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Recent Advances in Cationic Photopolymerization

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The paper reports important strategies to overcome limitation of cationic photopolymerization. First, it was possible to run emulsion cationic photopolymerization in water, taking the advantages of hydrophobic droplets of suitable dimension to avoid termination reaction, achieving capsules of about 200 nm. Subsequently a frontal polymerization reaction is used to promote the UV-induced crosslinking process of an epoxy composites via a radical induced cationic frontal polymerization.

Keywords: Cationic photopolymerization, Emulsion polymerization, Frontal polymerization

1. Introduction

Cationic photopolymerization is an interesting UV-induced process since the mechanism is characterized by important advantages such as absence of oxygen inhibition, low shrinkage upon curing, and good versatility of the crosslinked materials [1]. While the main applications are in the field of coating and the electronic industry, we have recently investigated the use of cationic UV-induced polymerization for the synthesis of polymeric particles and for the fabrication of polymeric composites.

To use this photoinduced polymerization technique in these fields it is important to overcome some of inner limitations, such as: the detrimental effect of water in cationic growing polymeric chain or the limit of penetration depth during irradiation curing.

Emulsion and mini-emulsion polymerization are the most used polymerization technique for the polymeric particles production, but cationic process is strongly inhibited by the presence of water, so in principle it would not be possible to carry a miniemulsion polymerization cationic reaction in aqueous media. We investigated the cationic miniemulsion photopolymerization of triethylene glycol divinyl ether (DVE3) in aqueous phase [2].

Another recent advancement in cationic UV-curing is the use of the polymerization technique for the fabrication of polymeric composites. In this case, the main limitation of UV-induced crosslinking reactions is related to the hindering of UV-light penetration towards thickness of the formulations, which limits this polymerization technique in the preparation of thick composite materials. This limitation has been overcome by the introduction of a Radical Induced Cationic Frontal Polymerization (RICFP) process. The suggested mechanism put together the so-called Radical Induced Cationic Polymerization (RICP) with Frontal Polymerization (FP). UV-cured bulk epoxy composites were successfully produced by Radical Induced Cationic Frontal Polymerization (RICFP); it was shown that the FP is started by the dissociation of a radical, thermal initiator (RTI) promoted by the heat released during surface UV-induced cationic ring-opening polymerization. Subsequently, the carbon-centered radicals are oxidized to carbocations by the presence of the iodonium salt in a RICP mechanism [3].

2. Emulsion cationic photopolymerization in water

Polymeric particles or capsules can be obtained by means of 2 different approaches: the first one involves the processing of preformed polymers, whereas the second one is based on the in-situ polymerization of a monomer [4,5]. The latter can be commonly carried out by means of emulsion and miniemulsion polymerizations [6], where

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polymerization reaction starts in the monomer droplets (miniemulsion polymerization) or in the micelles (microemulsion polymerization), while the initiator is solubilized in the continuous phase.

Even if most of the literature papers on emulsion polymerization are focused in thermal initiated process, the use of light to trigger polymerization in emulsion conditions is very attractive. The photoinitiated polymerization reaction shows higher reaction rate in comparison with thermal process, because of the rapid and energy efficient initiation, as well as a higher colloidal stabilization, since the reaction is occurring formally at room temperature.

The main issue related to the use of cationic photopolymerization process in emulsion is due to the presence of water that inhibits the carbocationic growing chains.

Even if it is not common, some data are reported in literature on cationic polymerization reaction occurring at water interface inside an emulsion droplet [7]. Piradashvili et al. suggested the use of water-tolerant catalyst such as the Lewis acid $Yb(OTf)_3$ to achieve the synthesis of epoxy functionalized microspheres through emulsion cationic polymerization. Cationic ring-opening epoxy photopolymerization was performed in water by Crivello under aqueous suspension conditions [8, 9]. In those papers Crivello suggested the use of a silicone epoxy monomer and an appropriate cationic photoinitaitor soluble in the hydrophobic monomer. By maintaining the dimension of the monomer droplet big enough, the chain-transfer and inhibition promoted by water predominate over polymerization only at the droplet surface. The authors demonstrated that by decreasing the average particles diameter of the droplets below 1 μm the side reaction was dominating over propagating in the bulk droplets, preventing the formation of solid particles.

