (BDDA)^[30] and diethyleneglycoldiacrylate (DEGDA)^[31] are some examples of acrylate monomers.

Trifunctional and tetrafunctional monomers are also used but to a lesser extent. Examples of a trifunctional monomer are

acrylate or methacrylate esters of glycerol, such as pentaerythritoltriacylate (PETA), widely used in printing inks. A tetrafunctional monomer example is pentaerythritol tetraacrylate, used in adhesives and coatings.^[32] However, in most of the cases a mixture of various monomers is used.

Another type of monomers used in free radical polymerizations are the vinyl ethers. Compared to acrylates, vinyl ethers show the advantages of high diluting power and low toxicity.

Table 3. Commonly used oligomers for photopolymerization by free radical mechanism.

Type	Chemical structure	Merits	Drawbacks
Polyurethane		Versatility, best combination of hardness and elasticity, weatherability and adequate H ₂ O resistance	Aromatic yellow, aliphatics costly, aliphatics toxic and plasticized by H ₂ O
Polyether		Fairly good adhesion, flexibility, elasticity and UV-resistance	Low glass transition
Polyester		Fairly good adhesion, versatility and hardness	Poor UV-resistance and hydrolytic stability
Epoxy		Adhesion, hydrolytic stability, hardness and acid resistance	Poor UV-resistance and high viscosity

Diethyleneglycol divinyl ether (DEGDE), cyclohexane dimethanol divinyl ether (CHDMDE), and triethylene glycol divinyl ether (TEGDE) are some examples of this type of monomers.^[33] Styrene, which is the most widely used reactive diluent for unsaturated polyester resin systems, and *N*-vinyl pyrrolidone are two remarkable reactive diluents. Styrene shows a good performance, with a relatively low cost and is highly flexible when cured.^[32,34]

For oligomers, also called prepolymers, and in the same way as with monomers, acrylated ones are most frequently used for photopolymerization by free radical mechanism due to their higher reactivity, lower volatility, environmental degradation resistance, low color and chemical resistance in comparison with other oligomers.^[35] The chemical structure of the oligomers has influence on the viscosity of the reaction mixture, which affects both the propagation and the termination polymerization steps. Thus, the final properties of the obtained material depend on the oligomer structures.

There are four basic structures for acrylated oligomers employed in photopolymerization that contains the following chemical groups: polyurethane, polyethers, polyesters, and epoxy resins. **Table 3** shows the structures of these chemical groups and the merits and drawbacks for all of them. The typically used oligomers are composed by these chemical groups and acrylated groups on the extremes of the structures. The functionality (number of acrylated groups) can be two, three, four or higher and the basic chemical structures can be more complex.^[21]

2.1.2. Ionic Curing Mechanism

UV-induced free-radical polymerization has enjoyed commercial success over ionic polymerization. However, the UV-induced ionic curing systems are finding increasing application in several specialized fields due to their advantages compared to free radicals: no oxygen inhibition, minimal sensitivity to water and the ability to polymerize vinyl ethers, oxiranes (epoxides), and other heterocyclic monomers that do not polymerize by a free radical mechanism.^[36] In addition, ionic photopolymerization has the ability for dark cure, cation-initiated polymerization can continue after exposure to the radiation source until the reactive cations become immobilized.

Moreover, the shrinkage of the polymers during ionic photocuring is lower than in free radical photocuring, showing cured material, in general, high mechanical properties and good adhesion to various substrates.^[37]

In the same way as free-radical polymerization systems, two types of compositions curing by ionic mechanism can be obtained: cationic and anionic photopolymerization systems. It is worth to mention that the possibility that photoinitiated polymerization can occur through an anionic mechanism has long been overlooked and, even today, literature reports on anionic photopolymerization are rare.^[18]

Cationic photopolymerization was discovered by Prof. Crivello^[38–40] in the late 1970s. This mechanism is initiated with photoinitiators that can absorb UV light to create reactive cations that initiate the polymerization reaction. Onium salt-type photoinitiators were first used. They have general structure that consists of an organic cationic moiety with a positive charge on a heteroatom and a counter anion in the structure. This category includes aryldiazonium, diaryliodonium, triarylsulfonium, alkyl-arylsulfonium, phenacylsulfonium, phosphonium, ammonium, and addition-fragmentation-type onium salts, among others.^[41] Some examples such as (4-methylphenyl) [4-(2-methylpropyl)phenyl] iodonium hexafluorophosphate,^[42] diphenyl(4-methoxyphenyl)sulfonium hexafluoroantimonate,^[43] or *N*-ethoxy-2-methylpyridinium hexafluorophosphate^[44] are shown in Table 1.

The difference between anionic and cationic photopolymerization only lies in the photoinitiator, anionic photopolymerization working in the same way as cationic photopolymerization. The initiation mechanism is the photoinduced release of a reactive anion, which is added to the monomer. The polymer is then formed through the repetitive addition of monomers to the growing anionic chain. This mechanism has been found to photoinitiate the polymerization of methyl 2-cyanoacrylate (CA) using crystal violet leuconitrile (CVCN) and of malachite green leucohydroxide (MGOH)^[45] (Table 1). More recent studies have revealed other compounds such as ketoprofen^[46] or more complex compounds such tertiary-amine-releasing systems, aromatic formamides, cobalt–amine complexes, amine–imides, and aminoketones.^[20] The most relevant ionic photoinitiator structures can be found in the references included in Table 1.

In the case of monomers used in cationic photopolymerization, different types have been proposed and

reported in literature, mainly epoxides, vinyl ethers and propenyl ethers.^[36] Vinyl ethers are really attractive since their photopolymerization is rather fast and photocuring rates are in many cases faster than for the corresponding free-radical photopolymerization of acrylic monomers. However, their synthesis is expensive. A good alternative is the use of propenyl ethers, which show good reactivity. Some examples of vinyl and propenyl ethers typically used are diethyleneglycol divinyl ether, trimethylolpropane tripropenyl ether, and trimethylolpropane dipropenyl ether,^[47,48] which are shown in Table 2.

Epoxides are another type of monomers employed in cationic photopolymerization due to their high mechanical properties, relatively low shrinkage, and chemical and thermal resistance. Nevertheless, epoxy matrix suffers from fragility and low toughness. 3,4-Epoxy cyclohexylmethyl-3',4'-epoxy cyclohexane carboxylate and dicycidylether derivative of bisphenol A (ADE) are some examples^[49,50] shown in Table 2.

It should be noted that the oligomers employed in ionic photopolymerization, both cationic and anionic, show similar structures to the mentioned monomers but with a large chain structure, high functionality and more voluminous groups leading to higher viscosity.^[28]

2.2. Cure Extent Evaluation

Control the UV curing process is as important as the choice of the photoinitiator and the monomers and oligomers to be used. Photopolymerization typically occurs within seconds or minutes, being an important issue to study the kinetics of photo-polymerization both quantitatively and qualitatively. In that, the most used methods to evaluate the cure extent are differential scanning photocalorimetry (photo-DSC), real-time infrared spectroscopy (RT-IR), and confocal Raman microscopy.

