Non-Conventional Curing of Organic-Inorganic Hybrids

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Summary: Infrared and microwave curing of organic–inorganic hybrid materials was studied, in order to achieve the maximum conversion without detrimental effects due to the overheating or to the long-time permanence at high temperature.
Partially cured poly(ethylene oxide)/silica hybrids were prepared by hydrolysis and subsequent condensation of precursors for 30 minutes isothermal heat treatment at 70°C. The conversion after the preliminary treatment is still low and requires an additional heating to complete the reaction. Three different thermal treatments were investigated: conventional heating, infrared heating and microwave heating.
DSC characterisation of the obtained samples evidenced a drastic reduction of the treatment time when microwaves were used, requiring only a few seconds, compared to the hours-lasting conventional treatments.

Keywords: curing of polymers; infrared curing; microwave curing; organic-inorganic hybrids; radiation

Introduction

Plasticized poly(vinyl chloride) (PVC) is largely used in the production of medical devices such as intravenous fluid bags and tubing, blood and plasma bags, enteral feeding and dialysis equipment, catheters, and gloves[1]. Di-ethylhexyl phthalate (DEHP or DOP) is the one most commonly used as plasticizer in the production of medical devices for its processing advantages. A complete and critical review[2] on the health risks by DEHP leaching form plasticized PVC indicated that, in some instances, humans can be exposed to clinically important concentrations of DEHP through PVC medical devices and experimental results suggest that DEHP exposures resulting from medical care may lead to adverse health effects in certain groups of patients.

An effective method to reduce the plasticizer leaching from PVC devices was recently proposed by Messori *et al.*[3] α,ω-triethoxysilane terminated poly(ethylene oxide) (PEO-Si) was prepared and used to produce organic/inorganic hybrids by the sol-gel process. These hybrids were used as coatings for flexible PVC tubes in order to reduce the plasticizer leaching and extraction tests carried out with hexane indicated that all coating

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compositions investigated were able to strongly reduce (about one order of magnitude) the leaching of DEHP in hexane. One of the main drawbacks of this approach is represented by the long curing time of the organic-inorganic hybrid coating which can require up to 24 hours thermal treatment at relatively high temperature, eventually leading to distortion of the plasticized PVC substrate. At the best of our knowledge no paper are reported in the scientific literature about the use of non conventional curing methods of organic-inorganic hybrids. For this reason, aim of the present work was the investigation of non-conventional curing treatments such as microwave and infrared irradiation alternatively to the classical thermal curing in order to achieve the maximum conversion without detrimental effects due to the overheating and/or to the long-time permanence at high temperature.

Experimental

Materials

α,ω-hydroxyl terminated poly(ethylene oxide) (PEO, purchased from Fluka and with a number average molecular weight of about 1000 g/mol), 3-isocyanatopropyltriethoxysilane (ICPTES, Fluka), tetraethoxysilane (TEOS, Aldrich), hydrochloric acid at 37% concentration (Carlo Erba) and ethanol (EtOH, Carlo Erba) were used without further purification.

Preparation of α,ω-triethoxysilane terminated poly(ethylene oxide) (PEO-Si)

α,ω-triethoxysilane terminated poly(ethylene oxide) (PEO-Si) was prepared by bulk reaction of PEO with ICPTES (molar ratio of 1:2). The reaction was carried out in a 50 ml glass flask equipped with a calcium chloride trap and under magnetic stirring, at 120°C, for 3 hours as already reported in a previous paper.[3]

Preparation of PEO/silica hybrids

PEO-Si/TEOS mixtures were dissolved in EtOH at a concentration of 40% wt/vol, then water (for the hydrolysis reaction) and hydrochloric acid (as catalyst) were added at the following molar ratios with respect to ethoxide groups of PEO-Si and TEOS: EtO-:H_2O:HCl=1:1:0.05.

A typical preparation was as follow: PEO-Si (1.20 g) and TEOS (0.80 g) were added to 3 ml of EtOH in a screw-thread glass vial and mixed until a homogeneous solution was obtained. Then water and HCl (37%wt solution) were added under vigorous stirring at

room temperature for about 10 min. The closed vial was placed in air circulating oven at the temperature of 70°C for 30 minutes in order to allow only a partial progress of the sol-gel reaction. The clear solution was then cast into a closed polytetrafluoroethylene dish and the solvent was slowly evaporated at room temperature for about one week.

The final hybrids were characterized by a final organic/inorganic weight ratio of 7/3, assuming the completion of the sol-gel reactions reported in the Scheme 1.