In our work we propose the synthesis of polymeric nanocapsules by miniemulsion cationic photopolymerization of divinyl ether in water. The reaction was triggered at the interface between the continuous (water) and the dispersed (monomer in hexadecane) phase. The monomer used, tirethylenglycol divinyl ether (DVE3), is characterized by a moderate polarity, and it was previously added in the hexadecane oleophobic phase. The onium salt (triarylsulfonium hexafluoroantimonate salts) is soluble in the oily phase and insoluble in the water. Once the dispersed phase was added to the aqueous one, DVE3 tend spontaneously to move towards the interface between hexadecane and water. This affords an interfacial polymerization that leads to the formation of microcapsules. The overall process is schematized in Fig. 1.

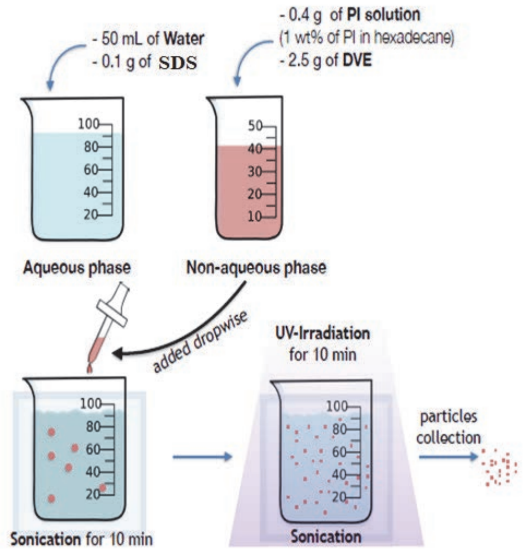

Fig. 1. Scheme of the process of cationic emulsion polymerization in water.

Formulation and process parameters were properly investigated to control the polymeric capsules dimensions. The selection of the proper surfactant is of enormous importance since it is responsible for interface stabilization. In this work we investigated both ionic (sodium dodecyl sulfate, SDS) and non-ionic (polyvinylpyrrolidone PVP, and Pluronic) surfactants. It was observed that non-ionic surfactants led to a significant increase in the average diameter of the nanocapsules probably because of the higher interfacial tension of the droplets. the minimum amount of surfactant for the formation of a stable and homogeneous miniemulsion was identified as 7% relative to the dispersed phase. The photoinitiator content was fixed at 1 wt% with respect to the monomer content. By increasing the photoinitiator content there was a noticeable increase in the nanocapsule size and PDI.

The effect of sonication time was taken into consideration, ranging from 2.5 up to 25 minutes. Both DLS and TEM analysis showed a marked decrease in size followed by a plateau by increasing sonication time. Ultrasound exposure of 15 min originated the smallest particles obtainable from this system. Longer US times did not change nanocapsules size because droplet coalescence likely balanced rupture. A threshold irradiation time of 10 minutes was evidenced to have a full monomer conversion avoiding additional crosslinking among the particles leading to a loss in size uniformity; a considerable increase in the dimension and polydispersity index was detected for long UV irradiation times.

Therefore, the smallest average diameter of polymeric capsules was provided in the presence of SDS as surfactant, by ultrasonication for 15 minutes and UV-irradiation for 10 minutes. As can be seen from the dimensional distribution of the nanocapsules in Fig. 2, the population was characterized by a single peak around 220 nm (measured by DLS). The TEM and EM analysis agree with the DLS collected data.

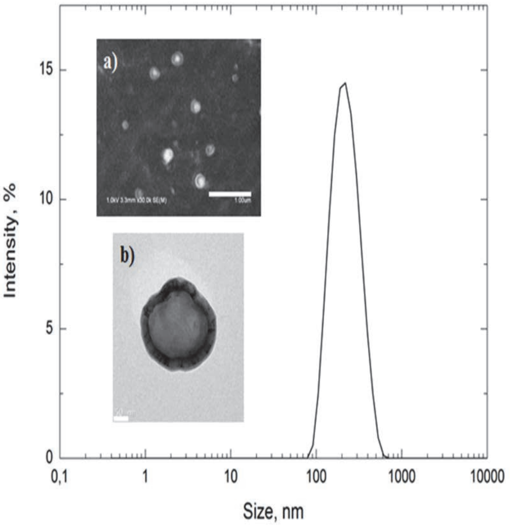

Fig. 2. Dimensional distribution of the sample based on SDS. Images of nanocapsules obtained by (a) FESEM and (b) TEM.