Differential scanning photocalorimetry measures the heat flux evolved by the photo-initiated exothermal reaction as a function of time at a given temperature. It is very well suited for the determination of kinetic parameters, such as enthalpy, degree of conversion, rate constants, and Arrhenius parameters, among other relevant parameters.^[21] There are several cases where the extent of the cure has been evaluated by this technique. Photo-DSC has been used to study the cure kinetics of UV-initiated cationic photo-polymerization of epoxy resin monomers in presence of different photoinitiators and to investigate the photo-reactivity with respect to their chemical structure.^[51] The effect of the presence of a hyperbranched OH-functionalized polymer (HBP) on the kinetics of cationic photopolymerization of an epoxy system was also investigated using Photo-DSC and RT-IR.^[52] Similarly, Photo-DSC was applied to study the gelation and photopolymerization of some multifunctional acrylates.^[53]

The development of the Real-Time Infrared Spectroscopy technique has improved the ability to monitor UV-curing processes. RT-IR, with its milliseconds resolution time, has been successfully used to monitor photopolymerizations occurring within a fraction of a second. RT-IR spectroscopy involves the exposure of a photopolymerizable sample simultaneously to IR and UV radiations. Therefore, this technique enables to monitor the specific changes in chemistry during UV-curing by

following the decay of the stretching vibrations of the reactive functional groups. Thus, from the recorded profile the degree of conversion can be evaluated, i.e., the amount of unreacted functional groups that remain in the UV-cured polymer.^[21,54]

RT-IR spectroscopy is being used for several years, for example, for the characterization of the UV curing kinetics of a thiol-ene system containing trimethylolpropane tris(2-mercaptoacetate) and trimethylolpropane diallyl ether.^[55] Real-Time FTIR-ATR spectroscopy has been also used to study the kinetics of photopolymerization reactions induced by monochromatic UV light testing various photoinitiator systems.^[56] The evaluation of the photopolymerization kinetics obtained by Photo-DSC and RT-IR techniques does not necessarily provide comparable results due to the absence of temperature control during RT-IR analysis or the different amounts of material employed.^[57]

RT-IR and photo-DSC techniques do not provide information about the cure extent throughout the film thickness. Thus, another technique has been developed, which allows the measurement of chemical bonds throughout the film thickness, confocal Raman microscopy. This technique combines the chemical information from vibrational spectroscopy with the spatial resolution of confocal microscopy.^[58] Thus, it has been used to characterize UV cured coatings, in one case depth profiles of acrylate curing conversion were recorded in order to elucidate the interaction of photoinitiator, photostabilizer, and irradiation source^[58] and to investigate the aluminum flakes in metallic coatings.^[59]

2.3. Printing Technologies for UV Curable Polymers

Among the several existing 2D and 3D printing technologies, just few of them have been consolidated in industry as potentially useful techniques such as offset lithography, flexography, inkjet printing, xerography, or rotogravure. Printing processes can be divided into two different groups: the ones that use a master image carrier or a printing plate (e.g., screen printing and spray coating) and the ones that use computers digital files to create the pattern (e.g., inkjet printing or stereolithography, among others).^[60–62]

In 2D printing, the layers are cured right after the complete image is printed. The curing is carried out in a different way depending on the nature of the ink, focusing the present review on the ones cured by UV light. In 3D printing technologies instead, the curing of the resin is performed layer by layer until the whole 3D object is created. In this case there are specific UV curing techniques, such as stereolithography (SLA) or digital light processing (DLP), based on the spatially controlled solidification of a liquid resin layer by layer using UV laser and a UV DLP-based projector, respectively.^[63]

Inkjet, spray, and screen printing (Figure 3) are widely used 2D printing techniques that enable the usage of different type of inks. Inkjet printing (Figure 3a) is a nondirect contact deposition technique since drops are deposited from a certain distance with respect to the substrate. A pattern is designed in the computer and the cartridge is moved all over the substrate following the pattern and depositing drops in the required places. This method allows the design of complex patterns with high-resolution customizing the material deposition volume

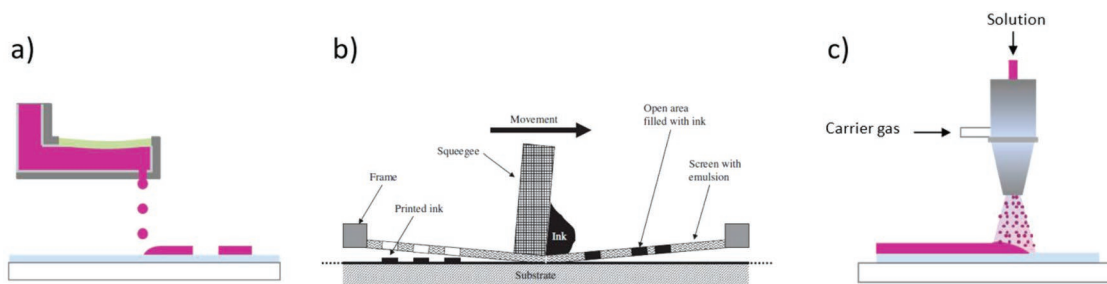


Figure 3. Graphical representation of a) inkjet printing, b) screen printing, and c) spray coating techniques. (b) Reproduced with permission.^[65] Copyright 2009, Elsevier.

and location, i.e., it provides the droplet-on-demand option (DOD). The material is deposited drop by drop, hence, for a continuous path drops need to overlap or touch each other. Multilayers can also be printed and the thickness of the layer can be controlled either in this way or changing the amount of the material in the drop.^[64] Inkjet printing allows high resolution, which can easily range from 300 dpi up to 1200 dpi. The inks are required to be of low viscosity (4–30 cP).^[65]

Screen printing (Figure 3b) is a printing technique where a mesh is used in order to transfer the pattern to the substrate. A squeegee is moved all over the substrate along the mesh, transferring the ink to the substrate. This technique allows the printing of complex patterns with a resolution of about 100 μm . Screen printing is characterized by a large wet film thickness and the requirement of relatively high viscosities (100–100 000 cP).^[65]

Similar to inkjet printing, spray coating (Figure 3c) is not a direct contact deposition technique and the material is deposited in micron size droplets. The liquid coming out from a nozzle is atomized by ultrasonic vibrations or pressure and the droplets are deposited randomly. An inert gas, such as nitrogen is used as a carrier gas. The nozzle is moved all over the substrate in order to cover the full surface. Depending on the solution flow rate and the moving speed of the nozzle, the thickness of the layer can be controlled. This deposition method does not allow complex patterns unless a mask with the desired pattern is used. This technique allows the use of inks with a large viscosity range (10–1000 cP).^[65]

Stereolithography (SLA), digital light processing (DLP), continuous liquid interface production (CLIP) and PolyJet (Figure 4) are 3D printing techniques based on UV curing processes for the fabrication of an object.^[66]

In stereolithography (Figure 4a) specific surface regions of photosensitive liquid resin undergo localized polymerization by exposure to a UV laser.^[67,68] The 3D object is fabricated by the photopolymerization of each layer on a platform. A UV laser beam scans the surface of the resin and selectively hardens the material corresponding to a cross section of the 3D product, which is fabricated from the bottom to the top. The required supports for overhangs and cavities are automatically generated and later manually removed. Once the object is completed, the excess resin is drained to be reused. The main advantages of SLA are accuracy and resolution, where stereolithography is better than other solid free-form fabrication (SFF) techniques (in most SFF techniques the smallest printed details are in the 50 to 200 mm range, vs 20 mm in many commercially available

stereolithography set ups).^[63] The main disadvantage instead is the cost.

