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Characterization and Optimization of Ceramic Suspensions for 3D Printing based on Stereolithography

Pol Barcelona[1], Jose Antonio Padilla[1], Alejandro Martín[1], Mònica Martínez[1], Mercè Segarra[1], Elena Xuriguera[1]*

[1] *Centre DIOPMA, Departament de Ciència dels Materials i Química Física, IN2UB, Facultat de Química, Universitat de Barcelona,*
C/ Martí i Franquès 1, 08028 Barcelona, Spain

***E-mail:** xuriguera@ub.edu

Introduction

3D printing of ceramics is a growing field given the great versatility of the technique to achieve complex and/or personalized geometries. One of the most implemented technologies today is those based on photosensitive systems in which a polymer sensitive to UV-visible radiation is used as a carrier for the ceramic particles that will later make up the final piece. These technologies have become very affordable and are increasingly reaching more sectors that see an opportunity in their implementation.

The three-dimensional object is built up layer by layer, where new layers of material adhere to the previous layer by photopolymerization, generating a new surface. The sequence of multiple layers of a specific thickness, which is usually not greater than 100 µm, forms the three-dimensional object. In this case, the energy for the polymerization comes from a Digital Light Processing projector, *Figure 1*. Post-processes of burning the organic part and sintering must be carried out to obtain the ceramic piece once the printed piece in green is obtained.

The development of new ceramic materials that can be used in these technologies usually focuses on obtaining highly concentrated and stable ceramic suspensions that have the necessary rheological properties for each technology. Once formulated, factors such as layer thickness or UV light exposure time are studied to check their influence on the printing process, as well as on the thermal post-process.

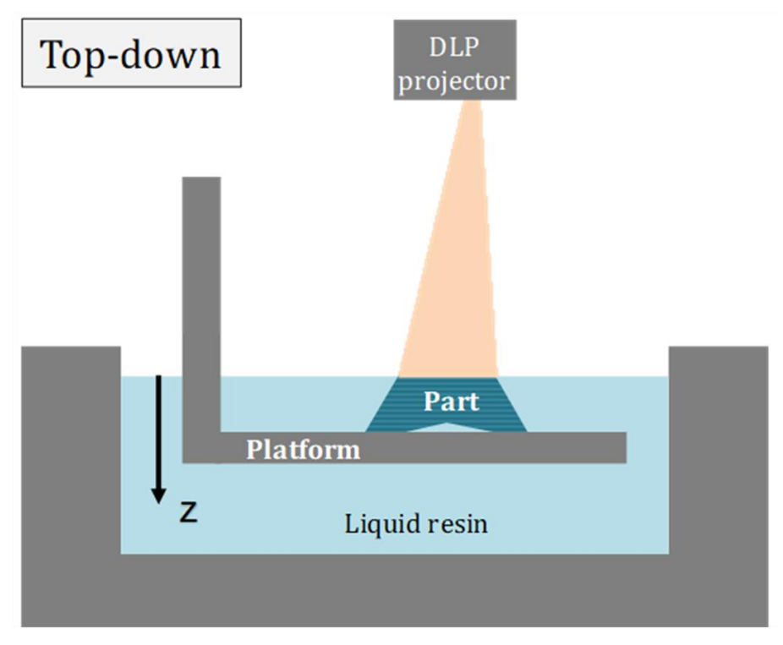

Figure 1. Schematic top-down DLP approach

Methodology

All measurements are carried out at rheometer Discovery HR2, *TA Instruments*, with a UV guide accessory, *Figure 2*, to perform fast sampling oscillation measurements at constant frequency and strain, 10 Hz and 0.01 % respectively.

The measurements have been made in a plate-plate system, with an upper 8 mm aluminum plate and a lower 20 mm PMMA plate, at different gap heights.