In summary, this study evidenced the possibility to control the nanocapsule size by acting on the sonication time and irradiation time.

3. Cationic photopolymerization of composites

Cationic photopolymerization of epoxy resin is a very interesting alternative to the use of amine or anhydride to promote crosslinking reaction. Under UV light onium salts can generate strong photolatent acid able to promote cationic ring-opening polymerization [10]. The main limitation of UV-induced crosslinking reactions is related to the hindering of UV-light penetration toward thickness of the formulations, which limits this polymerization technique in the preparation of thick composite materials [11]. This limitation has been overcome by the introduction of a radical induced cationic frontal polymerization (RICFP) process. The suggested mechanism puts together the so-called radical induced cationic polymerization (RICP) with frontal polymerization (FP).

By dispersing in the epoxy resin the thermal initiator tetraphenylethandiol (TPED, benzopinacol), and the iodonium salt *p*-(octyloxyphenyl)-phenyliodonium hexafluoro-antimonate (IOC8-SbF$_6$) upon irradiation the heat released by the surface UV-activated cationic ring opening polymerization promote a thermal frontal polymerization forming carbon radicals towards the thickness of the formulation. The carbon-cantered radical thermal-generated can be oxidized by the diaryliodonium salts forming a reactive carbocation which start the cationic ring-opening polymerization through the thickness of the formulations also in the presence of fillers (scheme reported in Fig. 3).

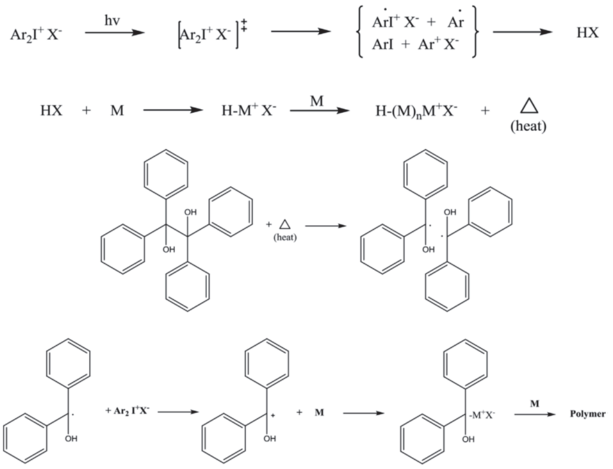

Fig. 3. Scheme of the radical induced cationic frontal polymerization process.

Formulations parameters were defined, and frontal polymerization was investigated with pristine bis-phenol-A-diglycidyl ether (BADGE) epoxy formulation containing 1% PAG IOC8-SbF$_6$ and 1% thermal radical initiator TPED. To analyze the influence of insulating nanosized fillers for composites in RICFP experiments, 80 nm SiO$_2$ nanopowder was used. The particles with high surface and small particle size were chosen to show the change in polymerization behaviour and product features in a homogenous dispersion.

By increasing the filler content there is a decrease of front velocity and a decrease of front starting time (see Fig. 4), attributable to the presence of silica filler which are thermally insulating.

The low thermal conductivity of SiO$_2$ impedes the heat diffusion in longitudinal direction of the front. Filler content of 1% phr has only marginal influence on the VF, whereas 2% phr already shows significant decrease of almost 10% compared to the unfilled system. Using 3% phr of SiO_2 further decreases the VF to 6.8 from initially 7.5 cm min^{-1}.

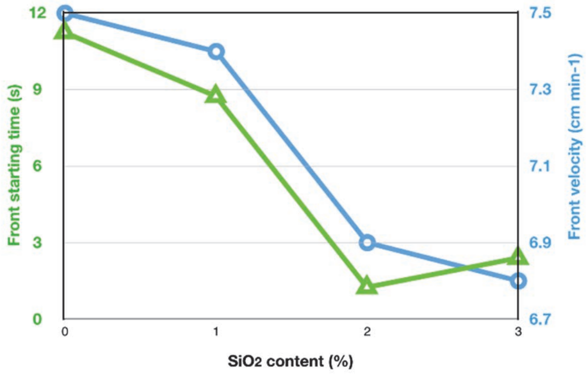

Fig. 4. Front velocity and front starting time as a function of filler content.