$Si(OEt)_4 + x\ H_2O \rightarrow Si(OEt)_{4-x}(OH)_x + x\ EtOH$

$(EtO)_3Si\text{-}PEO\text{-}Si(OEt)_3 + (x+y)\ H_2O \rightarrow (EtO)_{3-x}(HO)_xSi\text{-}PEO\text{-}Si(OEt)_{3-y}(OH)_y + (x+y)\ EtOH$

$\equiv Si\text{-}OH + EtO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + EtOH$

$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$

Scheme 1. Reaction scheme of the sol-gel process.

Curing treatments

Partially cured hybrids were subjected to different post-curing treatments:

a) conventional heating in an air circulating oven (WTB Binder) at 100°C for 30 and 90 minutes, respectively;

b) infrared heating by using a Philips Infraphil PAR38E (1000 nm peak) at irradiation times ranging from 20 to 60 minutes;

c) microwave heating by using a Milestone MLS 1200 - Multi-mode at irradiation times ranging from 1 to 15 minutes and by using an Alter TE10n Applicator - Single-mode 2.45 GHz at irradiation times ranging from 5 to 30 seconds.

Characterization

Differential Scanning Calorimetry (DSC) was performed with a TA DSC2010 instrument in the range -100 ÷ +150°C with a heating rate of $10°C \cdot min^{-1}$. The extent of the residual curing reaction was determined during the first heating scan on the basis of the endothermic peak corresponding to the volatilization of EtOH and water formed during the completion of the sol-gel reaction. A second heating scan was performed in the case of hybrids in order to evaluated the presence of further sol-gel reaction or melting transitions. Just before the measurements all samples were accurately dried under dynamic vacuum at 40°C for 1 hour in order to eliminate any volatile product.

Results and Discussion

Typical DSC thermograms of PEO-Si/SiO_2 after infrared heating and for different time of irradiation are reported in Figure 1. The endothermic peak shown from about 50 to 160°C can be correlated to the vaporization of volatile products such as water and EtOH formed during the heating scan according to the reaction scheme for the sol-gel process proposed in Scheme 1. That endothermic peak can be considered as an indirect indication of the residual degree of cure present in the hybrid after the preliminary treatment of PEO-Si and TEOS in solution at 70°C for 30 minutes: it is well evident its decreasing by increasing the irradiation time.

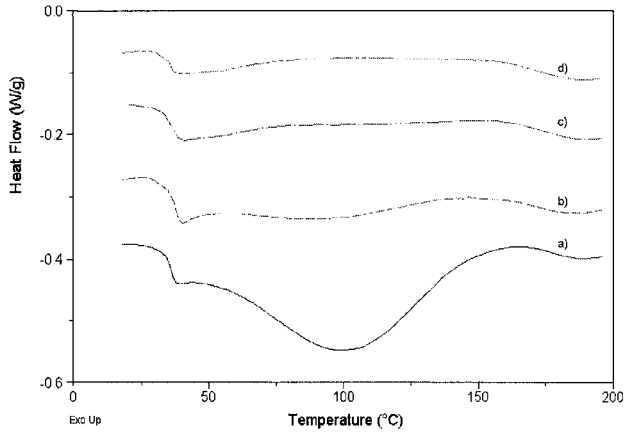

Figure 1. DSC thermograms of PEO-Si/SiO_2 infrared irradiated for a) 0 min; b) 20 min; c) 40 min and d) 60 min.

Quantitative evaluation of the conversion degree at different irradiation time and treatment can be calculated by integration of the endothermic peak above mentioned. The corresponding enthalpy values are reported in the following Table 1 and Figure 2.

In all cases a complete curing was achieved as indicated by the approaching zero enthalpy values for the higher irradiation times. Dramatic differences in terms of time necessary to reach complete cure (full cure time, FCT) were clearly evident among different types of curing. If we consider that complete curing was achieved for enthalpy values of 2 J/g or less, conventional thermal curing carried out at 100°C in an air circulating oven typically require more than one hour to achieve complete curing. Curing carried out by infrared irradiation was very similar to above mentioned conventional heating showing comparable FCT values.

Table 1. Enthalpy of PEO-Si/SiO_2 samples at different curing times and treatments (from DSC analysis).

Type of treatment	Treatment time	Enthalpy (J/g)
None	-	44.0
Oven	1800	4.0
	5400	0.1
IR	1200	5.8
	2400	1.7
	3600	2.2
	5400	1.0
MW 200 W	60	3.5
	300	3.0
	600	2.9
	900	2.0
MW 500 W	5	2.0
	10	0.7
	30	1.6

Significant decreasing of FCT was observed for microwave irradiation. In the case of low energy microwave irradiation (200 W) the time necessary to reach complete curing is lowered to 15 minutes. Better results were obtained with high energy microwave irradiation (500 W) for which complete conversion was obtained in a few seconds.

