PRODUCTION OF POLYMER/CLAY NANOCOMPOSITE FOAMS WITH IMPROVED FIRE BEHAVIOUR USING SUPERCRITICAL FLUID TECHNOLOGY

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In this study, supercritical CO_2 is successfully used as foaming agent to prepare poly(styrene-co-acrylonitrile) (SAN) foams containing a low amount of well-dispersed nanoclay (5wt%). This kind of nanofiller has an influence both on material cellular morphology and fire property. In fact, SAN foam filled with nanoclay has smaller cells and higher density compared to unfilled foam. Moreover, the nanocomposite foam burns more slowly and without producing any burning droplets, which is highly desirable when considering housing applications.

INTRODUCTION

Polymeric foams are attractive materials due to their low weight, high impact resistance, thermal insulation, etc. However, these materials, mainly composed of voids, are highly flammable, which prevents their use in several applications, like house decoration. Usually, high amounts of halogenated flame retardant are added in order to overcome this problem. But due to environmental and health concerns, there is now a need for both friendlier and more efficient flame retardants. Phosphorous and nitrogen-based compounds, like melamine, are currently investigated as potential alternatives. For a few years, lamellar nanoclays are also driving an increasing interest due to their ability to enhance polymers combustion behaviour with only a few percent of well-dispersed filler while increasing the material strength. Only a few works have already dealt with the combustion behaviour of polymer/clay nanocomposite foams so far [1,2].

In this work, we have used supercritical carbon dioxide (CO_2) as the physical blowing agent in order to prepare poly(styrene-*co*-acrylonitrile)/clay nanocomposite foams. This gas has been chosen because it is more environmentally friendly than CFC and it has a good affinity with slightly polar polymers, like SAN. Furthermore, microcellular foams with very regular porosity can be obtained, with cells size going from 500µm down to 1µm. Adding nanoclays can even lead to smaller cells due to their heterogeneous nucleating ability.

The effect of nanoclay on the sample porosity is investigated, and the foams burning behaviour are then evaluated qualitatively.

MATERIALS AND METHODS

Nanocomposite preparation : PCL/Cloisite®30B masterbatch (53 wt% in inorganics), previously prepared by in situ polymerization in $scCO_2$ [3], was melt blended into SAN in a counter-rotating mixer at 175°C for 5min at 70rpm in order to reach 5wt% in inorganics [4]. The nanocomposite is then molded into 3mm thick sheets at 175°C for 5min.

Batch foaming process : The nanocomposite is left to soak for 22h at 40°C under 300bar of CO_2 in a 250ml high pressure reactor. Then, the vessel is depressurized rapidly and the saturated sample is directly dipped in an oil bath at 100°C for 3 min to induce foaming. The foam is then quenched in an ice/water bath.

Characterization : Nanocomposite characterization can be found in ref. 4. The foam porosity is observed with scanning electron microscopy (SEM; JEOL JSM 840-A) after metallization with Pt. The burning test is made on 7x1x0,5cm foams cut with a bevelled edge. The samples are ignited with a lighter and the burning time is recorded.

RESULTS

SAN foamed with $scCO_2$ has regular porosity with cells size around 1-2µm. When adding 5wt% of nanoclay, denser nanocomposite foam is obtained, due to the increased viscosity while adding well-dispersed nanofiller, and with cells size below 1µm.

Striking differences in the burning behaviour are observed for those two foams during the burning test. On one hand, pure SAN foam burns fast with the production of burning droplets which facilitates fire propagation. On the other hand, SAN/5%MB30B foam burns more slowly with the formation of a carbonaceous char which prevents burning droplets formation.