Radical induced cationic frontal polymerization was also investigated for the epoxy samples prepared with two plies of glass fibres disposed with orientation of 0° and 90°. The lamp was turn-on for 10 s. The heat front was propagating towards the entire composite very clearly and quickly. A fully crosslinked composite was obtained in less than a minute. The UV-crosslinked epoxy composite was compared with the same composite thermally cured.

Table 1. Thermo-mechanical properties of UV-cured and thermally cured epoxy composite.

Sample	***Tg* (°C)[1]**	**Tensile Strength (MPa)[2]**	**Tensile Modulus *E* (GPa)[2]**
UV-Cured	105	367±14	23.5±1.3
Thermally Cured	95	345±23	21.8±2.8

[1]Determined as the maximum of tanδ curves from DMTA analysis. [2]Measured by stress-strain curves.

In Table 1, the *T*g, determined as the maximum of tanδ curve, the tensile strength and tensile modulus, measured by stress-strain curves, are collected for the investigated samples. The data showed that the UV-cured samples are characterized by a slightly higher mechanical performance, in accordance with the higher *T*g recorded by DMTA.

In summary we demonstrated the feasibility of using UV-light to achieve epoxy composites containing silica or glass fibres. The important advantage of this crosslinking method is related to the very fast polymerization process compared with thermal curing, which allows to get high productivity maintaining the good thermo-mechanical properties of the epoxy composites.

4. Conclusion

With this paper it is intended to demonstrate the possibility to extend the use of cationic photopolymerization in different areas. It is shown how to overcome important limitation of this process related to the presence of water and to the possibility to crosslink with light thick composite materials. Specific strategies have been followed to run cationic emulsion polymerization reaction in water, taking the advantage of hydrophobic droplets of suitable dimension to avoid termination reaction, achieving capsules of about 200 nm.

A frontal polymerization reaction is used to promote the UV-induced crosslinking process of an epoxy composites via a radical induced cationic frontal polymerization. The thermo-mechanical properties of the achieved composites showed comparable behavior with thermal crosslinked composites.

This paper shows recent advancement of cationic photopolymerization knowledge and suggests the use of this technique in different field.

References

1. M. Sangermano, N. Razza, and J. V. Crivello, *Macromol. Mater. Eng.*, **299** (2014) 775.
2. F. Artusio, M. Bazzano, R. Pisano, P. E. Coulon, G. Rizza, T. Schiller, and M. Sangermano, *Polymer*, **139** (2018) 155.
3. N. Klikovits, R. Liska, A. D'Anna, and M. Sangermano, *Macrmol. Chem. Phys.*, **218** (2017) 1700313.
4. C. Vauthier and K. Bouchemal, *Pharm. Res.*, **26** (2009) 1025.
5. B. V. N. Nagavarma, K. S. Y. Hemant, A. Ayaz, L. S. Vasudha, and H. G. Shivakumar, *Asian J. Pharm. Clin. Res.*, **5** (2012) 16.
6. M. S. El-Aasser and C. M. Miller, Principles and applications, in: J. M. Asua (Ed.), Polymeric Dispersions, Kluwer Academic Publisher, Dordrecht, 1997, pp. 109-126.
7. K. Piradashvili, E. M. Alexandrino, F. R. Wurm, and K. Landfester, *Chem. Rev.*, **116** (2015) 2141.
8. B. Falk and J. V. Crivello, *Chem. Mater.*, **16** (2004) 5033.
9. B. Falk and J. V. Crivello, *J. Appl. Polym. Sci.*, **97** (2005) 1574.
10. M. Sangermano, N. Razza, and J. V. Crivello, *Macromol. Mater. Eng.*, **299** (2014) 775.
11. M. Sangermano, "UV Cured nanostructured epoxy coatings" in "Epoxy polymers" new materials and innovations", J. P. Pascault and R. J. J. Williams Eds., Wiley, Weinheim, 2010.