Synthesis of chemical blowing agents for the development of light weight acrylate-based 3D printing inks

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The 3D printing technique is a common technology for the production of complex and precise products. The printed product is built up of numerous thin layers which are individually printed and cured before applying the next layer (e.g. working principle of the polyjet technology). The addition of a blowing agent to the ink blend and subsequently foaming of the individual layers before curing would open up the possibility of being able to produce light-weight products which would be a further improvement of the 3D printer possibilities.

Basis for the development of the ink mixture is an acrylate based 3D printer ink system. Therefore, a large part of the commonly used chemical blowing agents, typically consisting a reactive nitrogen functionality, are unusable since a reaction of the acrylate monomers and the blowing agent would take place.

There are only a few widely used blowing agents which have no reactive nitrogen functionality, so it is necessary to customize the blowing agent specifically to the ink mixture.

Experimental

The adapted structures are based on sulfonyl hydrazide blowing agents. These have a terminal primary nitrogen functionality which can react with the ink mixture without further modification of the blowing agent.

Thus, according to [1-2], benzenesulfonyl hydrazide (BSH) and 4,4‘-Oxybis(benzenesulfonyl hydrazide) (OBSH) are functionalized with methacryloyl chloride (MAC) as shown in Figure 1. This modification is not only intended to block the reactive nitrogen functionality, it also provides better compatibility with the ink system due to the higher similarity of the blowing agent and the acrylate monomers.

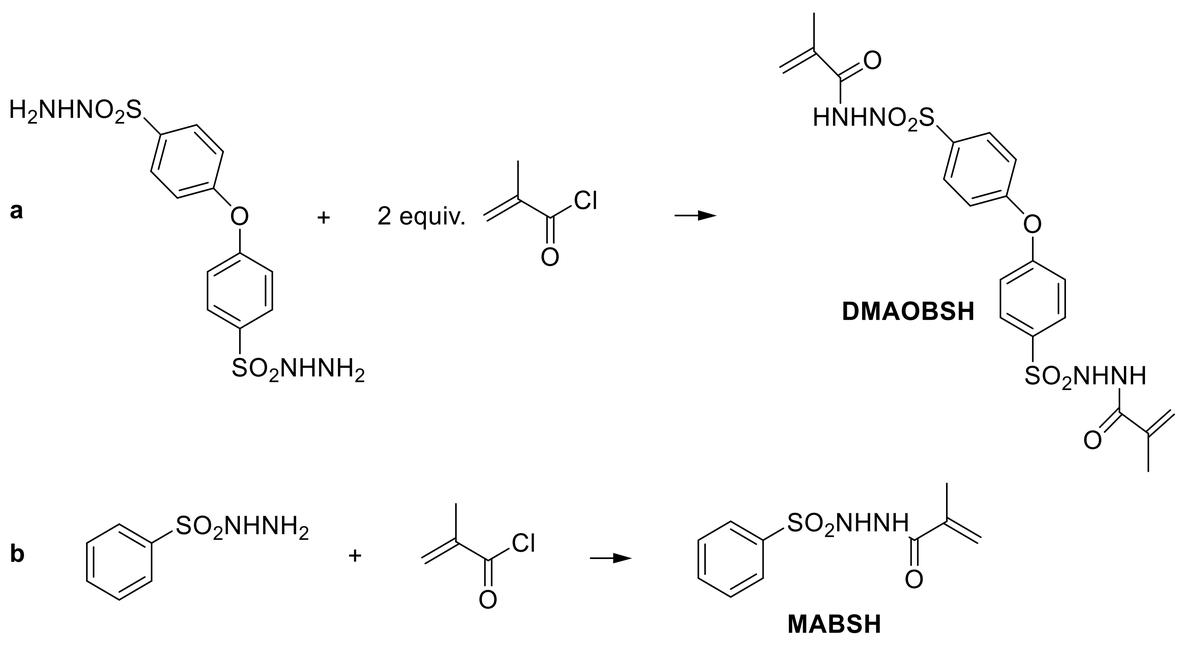

Figure 1: Modification of OBSH (**a**) and BSH (**b**).