Digital light processing (Figure 4b) is similar to stereolithography, being the light source the main difference. DLP uses a more conventional light source and it is applied to the whole photopolymer resin in a single pass, leading to a faster process than SLA. The DLP projector displays the image of the 3D model onto the liquid polymer. The exposed liquid polymer hardens, built plate moves down and the liquid polymer is once more exposed to light. The process is repeated until the 3D model is complete and the vat is drained of liquid, revealing the solidified model. As for SLA, in DLP support structures are required and parts with high resolution are fabricated.^[69] DLP and SLA printing techniques allow the use of resins in a large viscosity range (100–10 000 cP).^[66] However, expensive and limited materials are some drawback of this techniques compared with thermal-based 3D printing techniques such as FDS, which has the advantages of low cost, good strength and multimaterial capability.^[70]

The SLA or DLP techniques can be used with a wide variety of monomers and resin systems.^[71]

Continuous liquid interface production (Figure 4c) is another UV curing based 3D printing technique. It is a bottom-up continuous process where the UV light beam passes through a window at the bottom part of the vat with the resin illuminating a cross section of the object. In order to avoid the attachment of the solidified resin to the window, there is a oxygen inhibited dead zone. This process allows the fabrication of smooth surfaces.^[72]

PolyJet (Figure 4d) is an additive manufacturing printing technique. The photopolymer is deposited and subsequently the UV light cures the material until the 3D object is completed layer by layer. A roller embedded into the printhead smooths the deposited droplets into a flat layer. UV lamps, which are also mounted in the printhead, fully cures the jetted photopolymer droplets. PolyJet support material is a separate composition formulated to release from the part when jetted off or dissolved with water.^[73–75] Similar to thermal-based 3D printing techniques, the build orientation can significantly affect elastic modulus and fracture stress but tensile strength is relatively insensitive to printing direction.^[66]

During the printing processes, some common problems that can occur include bad adhesion of the resin/ink to the substrate (or between layers in the case of UV-based 3D printing techniques), deformations, cracks or porous appearance in the printed pieces or even incomplete cured materials. Those

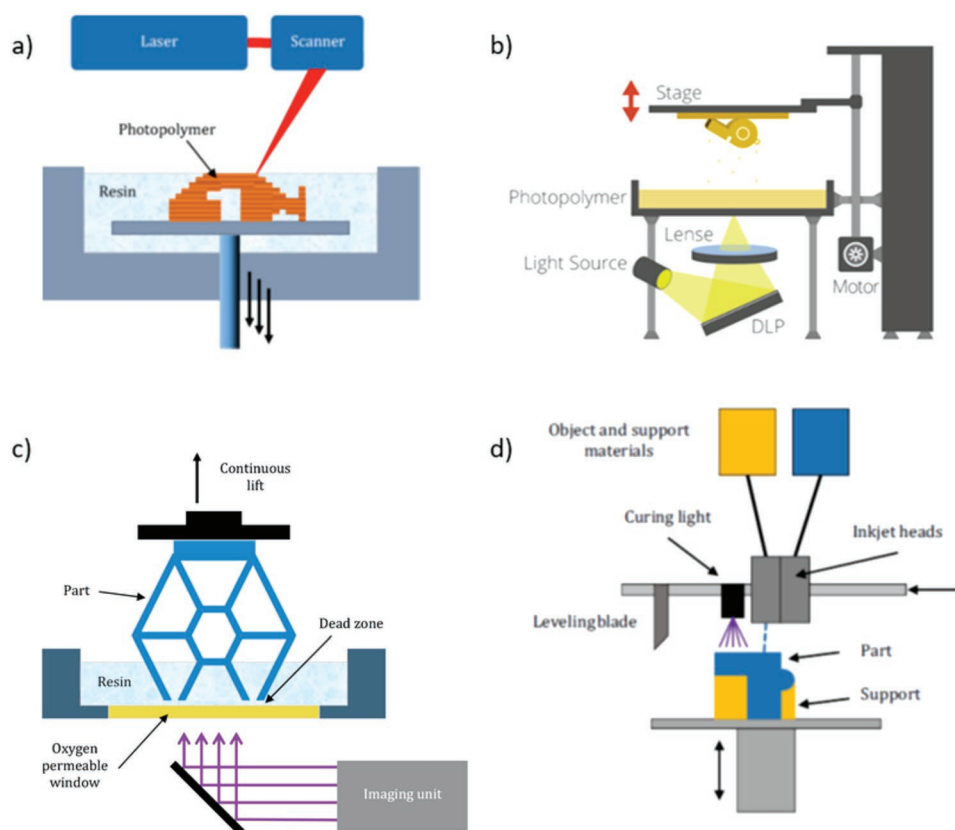


Figure 4. Schematic representation of a) stereolithography, b) digital light processing, c) continuous liquid interface production, and d) Polyjet. Panels a) to d) reproduced with permission.^[66] Copyright 2016, Elsevier.

problems can be addressed by optimizing the printing parameters. Possible solutions can also include modifications of the design of the piece to print, variations of the printing process conditions (temperature, humidity, etc.), adequate surface treatments or include a postcuring process.

3. UV Cured Smart Materials

Chromic, self-healing, shape-memory, piezoresistive, and piezoelectric materials (Table 4) are some examples of UV curable smart materials that are described in the following.

The **piezoresistive effect** represents the variation of the electrical resistivity of a material when mechanical strain is applied. In UV curable materials, typically polymer based materials, this smart behavior is obtained by the addition of a filler into the polymeric matrix, which is the main responsible for a larger piezoresistive response. Further, the filler also improves or changes some properties such as mechanical or thermal properties of the polymeric UV curable material. Commonly used materials for piezoresistive responsive composites are carbon based materials such as carbon nanotubes (CNTs), graphene or carbon fillers (CFs). Silver fillers, microcrystalline silicon or 3, 4-polyethylenedioxythiophene-polystyrene sulfonic acid (PEDOT/PSS) are some other alternatives.^[1]

CNTs are the most widely used fillers for piezoresistive composites, improving mechanical properties, electrical and

thermal conductivities.^[76] Thus, multiwalled carbon nanotubes (MWCNTs) and a commercial available UV curable epoxy photoresin (SU-8) were used to create a flexible organic piezoresistive micro-electro-mechanical system (MEMS) strain sensor with enhanced sensitivity^[77] (Figure 5). The electrical resistance changes versus strain of these CNT/SU-8 piezoresistive materials shows linear and nonlinear regions at low and high strain, respectively. It is also highlighted the role of the MEMS design in the enhancement of the final sensing performance of the devices, reaching gauge factors up to 200 for optimized sensor geometries, resulting in highly sensitive piezoresistive materials for flexible electronic applications.

Piezoresistive nanocomposites were also obtained by dispersing and aligning simple-walled carbon nanotubes (SWCNTs) in a blend of two different photopolymerizable monomers which consisted of urethane dimethacrylate (UDMA) and 1,6-hexadienol dimethacrylate (HDDMA).^[78] Dielectrophoresis technique was used under the application of AC electric fields obtaining aligned CNTs/polymer nanocomposites. The influence of the degree of alignment of CNTs on the electrical conductivity and piezoresistive response in both the aligned and transverse to alignment directions were assessed, being obtained the best piezoresistive sensitivity for aligned specimens.

More complex piezoresistive structures were also developed by UV curing and using CNTs. A piezoresistive sandwich type sensor that include three different layered materials a

Table 4. Summary of the most relevant UV-curable smart materials presented in the literature.