Lightningcure^{TM} LC8, *HAMAMATSU*, was used as a UV light source for the rheological analysis. All samples have been measured at a steady state for one minute before irradiation, and another minute while they were being irradiated over a large spectrum of UV-visible wavelengths at two different intensities. The irradiance was measured with a radiometer at the measuring point.

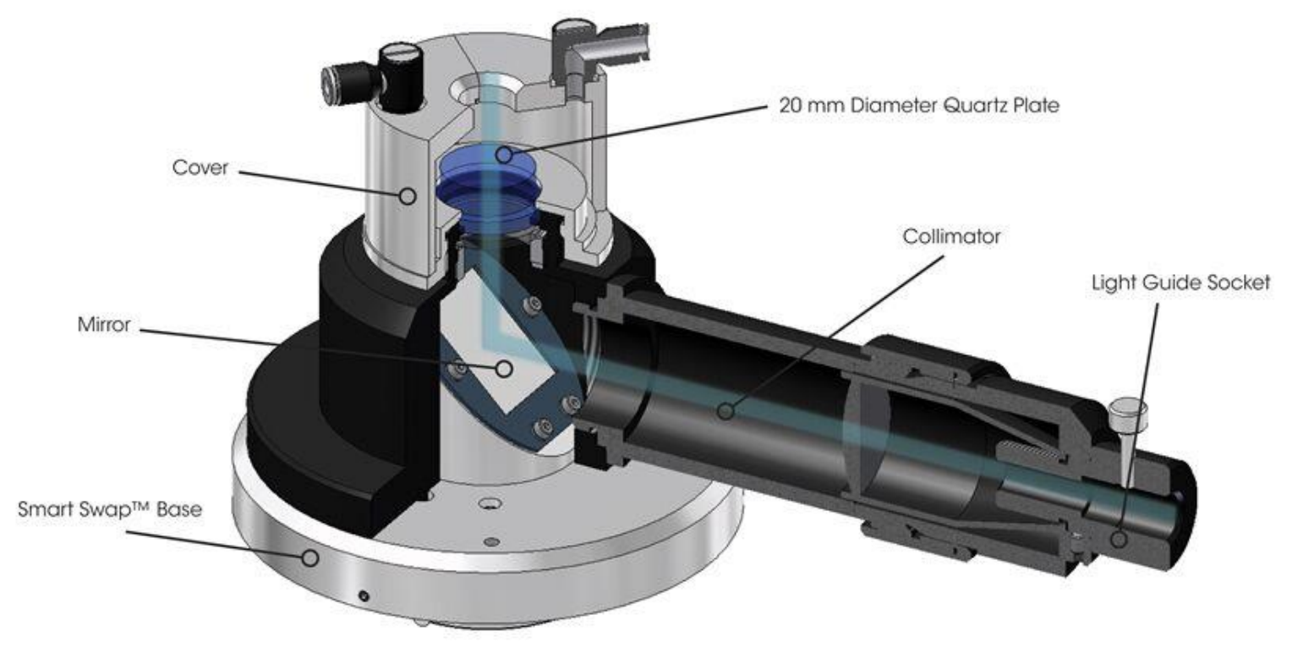

Figure 2. UV rheology accessory. *TA Instruments*

SPOT-LV, *Spot A Materials*, was used as the photosensitive resin in this study. The resin has been studied as received, and as part of ceramic suspensions.

For the suspensions, alumina ceramic particles with a d_{50} of 3 µm have been used, *Sharlab*. Before the addition of the ceramic, dispersant BYK W 969, *BYK Additives & Instruments*, was added to the resin, at a content of 2 wt% concerning the subsequent solid load.

Two suspensions of 67 wt% (37 vol%) and 80 wt% (52.6 vol%) of alumina were studied. All the suspensions have been prepared by sonication of the dispersant and the resin and subsequent incorporation and mixing of the solid load in a ball mill for 48 hours.