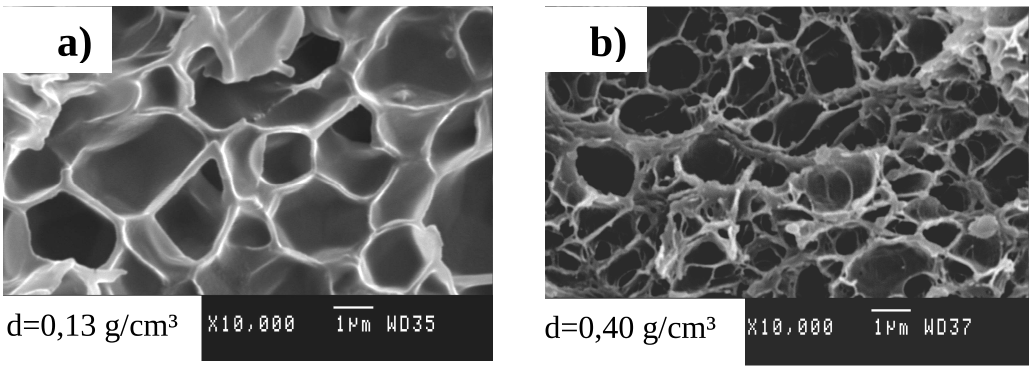

Figure 1 : SEM analysis of a) SAN and b) SAN/5%MB30B foams, prepared by batch foaming with $scCO_2$.

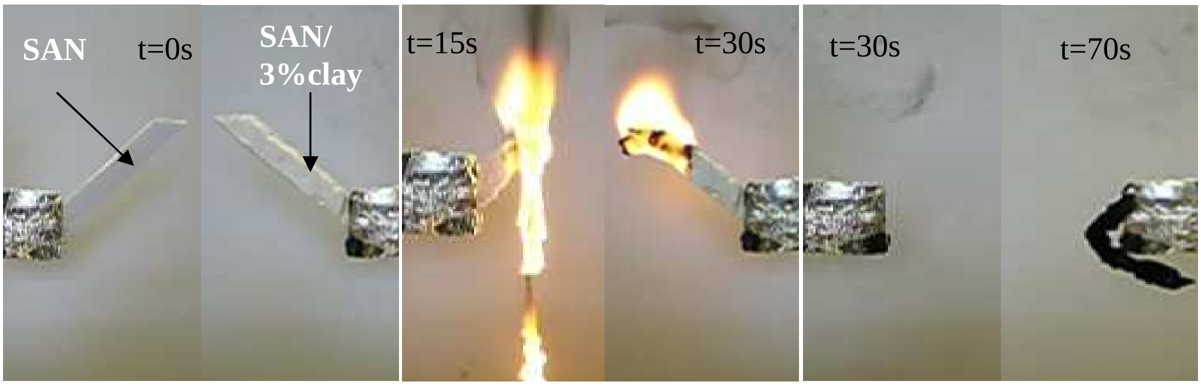

Figure 2 : Burning behaviour of left: SAN and right: SAN/5%MB30B foams, prepared by batch foaming with $scCO_2$.

CONCLUSION

This work demonstrates that the addition of only 5wt% of nanometric filler can enhance significantly the burning behaviour of highly flammable materials like polymeric foams. The formation of burning droplets – responsible for fast fire propagation – can be avoided thanks to the carbonaceous char formed during nanocomposite combustion. However, self-extinction is not observed for such nanocomposite foams. The combination of lamellar nanoclays with classical flame retardants is seen as a promising route in order to obtain very fire-resistive materials with low additive loadings [1].

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REFERENCES

[1] WANG, J. Q., CHOW, W. K., J. Appl. Pol. Sci., Vol. 97, **2005**, p. 366

[2] ZAMMARANO, M.; GILMAN, J.W.; KRAMER, R.H.; HARRIS, R.; OHLEMILLER, T.J.; SHIELDS, J.R., Proceedings of 19^{th} BCC Conference, **2008**

[3] URBANCZYK, L., CALBERG, C., STASSIN, F., ALEXANDRE, M., JÉRÔME, R., JÉRÔME, C., DETREMBLEUR, C., Polymer, Vol. 49, **2008**, p. 3979

[4]. URBANCZYK, L., CALBERG, C., BENALI, S., BOURBIGOT, S., ESPUCHE, E., GOUANVÉ, F., DUBOIS, PH., GERMAIN, A., JÉRÔME, C., DETREMBLEUR, C., ALEXANDRE, M., J. Mater. Chem., Vol. 18, **2008**, p. 4623