Classification	Shape	Polymer	Filler	Description	Reference
Piezoresistive	Film	Commercial epoxy resin (SU-8)	MWCNTs	MWCNTs and SU-8 are used to fabricate a flexible organic piezoresistive micro-electro-mechanical system (MEMS) strain sensor with enhanced sensitivity.	[77]
Piezoresistive	Film	UDMA and HDDMA	SWCNTs	UDMA and HDDMA in combination with SWCNTs are used to obtain piezoresistive nanocomposites, aligned (better properties) and randomly oriented filler.	[78]
Piezoresistive	Sandwich type	Commercial acrylic resin (TangoPlus)	MWCNTs	MWCNTs/TangoPlus composites for the electrodes and a Ionic Liquid/polymer composite for the internal layer that are between the two electrodes are used to fabricate a new piezoresistive sensor with sandwich type structure.	[79]
Piezoelectric	Film	Commercial acrylic resin (Ebecryl 150)	ZnO nanostructures	Ebecryl 150 and four different morphologies of ZnO filler is used to develop piezoelectric films that, despite the low ZnO content, show interesting piezoelectric properties (in particular, the devices containing flower-like nanostructures).	[82]
Piezoelectric	Film	HDDA	PVDF	HDDA and PVDF are used to obtain a photocurable ink (35 wt% of PVDF particles) employed to create 3D printed piezoelectrically active thick film with an optimized piezoelectric voltage coefficient (g_{33}).	[81]
Shape-memory	Film	DGEBA	PCL fibers	DGEBA and PCL fibers are used to obtain shape memory films with shape recovery ratios between 88 and 100% by electrospinning and UV curing.	[84]
Shape-memory	Helical thread structure	Epoxy polymers	-	Different epoxy polymers are used to develop a helical thread structure with functional graded shape memory parts that have spontaneous and sequential shape recovery abilities at 100 °C in 6.5 s.	[85]
Self-healing	Film	Complex polyol	-	Complex polyol structure polymer is used to obtain films with self-healing properties, they could be repaired in a short time by hot air gun and maintained high repair efficiency.	[87]
Self-healing	Film	Polyimide sheets and Epoxy polymer	-	Polyimide sheets and epoxy photocurable resin are used to obtain self-healing films using a layer-by-layer technique.	[88]
Photochromic	Film	PEUDA	ACV ²⁺	ACV ²⁺ in PEUDA matrix are used to obtain by UV curing a cross-linked polyviologen film that after UV illumination for 60 s it can swiftly change its color from pale yellow to deep blue.	[90]
Electrochromic	Sandwich structure	PEUDA	ACV ²⁺ and electrolyte gel	ACV ²⁺ in PEUDA matrix in addition to gel electrolyte film are used to obtain electrochromic sandwich structure that can undergo reversible color change in response to the external voltages of -2.0 and 2.0 V.	[90]

TangoPlus FLX930 photoresin for the top and bottom of the structure, a MWCNTs/TangoPlus composite for the electrodes and an Ionic Liquid/polymer composite for the internal layer that are between the two electrodes was fabricated.^[79] All materials used in that study are UV-curable. 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) is the Ionic Liquid

(IL) employed and 2-[[[(butylamino)carbonyl]oxy]ethyl acrylate (BACOEa) is the used polymer. The performance of the piezoresistive sensors was investigated as a function of the degree of crosslinking and polymerization of the IL/polymer composites. As the compressive strain was increased, the distance between the two electrodes decreased, the variations in polymer

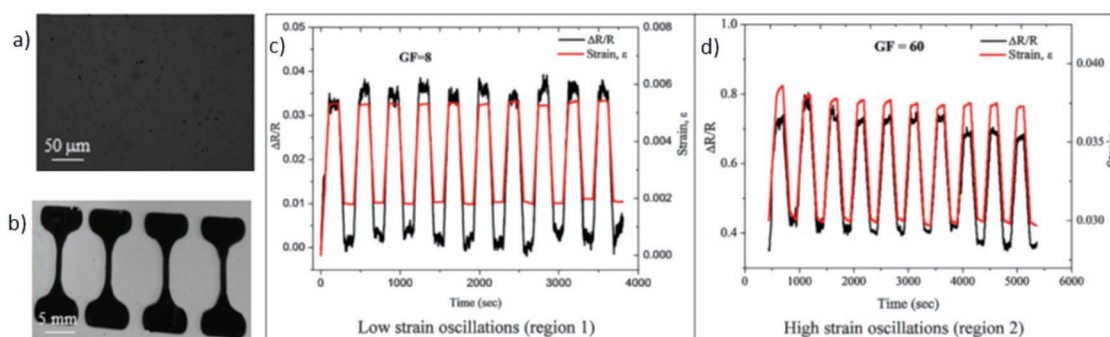


Figure 5. a) The 1 wt% CNT/SU-8 thin film sample, b) the dog-bone shaped specimens of the same sample, and the $\Delta R/R$ response of a 0.8 wt% CNT/SU-8 thin film for tensile/compressive strain oscillations between c) 0.2–0.55% and d) 3–3.7%. Panels a) to d) reproduced with permission.^[74] Copyright 2014, Elsevier.

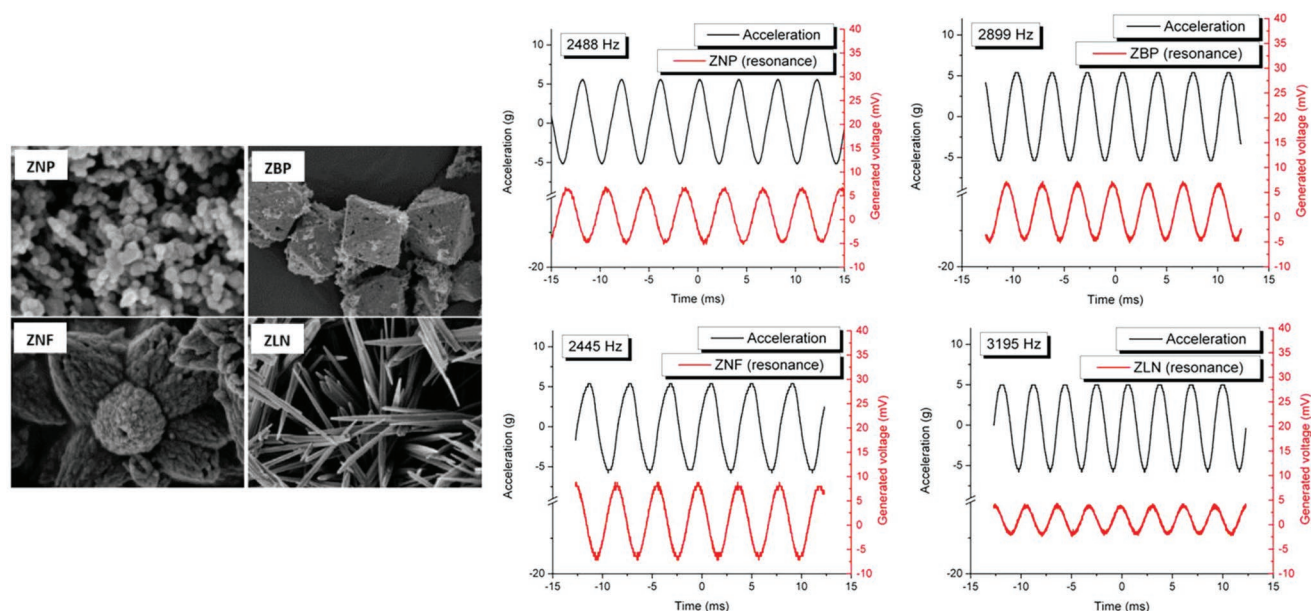


Figure 6. Micrographs of ZnO nanostructures used for the development of piezoelectric UV curable composites and their generators output voltage at resonance frequency. Reproduced with permission.^[79] Copyright 2017, Elsevier.

chains and IL resulting in a decrease of the electrical resistance of the sensors. It is confirmed that the sensitivity of the sensors is affected by the degree of crosslinking and polymerization of the IL/polymer composites.