UV-Rheology for Photosensitive Resins

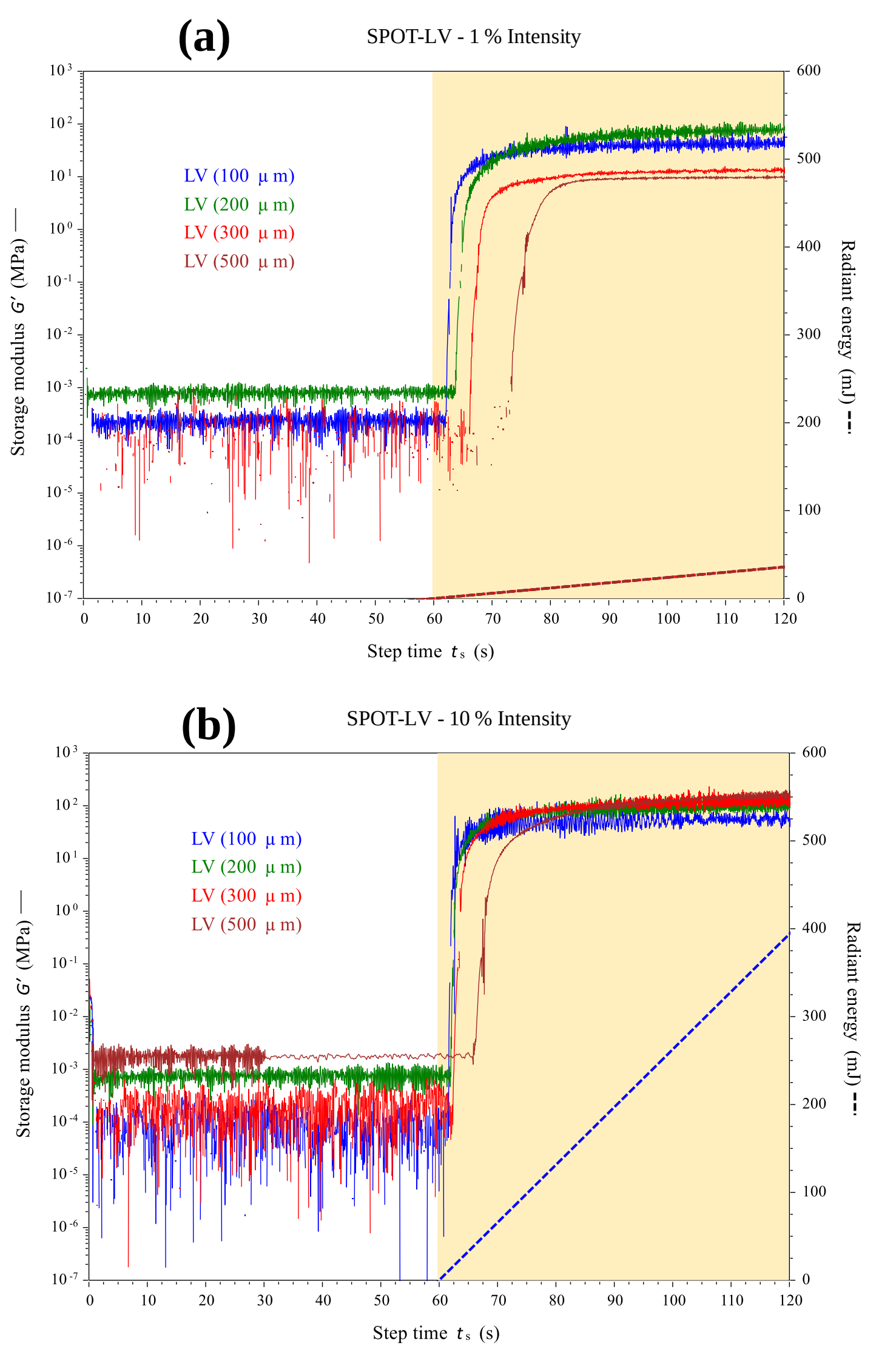

Figure 3. Storage modulus evolution of SPOT-LV for different layer thicknesses at 1 (a) and 10 % (b) of intensity. Gold shading corresponds to irradiation time. The dashed line shows the energy received over time.