Results

The results of the thermal analysis show that the foaming properties of the blowing agents are preserved as shown in Figure 2.

Moreover, especially in the case of OBSH, they improve the decomposition behavior, since a rapid decomposition reaction is not desired. Further the onset for the decomposition temperature and the energy required for the disintegration of the blowing agent are in the ideal range for the application in the acrylate based ink mixture.

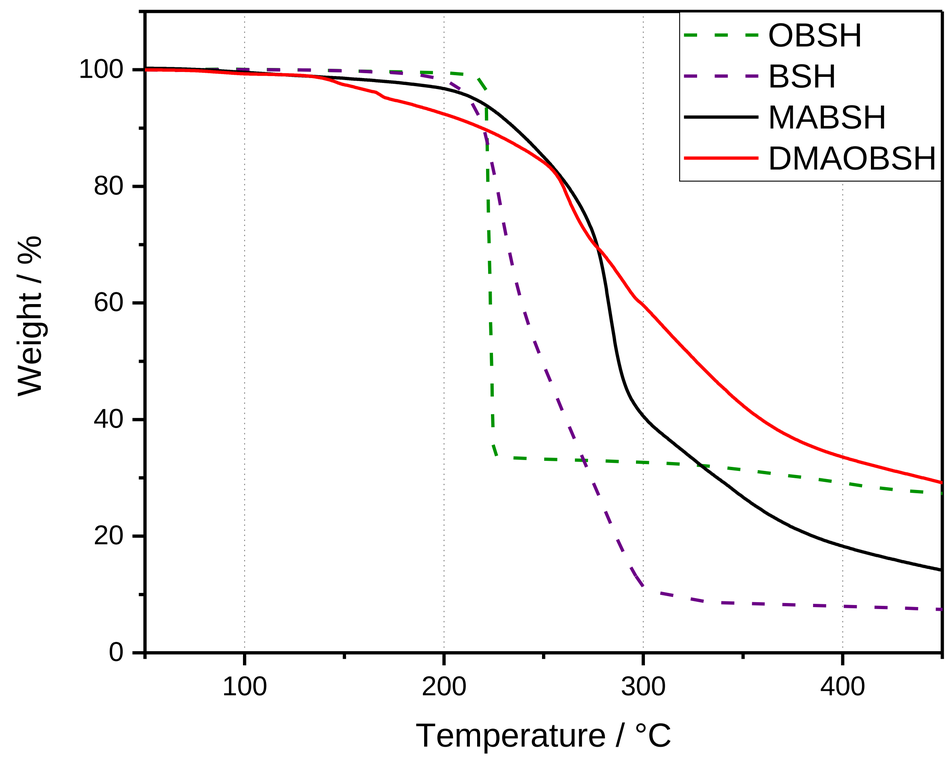

Figure 2: Comparison of the TGA analysis of OBSH, BSH, MABSH and DMAOBSH.

Conclusion

The functionalized blowing agents developed, showed good stability in various thermal analyses and the foaming action is retained as desired. The functionalization increased the onset of the decomposition temperature to 212°C and lowered the rate of disintegration, both changes being an improvement over the commercial blowing agents.

First printing tests of the ink blends with the new blowing agents have shown a good printability (Figure 3). The blowing agent is fully dissolved and it is possible to print thin layers followed by a subsequently foaming step and the final curing of the acrylate monomers.

Figure 3: Printed layer before (left) and after (right) the foaming step.

References

[1] Jeong J., Yang J., Ha S., Cho J., Chung I., Synthesis and characterization of polymeric foaming agent containing sulfonyl hydrazide moiety, *Polym. Bull*., (**2012**), *68*(5), 1227–1238.

[2] Jeong J., Kim T., Cho J., Chung I., Synthesis and decomposition performance of a polymeric foaming agent containing a sulfonyl hydrazide moiety, *Polym. Int*, (**2012**), *51*, 1094-1100.