Piezoelectric materials have been also investigated in UV curable smart materials. The **piezoelectric effect** is the ability of certain materials to generate voltage when subjected to a mechanical stress, or to generate a mechanical strain when subjected to an electric field.^[80] The piezoelectric effect in photocurable materials is achieved using piezoelectric fillers such as polycrystalline ceramics (lead zirconium titanate, lead lanthanum zirconium titanate, and barium titanate), single crystals (quartz, and zinc oxide), or some polymers (polyvinylidene fluoride).^[81]

UV-cured composite films containing zinc oxide (ZnO) nanostructures with different morphologies were presented by Malucelli et al.^[82] The UV curable material is a commercially available acrylic resin, namely bis-phenol A ethoxylate diacrylate (Ebecryl 150), and the studied morphologies of ZnO fillers included nanoparticles (ZNP), bipyramidal structures (ZBP), flower-like structures (ZNF), and long needles (ZLN) (**Figure 6**). The different morphologies of the ZnO nanostructures were found to significantly affect the thermo-oxidative stability and the glass transition temperature of the UV-cured films. All the UV-cured nanocomposite films, despite the low ZnO content, showed interesting piezoelectric properties. In particular, the devices containing flower-like nanostructures exhibited the highest root mean square voltage both at 150 Hz and at the resonance frequency (about 0.176 ± 0.001 and 0.914 ± 0.001 mV, respectively).

A better integration between the UV curable polymer matrix and the filler can be achieved, if the filler is a polymeric material such as polyvinylidene fluoride (PVDF). PVDF has been widely applied due to its stable and high piezoelectric coefficient.^[6] PVDF also presents a unique combination of properties

in comparison to other piezoelectric materials, such as excellent mechanical flexibility, chemical stability, biocompatibility, and solution based processability. Therefore, an all-polymer-based piezoelectric photocurable resin (V-Ink) based on 1,6-hexanediol diacrylate (HDDA) and PVDF was developed,^[81] being suitable for additive manufacturing processes. The optimized V-Ink contains 35 wt% of polyvinylidene fluoride particles suspended in the photocurable resin. A 3D printed piezoelectrically active thick film was demonstrated with an optimized piezoelectric voltage coefficient (g_{33}) of 105.12×10^{-3} V m N⁻¹.

Shape-memory polymers (SMPs) are other smart materials that can be obtained by UV curing but are not electrically active. Shape-memory polymers are materials capable of reacting to external stimuli, such as temperature, magnetic or electric fields, and solvents, to return from a pre-programmed shape to their original form.^[83] Temperature is the most studied one.

Poly (ϵ -caprolactone) (PCL) based shape memory polymer blends have been the focus of recent research. These materials show sharp and rapid shape memory-recovery response as a consequence of the melting/recrystallization of the PCL component as switching transition. For that, PCL has been used as a shape memory material and diglycidyl ether of bisphenol A (DGEBA) as an epoxy UV curable matrix to obtain shape-memory polymeric composites.^[84] Electrospinning technique was used to create PCL fibbers into an epoxy DGEBA matrix that was then UV cured. In this way, a film was obtained with a mat of fibbers with shape memory response (at 60 °C). Shape fixity ratios range from 95% to 99% and shape recovery ratios between 88% and 100%, respectively. This shape memory behavior can be observed in **Figure 7**.

Some other investigations are based on materials that do not use any filler and the shape memory effect is achieved only by the polymer. This is the case of^[85] where seven epoxy polymers with different glass transition temperatures were used to create a functional gradient shape memory “helical thread” structure,



Figure 7. Photographs of a) initial shape, b) fixed shape after folding the mat three times in half at 60 °C, and c) recovery shape after heating again to 60 °C. Panels a) to c) reproduced with permission.^[81] Copyright 2017, Elsevier.

where shape recovery is thermally triggered. The feasibility of using 3D printing technique to fabricate functional graded SMPs with both spontaneous and sequential shape recovery abilities was demonstrated. The SMP components, with properly assigned spatial variation of the thermodynamical property distribution, react rapidly to a thermal stimulus (at around 100 °C) and return to a specified configuration in a precisely controlled shape changing sequence in around 6.5 s. The sequential shape recovery process can be observed in **Figure 8**.

Self-healing materials effectively expand the lifetime of the product and have desirable economic and human safety attributes. Self-healing materials are polymers, metals, ceramics, and their composites that, when damaged through thermal, mechanical, ballistic, or by other means, have the ability to heal and restore the material to its original set of properties.^[86]

Combining self-healing characteristics with the UV-curing advantages (an environmental friendly, energy saving, and efficient technology), self-healing UV curable materials become in an interesting research area. In this way, a novel UV-curable self-healing oligomer was designed on the basis of a quadrupolar hydrogen bonds system.^[87] The oligomer is formed by reacting a mixture of a hydrogen bonding group and a photosensitive monomer with three-arm polyols. The oligomer coating could be repaired in a short time by hot air gun and maintained high repair efficiency (**Figure 9**). The coating could self-heal remarkably at a depth range from 3 to 4 μm . The polymer exhibited excellent thermal stability and significant weight loss occurred at a temperature of 270 °C, indicating that the healing process at 170 °C was safe for the material.

A skin structure exhibiting flexibility, self-healing and damage sensing was designed, fabricated and tested by Carlson et al.^[88] This coating is fabricated on a substrate of copper-clad polyimide sheets by a layer-by-layer technique using polyimide sheets and an UV curable epoxy polymer (used as both a structural adhesive and as the self-healing fill material). In addition,

this skin structure is integrated with an array of LC circuits and an integrated antenna coil that is used to detect and locate the damaged portion of the skin. If the skin is damaged, the UV-curable epoxy is released and is cured by sunlight.

Chromic materials are a type of materials capable of undergoing a change, often reversible, in the color due to a transformation between two forms.^[89] If this change in color occurs by the absorption of electromagnetic radiation, they are called photochromic material. If this change in color occurs by the application of an electric charge, they are called electrochromic material. These two type of smart materials are based on organic compounds with extended π -conjugation. The most investigated ones are the viologens (1, 1'-disubstituted-4, 4'-bipyridine salts) that are functional in their crystalline states, dispersed in appropriate matrixes or incorporated polymers by copolymerization or graft-modified reactions.^[90]

Acrylate-functional viologen (ACV²⁺) in polyether urethane diacrylate matrix (PEUDA) were used to obtain by UV curing a cross-linked polyviologen film with excellent photochromic and electrochromic performances.^[90] The photochromic effect appears after UV illumination for 60 s, when the cross-linked PACV²⁺ film can swiftly change its color from pale yellow to deep blue. In addition, the optical transmission of cross-linked PACV²⁺ film at 610 nm did not change significantly and still retained about 63.6% after 30 cycles. The cyclic voltammetry experiment showed that the film can undergo repetitively electrochemical redox reactions with good reversibility beyond the 10th scan.

Furthermore, when a gel electrolyte film was added to the PACV²⁺ film, an electrochromic sandwich structure film was obtained (**Figure 10**). The gel electrolyte film is a mixture of acetonitrile (MeCN), polymethyl methacrylate (PMMA), propylene carbonate (PC) and LiClO₄. The electrochromic device composed of the PACV²⁺ film and gel electrolyte film undergoes reversible color change in response to the external voltages

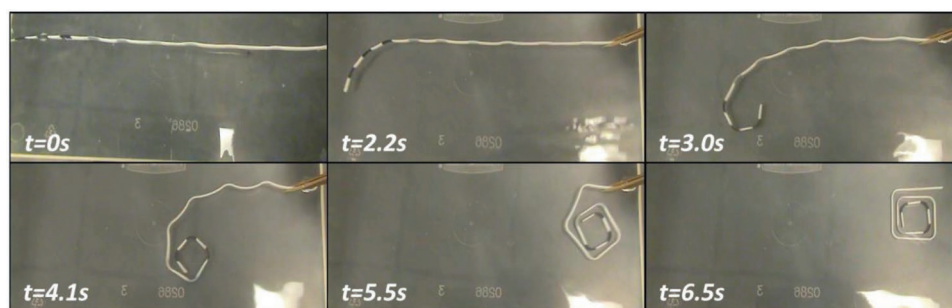


Figure 8. Series of photographs showing the spontaneous and sequential shape recovery process of the helical SMP component. Reproduced with permission.^[82] Copyright 2015, Elsevier.