The results show for all cases how the resin goes from a stationary state with constant modulus to increasing the modulus in a very short time up to 6 orders of magnitude once the sample begins to be irradiated.

If the results are compared for the same intensity at different gap heights, it can be seen how the increase of the modulus is delayed in time due to the major energy requested.

It can also be seen in *Figure 3b*, that at low intensity, higher layer thicknesses do not reach the highest modulus values, since the supplied energy is not enough to reach a complete conversion. The same did not happen at higher intensity, *Figure 3b*, where all layer thicknesses can reach the maximum conversion.

Comparing the results at both intensities, it can be confirmed that the higher the intensity, the faster the conversion, as expected.

While the curing process is observed through the irradiation process, the shrinkage in the normal direction of the light can be observed through the force that it generates on the plates of the rheometer. In this way, Figure 4 shows the evolution of the gap during the curing process for the SPOT-LV resin.

It can be seen how the higher the intensity, the linear shrinkage is higher, as well as that the shrinkage process is faster and more abrupt.

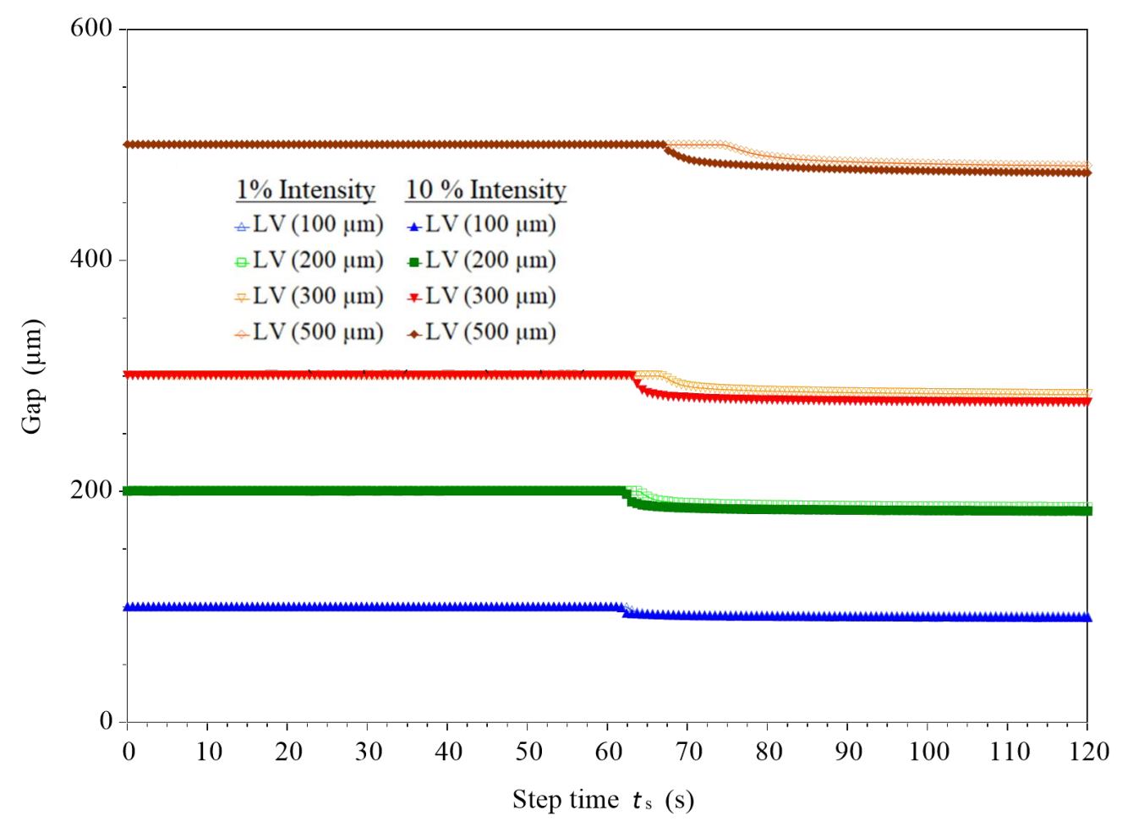

Figure 4. Gap evolution for different layer thickness and intensity through time.