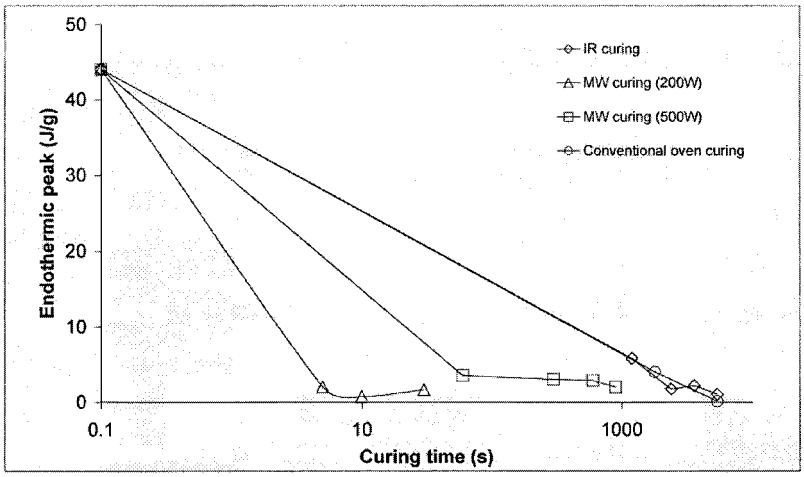

Figure 2. Enthalpy of PEO-Si/SiO_2 samples at different curing times and treatments (from DSC analysis).

Moreover, a strong dependence on the microwave applicator was observed. The Milestone furnace is a multimode applicator, where multiple reflections allow the microwaves to be absorbed by the sample. However, as shown in Figure 3, the Specific Absorption Rate - SAR (W/kg), calculated by the electromagnetic field simulation using the software Concerto 3.5, is significantly lower than the values achievable in a single mode applicator, at the same power level. This could explain the faster treatment time achieved in the single mode applicator, considering that, beside a higher electric field, the microwave heating is more homogenous. In case of non homogenous heating, the sample characterisation by DSC, which is based on averaging on the sample's mass, can be affected by the presence of untreated regions, leading to the permanence of peaks.

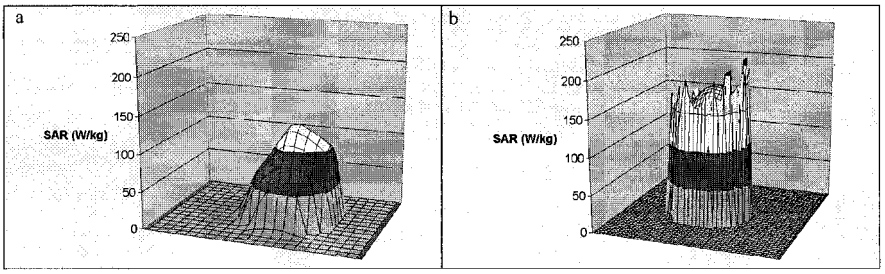

Figure 3. Calculated Specific Absorption Rate (SAR) of a disc-shaped sample exposed to 500W microwave power in: a) multimode applicator and b) single mode applicator.

Conclusions

Partially cured poly(ethylene oxide)/silica hybrids were prepared by sol-gel process. In order to increase the degree of cross-linking different post-curing treatments were carried out by conventional heating, infrared heating and microwave heating. DSC characterisation of the obtained samples evidenced a drastic reduction of the treatment time when microwaves at the ISM frequency of 2.45 GHz were used, requiring only a few seconds, compared to the hours-lasting conventional and infrared treatments. Moreover, microwave heating selectivity, due to the dielectric properties mismatch between the coating and the candidate substrates to be used, offers interesting possibilities of scale-up of the process to many low-loss dielectrics.

[1] W. Huber, B. Grasl-Kraupp, R. Schulte-Hermann, *Crit. Rev. Toxicol.* **1996**, *26*, 365.
[2] J. A. Tickner, T. Schettler, T. Guidotti, M. McCally, M. Rossi, *American Journal of Industrial Medicine* **2001**, *39*, 100.
[3] M. Messori, M. Toselli, F. Pilati, E. Fabbri, P. Fabbri, L. Pasquali, S. Nannarone, *Polymer* **2004**, *45*, 805.