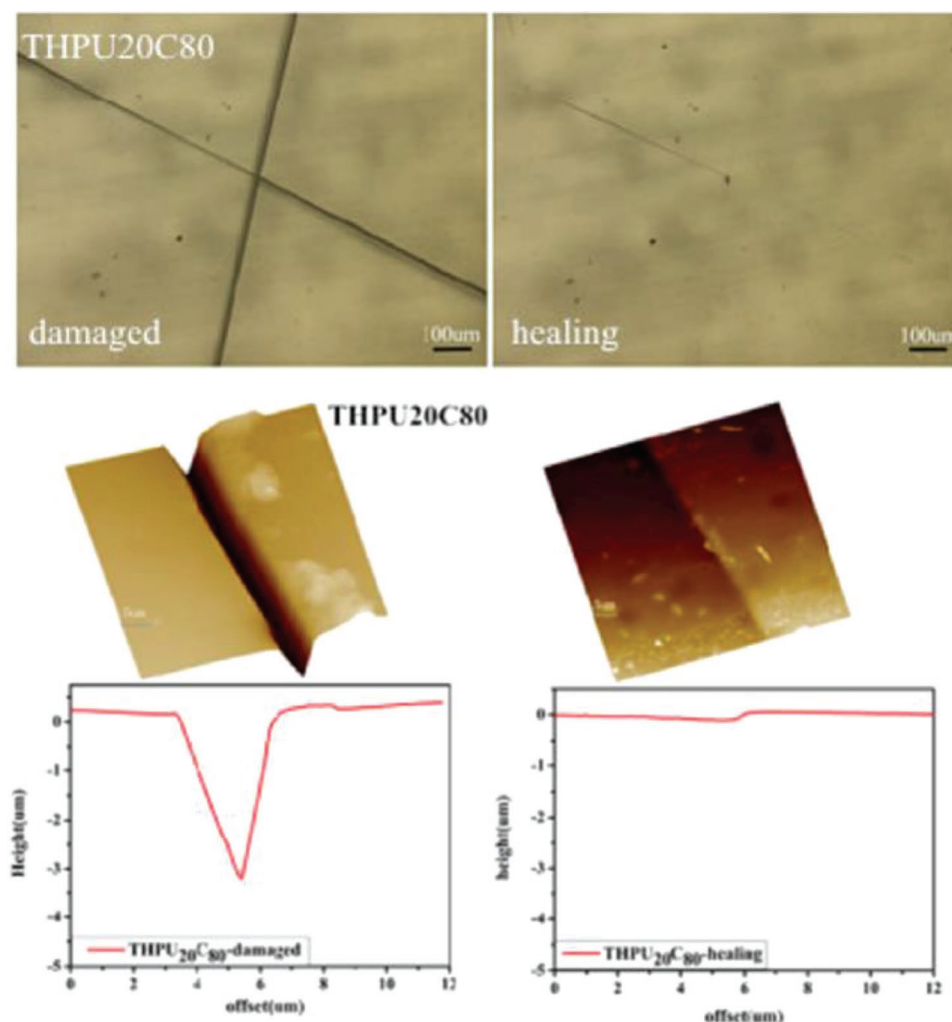


Figure 9. Optical and atomic force micrographs of the oligomer THPU20C80 damaged and after healing. Reproduced with permission.^[84] Copyright 2016, Elsevier.

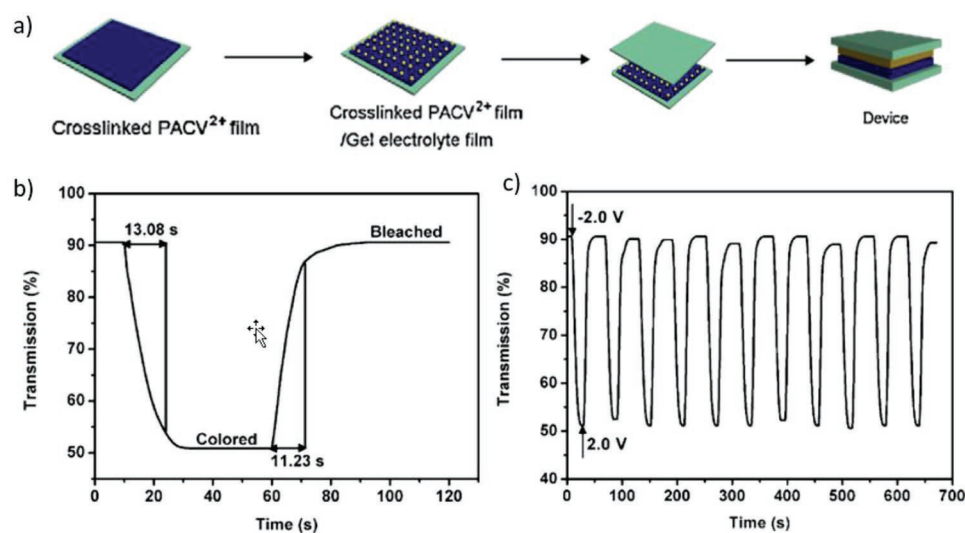


Figure 10. a) Schematic illustration for the construction of the electrochromic device, b) its coloring and bleaching response times, and c) the cyclic changes in optical transmissions at 610 nm obtained by cyclic application of the external voltages of -2.0 and 2.0 V. Panels a) to c) reproduced with permission.^[87] Copyright 2011, Elsevier.

of -2.0 and 2.0 V, respectively, while the contrast of EC device at 610 nm did not change significantly and still retained about 39.5% after 10 cycles.

A summary of the most relevant UV-curable smart materials presented in the literature is presented in Table 4. It can be noticed that UV curable smart materials are typically composed by a polymeric matrix and an active filler that provides this smart behavior (the filler can be also a polymer). There is no unique method for designing these UV curable materials, and strongly depends on the filler and the polymer matrix and, in particular, in the synthesis methods. In any case, parameters such as filler dispersion and distributions, compatibility between filler and polymer matrix and the polymer curing characteristics are among the most relevant parameters to be taken into account.

4. Summary, Conclusions, and Future Trends

Smart materials are attracting increasing interest based on the used for the Industry 4.0 and the Internet of Things concepts. Their properties allow them to be very suitable for sensor applications in several fields like aerospace, civil engineering and different industrial applications, with improved performance and integration. Further, in order to improve integration, additive manufacturing technologies are being implemented being therefore important the parallel development of suitable inks.

Depending on the composition of the ink, the curing process is achieved in a different way (including thermal treatments or cross-linking methods, among others), being UV-curable materials among the most suitable ones for smart materials development and integration. UV curable materials are based on photopolymers that are cross-linked when exposed to UV light. In contrast with solvent based materials, they present advantages like fast curing processes at room temperature with reduced VOC emissions, making then environmentally friendlier and really attractive for thin film processing in electronics and engineering.

Considering the indicated advantages, UV curable smart materials are becoming in a general research and implementation interest. Chromic, self-healing, shape memory, piezoresistive, or piezoelectric materials are some examples of it.

Printing technologies are in general additive manufacturing techniques where the material waste is minimized, considerably reducing thus the final cost of the product. Moreover, they are compatible for mass production and high-resolution designs can be processed. Depending on the printing technology, the image is transferred by means of a master image carrier or directly from the computers digital file. In 2D printing techniques like screen, inkjet, and spray printing the layer is cured right after it is printed. In 3D printing instead, the curing process is usually achieved layer by layer until the object is fully created. Stereolithography, digital light processing, continuous liquid interface production, and polyJet are some examples of 3D printing techniques based on UV curing processes.