UV-Rheology for Ceramic Photosensitive Suspensions

As in the resin without ceramic load, it is observed how the alumina suspensions take longer to reach the maximum modulus at a higher gap. In the most disadvantaged cases, minimum intensity and maximum gap, the maximum modulus is not always reached.

The results of the suspensions at 67 wt%, *Figures 5a* and *5c* , show a delay in the polymerization process in contrast to the resin without ceramic filler, *Figure 3*. This delay is mainly because of the backscattering effect produced by the surface of the particles, which decreases the real energy that is absorbed by the material.

On the other hand, is observed that the polymeric conversion with the higher solid load suspensions, at 80 wt%, is faster than the lower ones, 67 wt%. This effect can be observed comparing *Figures 5c* and *5d*, where suspensions at 67 wt% do not reach maximum conversion, and suspensions at 80 wt% reach it in a few seconds.

The increase of curing speed increasing ceramic concentration would be related to the lower amount of resin to be cured in the higher concentrations of alumina, making differences in backscattering effect of the two suspensions less relevant.

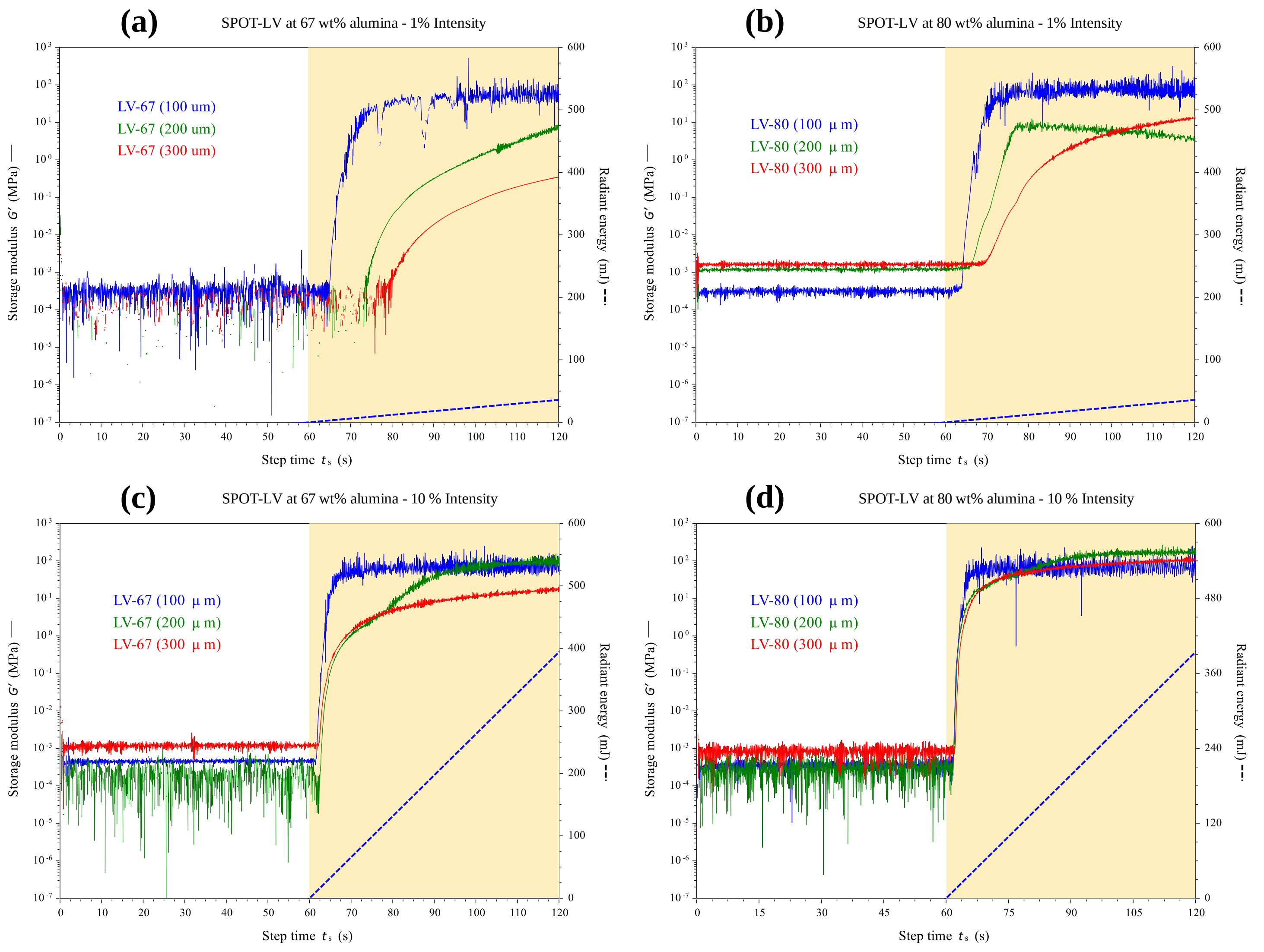

Figure 5. Storage modulus evolution for alumina suspensions at 1 % of irradiation intensity and a solid load of (a) 67 wt% and (b) 80 wt%; and at 10 % of irradiation intensity and a solid load of (c) 67 wt% and (d) 80 wt%.
Gold shading corresponds to irradiation time. The dashed line shows the energy received over time.

Table 1. Values of gap reduction and linear shrinkage for all measures at different intensities and initial gaps.

Material	Initial Gap (µm)	Final Gap 1 % (µm)	Final Gap 10 % (µm)	Shrinkage at 1% (%)	Shrinkage at 10 % (%)
SPOT-LV	100	91.7	90.7	8.3	9.3
	200	192.2	182.6	3.9	8.7