Despite UV curable smart materials being among the most promising technologies for the development and integration of sensors and actuators for advance technologies, the number of those materials is still small. This fact is mainly due to the

difficulty in reaching proper combination of UV-curable resins and nanofillers, leading to both suitable smart and multifunctional performance and processability. Thus, the key future challenges in this research field include the optimization of filler dispersion and distributions as well as the compatibility between fillers and polymer matrix, allowing also improved curing time and, therefore, processability.

Viscosity, density, surface tension, and contact angle on different substrates are parameters that are also affected when these smart and multifunctional UV-curable materials are developed, which influence their processability and integration into applications. In addition, depending on the nanofiller employed, the absorption of the UV light can be also affected. Thus, obtaining optimized materials in terms of functionality/smart response as well as processability requires a deep understanding on the filler-polymer interaction. In this way, the potential solutions and/or new approaches that are being investigated include the use of polymer coated fillers, new filler dispersion techniques or new fillers more compatible with UV-curable resin (i.e., that are not affected by and do not affect the UV curing process).

Thus, this review demonstrates both, the need to improve materials performance and the large potential for UV-curable smart and multifunctional materials for the next generation devices.

Acknowledgements

The authors thank the FCT (Fundação para a Ciência e Tecnologia) for financial support under framework of the Strategic Funding UID/FIS/04650/2013 and projects PTDC/EEI-SII/5582/2014 and POCI-01-0145-FEDER-028237. Funds provided by FCT in the framework of EuroNanoMed 2016 call, Project LungChek EN-Med/0049/2016, are also gratefully acknowledged. J.O. also thanks the FCT for the grants SFRH/BD/98219/2013. Finally, the authors acknowledge funding by the Spanish Ministry of Economy and Competitiveness (MINECO) through the project MAT2016-76039-C4-3-R (AEI/FEDER, UE) and from the Basque Government Industry and Education Departments under the ELKARTEK, HAZITEK, and PIBA (PIBA-2018-06) programs, respectively. This article is part of the special series on *Advanced Intelligent Systems* that showcases the outstanding achievements of leading international researchers on intelligent systems.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

multifunctional materials, polymer-based inks, printing technologies, smart materials, UV curing

Received: November 14, 2018
Revised: December 21, 2018
Published online: January 11, 2019

- [1] J. Oliveira, V. Correia, H. Castro, P. Martins, S. Lanceros-Mendez, *Addit. Manuf.* **2018**, 21, 269.
- [2] E. B. Murphy, F. Wudl, *Prog. Polym. Sci.* **2010**, 35, 223.