	300	284.0	276.6	5.3	7.8
	500	481.8	475.4	3.6	4.9
SPOT-LV 67 wt% alumina	100	96.0	95.7	4.0	4.3
	200	196.6	189.6	1.7	5.2
	300	300.0	281.3	0	6.2
SPOT-LV 80 wt% alumina	100	96.7	96.2	3.3	3.8
	200	196.6	192.0	1.7	4.0
	300	296.0	289.4	1.3	3.5

Table 1 presents de results of the gap reduction and linear shrinkage for all the rheological analyses. For all measurements, there is a clear increase in the shrinkage of the samples at higher irradiation intensity. This could be due to a higher conversion factor that lower intensities are not able to achieve.

At the same time, it is observed that for higher layer thicknesses, the percentage shrinkage is lower. This may be related to the non-uniform conversion of the entire layer to be cured, which produces different properties throughout the layer and can result in print defects.

Conclusions

- It is possible to follow the photoconversion process of resin and ceramic photosensitive suspensions through UV rheology.
- The intensity of irradiation affects the rate of conversion and the shrinkage of the material.
- The rheometer can follow the shrinkage of the material through the normal force that it generates.
- Low radiation intensities can lead to a lack of conversion of the final material, especially in photosensitive suspensions.
- For studied highly ceramic load, the backscattering effect from the particles is no longer predominant and the energy required for curing the suspension is related to the amount of photopolymer.
- Higher intensity of irradiation presents higher shrinkage at maximum conversion.
- Large layers thingness can cause inhomogeneities in the section of the material.
- The thickness of the layer and its contraction, as well as the intensity of radiation, are key factors in the DLP printing process.

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