- [3] R. Bogue, *Assem. Autom.* **2014**, 34, 16.
- [4] R. Bogue, *Assem. Autom.* **2012**, 32, 3.
- [5] M. Wollschläger, T. Sauter, J. Jasperneite, *IEEE Ind. Electron. Mag.* **2017**, 11, 17.
- [6] P. Martins, A. C. Lopes, S. Lanceros-Mendez, *Prog. Polym. Sci.* **2014**, 39, 683.
- [7] X. Qiu, S. Hu, *Materials* **2013**, 6, 738.
- [8] A. Benjeddou, *Int. J. Smart Nano Mater.* **2018**, 9, 85.
- [9] G. Grau, R. Kitsomboonloha, S. L. Swisher, H. Kang, **2014**, 5067.
- [10] G. Sossou, F. Demoly, G. Montavon, S. Gomes, *J. Comput. Des. Eng.* **2018**, 5, 3.
- [11] E. A. Clark, M. R. Alexander, D. J. Irvine, C. J. Roberts, M. J. Wallace, S. Sharpe, J. Yoo, R. J. M. Hague, C. J. Tuck, R. D. Wildman, *Int. J. Pharm.* **2017**, 529, 523.
- [12] E. Saleh, P. Woolliams, B. Clarke, A. Gregory, S. Greedy, C. Smartt, R. Wildman, I. Ashcroft, R. Hague, P. Dickens, C. Tuck, *Addit. Manuf.* **2017**, 13, 143.
- [13] M. Sangermano, A. Chiolerio, G. Marti, P. Martino, P. Martino, *Macromol. Mater. Eng.* **2013**, 298, 607.
- [14] C. Decker, *Polym. Int.* **1998**, 45, 133.
- [15] G. Mashouf, M. Ebrahimi, S. Bastani, *Pigm. Resin Technol.* **2014**, 43, 61.
- [16] A. Endruweit, M. S. Johnson, A. C. Long, *Polym. Compos.* **2006**, 27, 119.
- [17] A. Ravve, *Light-Associated Reactions of Synthetic Polymers*, Springer, New York, USA **2006**.
- [18] W. Schnabel, *Polymers and Light: Fundamentals and Technical Applications*, Wiley-VCH, Berlin, Germany **2004**.
- [19] J. P. Fouassier, *IEEE Electr. Insul. Mag.* **1996**, 12, 36.
- [20] J. P. Fouassier, J. Lalevée, *Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency*, Wiley-VCH, Weinheim, Germany **2012**.
- [21] A. Tiwari, A. Polykarpov, *Photocured Materials*, Royal Society of Chemistry, Cambridge, UK **2014**.
- [22] T. Sumiyoshi, W. Schnabel, A. Henne, P. Lechtken, *Polymer* **1985**, 26, 141.
- [23] A. Kajiwar, Y. Konishi, Y. Morishima, W. Schnabel, K. Kuwata, M. Kamachi, *Macromolecules* **1993**, 26, 1656.
- [24] N. Arsu, M. Aydin, Y. Yagci, S. Jockusch, N. J. Turro, *One component thioxanthone based Type II photoinitiators in Photochemistry and UV Curing: New Trends* (Ed: J. P. Fouassier), Research Signpost, Kerala, India **2006**, pp. 20–32.
- [25] Z. W. Wicks, J. F. N. Jones, S. P. Pappas, D. A. Wicks, *Organic Coatings: Science and Technology*, John Wiley & Sons, Inc., New York **2007**.
- [26] M. Sangermano, I. Roppolo, A. Chiappone, *Polymers* **2018**, 10, 136.
- [27] A. Wrzyszczyński, J. Bartoszewicz, G. L. Hug, B. Marciniak, J. Paczkowski, *J. Photochem. Photobiol., A* **2003**, 155, 253.
- [28] H. Itoh, A. Kameyama, T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, 34, 217.
- [29] J. Xu, Y. Jiang, T. Zhang, Y. Dai, D. Yang, F. Qiu, Z. Yu, P. Yang, *Prog. Org. Coat.* **2018**, 122, 10.
- [30] T. Scherzer, W. Knolle, S. Naumov, R. Mehnert, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, 208, 271.
- [31] C. Check, R. Chartoff, S. Chang, *React. Funct. Polym.* **2015**, 97, 116.
- [32] V. Shukla, M. Bajpai, D. K. Singh, M. Singh, R. Shukla, *Pigm. Resin Technol.* **2004**, 33, 272.
- [33] J. Chen, M. D. Soucek, W. J. Simonsick, R. W. Celikay, *Polymer* **2002**, 43, 5379.
- [34] A. B. Strong, *Fundamentals of Composites Manufacturing. Materials, Methods, and Applications*, Society of Manufacturing Engineers, Dearborn, MI **2008**.
- [35] R. Schwalm, *UV Coatings, Basics, Recent Developments and New Applications*, Elsevier, Amsterdam, The Netherlands **2006**.
- [36] J. Ortyl, R. Popielarz, *Polimery* **2012**, 57, 510.
- [37] V. K. Varadan, K. J. Vinoy, S. Gopalakrishnan, *Smart Material Systems and MEMS: Design and Development Methodologies*, John Wiley & Sons, Ltd., Chichester, UK **2006**.
- [38] L. Racicot, T. Kasahara, M. A. Ciufolini, *Org. Lett.* **2014**, 16, 6382.
- [39] J. V. Crivello, *Initiators—Poly-Reactions—Optical Activity*, Advances in Polymer Science, Vol. 62, Springer, Berlin **1984**, pp. 1–48.
- [40] J. V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, 37, 4241.
- [41] S. Shi, C. Croutxé-Barghorn, X. Allonas, *Prog. Polym. Sci.* **2017**, 65, 1.
- [42] B. Golaz, V. Michaud, Y. Leterrier, J. A. E. Mnsen, *Polymer* **2012**, 53, 2038.
- [43] S. R. Akhtar, J. V. Crivello, M. L. Schmitt, J. L. Lee, *Chem. Mater.* **1990**, 2, 732.
- [44] Y. Yaci, A. Kornowski, W. Schnabel, *J. Polym. Sci., Part A: Polym. Chem.* **1992**, 30, 1987.
- [45] V. V. Jarikov, D. C. Neckers, *Macromolecules* **2000**, 33, 7761.
- [46] Y.-H. Wang, P. Wan, *Photochem. Photobiol. Sci.* **2015**, 14, 1120.
- [47] M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, U. Annby, N. Rehnberg, *Polym. Int.* **2001**, 50, 998.
- [48] M. Sangermano, *Pure Appl. Chem.* **2012**, 84, 2089.
- [49] C. Decker, K. Moussa, *J. Polym. Sci., Part A: Polym. Chem.* **1990**, 28, 3429.
- [50] J. L. Stanford, A. J. Ryan, Y. Yang, *Polym. Int.* **2001**, 50, 1035.
- [51] V. Y. Voytekunas, F. L. Ng, M. J. M. Abadie, *Eur. Polym. J.* **2008**, 44, 3640.
- [52] C. Esposito Corcione, G. Malucelli, M. Frigione, A. Maffezzoli, *Polym. Test.* **2009**, 28, 157.
- [53] D. S. Esen, F. Karasu, N. Arsu, *Prog. Org. Coat.* **2011**, 70, 102.
- [54] C. Esposito Corcione, M. Frigione, A. Maffezzoli, G. Malucelli, *Eur. Polym. J.* **2008**, 44, 2010.
- [55] B. Chiou, S. A. Khan, *Macromolecules* **1997**, 30, 7322.
- [56] T. Scherzer, U. Decker, *Vib. Spectrosc.* **1999**, 19, 385.
- [57] P. Kerbouc'h, P. Lebaudy, L. Lecamp, C. Bunel, *Thermochim. Acta* **2004**, 410, 73.
- [58] W. Schrof, E. Beck, R. Königer, W. Reich, R. Schwalm, *Prog. Org. Coat.* **1999**, 35, 197.
- [59] W. Schrof, E. Beck, G. Etzrodt, H. Hintze-Brüning, U. Meisenburg, R. Schwalm, J. Warming, *Prog. Org. Coat.* **2001**, 43, 1.
- [60] H. Kipphan, *Handbook of Print Media*, Springer, Berlin, Germany **2001**.
- [61] A. J. Bard, L. R. Faulkner, *Printing on Polymers: Fundamentals and Applications*, William Andrew, Oxford, UK **2016**.
- [62] N. Saengchairat, T. Tran, C. K. Chua, *Virtual Phys. Prototyping* **2017**, 12, 31.
- [63] F. P. W. Melchels, J. Feijen, D. W. Grijpma, *Biomaterials* **2010**, 31, 6121.
- [64] E. M. Hamad, S. E. R. Bilatto, N. Y. Adly, D. S. Correa, B. Wolfrum, M. J. Schöning, A. Offenhäusser, A. Yakushenko, *Lab Chip* **2016**, 16, 70.
- [65] F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2009**, 93, 394.
- [66] J. W. Stansbury, M. J. Idacavage, *Dent. Mater.* **2016**, 32, 54.
- [67] D. C. Neckers, *CHEMTECH* **1990**, 20, 615.
- [68] H. Kaplan, *Photonics Spectra* **1990**, 24, 74.
- [69] Think3d, “Digital light processing (DLP) 3D printing technology overview,” can be found under <https://www.think3d.in/digital-light-processing-dlp-3d-printing-technology-overview/> (accessed: December 2018).
- [70] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, *Composites, Part B* **2017**, 110, 442.
- [71] C. Yan, Y. Shi, J. Yang, J. Liu, *Compos. Interfaces* **2010**, 17, 257.
- [72] D. Dendukuri, D. C. Pregibon, J. Collins, T. A. Hatton, P. S. Doyle, *Nat. Mater.* **2006**, 5, 365.
- [73] A. Cazón, P. Morer, L. Matey, *Proc. Inst. Mech. Eng., Part B* **2014**, 228, 1664.
- [74] M. Fahad, P. Dickens, M. Gilbert, *Rapid Prototyping J.* **2013**, 19, 230.

- [75] O. Ivanova, A. Elliott, T. Campbell, C. B. Williams, *Addit. Manuf.* **2014**, 1–4, 24.
- [76] P. C. Ma, N. A. Siddiqui, G. Marom, J. K. Kim, *Composites, Part A* **2010**, 41, 1345.
- [77] D. Thuau, C. Ayela, P. Poulin, I. Dufour, *Sens. Actuators, A* **2014**, 209, 161.
- [78] E. C. Sengezer, G. D. Seidel, R. J. Bodnar, *Smart Mater. Struct.* **2017**, 26, 095027.
- [79] J. Lee, M. O. Faruk Emon, M. Vatani, J. W. Choi, *Smart Mater. Struct.* **2017**, 26, 035043.
- [80] V. F. Cardoso, C. Ribeiro, S. Lanceros-Mendez, *Advanced Piezoelectric Materials: Science and Technology*, Elsevier, Duxfor, UK **2017**.
- [81] X. Chen, H. O. T. Ware, E. Baker, W. Chu, J. Hu, C. Sun, *Proc. CIRP* **2017**, 65, 157.
- [82] G. Malucelli, A. Fioravanti, L. Francioso, C. De Pascali, M. A. Signore, M. C. Carotta, A. Bonanno, D. Duraccio, *Prog. Org. Coat.* **2017**, 109, 45.
- [83] C. Liu, H. Qin, P. T. Mather, *J. Mater. Chem.* **2007**, 17, 1543.
- [84] A. Iregui, L. Irusta, O. Llorente, L. Martin, T. Calvo-Correas, A. Eceiza, A. González, *Eur. Polym. J.* **2017**, 94, 376.
- [85] K. Yu, A. Ritchie, Y. Mao, M. L. Dunn, H. J. Qi, *Procedia IUTAM* **2015**, 12, 193.
- [86] R. P. Wool, *Soft Matter* **2008**, 4, 400.
- [87] R. Liu, X. Yang, Y. Yuan, J. Liu, X. Liu, *Prog. Org. Coat.* **2016**, 101, 122.
- [88] J. A. Carlson, J. M. English, D. J. Coe, *Smart Mater. Struct.* **2006**, 15, N129.
- [89] R. J. Mortimer, A. L. Dyer, J. R. Reynolds, *Displays* **2006**, 27, 2.
- [90] L. P. Gao, G. J. Ding, Y. C. Wang, Y. L. Yang, *Appl. Surf. Sci.* **2011**, 258, 1184.