Textiles Thermosetting by Microwaves

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Summary: Thermosetting is an important part of the finishing of thermoplastic poly(ethylene terephthalate) (PET) fabrics and garments that confers stability in dimensions and shape as well as appropriate hand to the final product. Conventional thermosetting methods for PET include hot air and steaming treatments.
In the present work we used solid state NMR as well as DSC methods in order to investigate any differences in the behaviour of PET chips when annealed with either a conventional or a microwave technique.

Introduction

The everyday increasing interest in microwave applications in the industrial sector lies in the possibilities to perform very fast manufacturing cycles, to reduce production costs, to decrease power consumption, to improve the quality of the existing products, and to increase the efficiency and productivity of the processes. Most of the benefits deriving from microwave applications, however, become evident only after a careful laboratory experimental work, and

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preliminary economical cost-benefits analysis is always full of uncertainties, being difficult the extrapolation of experimental data to the larger industrial scale. The advantages of a well designed microwave system, however, are still numerous and appealing; in particular:

- uniform and homogenous heating
- temperature profile inversion
- materials treatment at surface temperature lower than conventional
- high power densities, localised and in short times

Thermosetting is an important part of the finishing of poly(ethylene terephthalate) (PET) fabrics or garments to impart dimensional stability, shape, and appropriate hand to the product during using. Conventional methods for setting dimensional stability include either hot air or steaming treatments.

The aim of the present work is to verify whether microwave technology can be applied to thermoplastic PET thermosetting and to evaluate the quality of the obtained products with this kind of technique that leads to undoubted economical advantages deriving from the rapid heating rate.

Experimental

Sample preparation

The PET under study is and industrial product obtained in chips from Montefibre SpA. It shows to be not highly crystalline, as evidenced both from X ray diffractometry (not shown), solid state NMR and DSC analysis.

The PET chips as received were subjected to different annealing treatments at temperatures from 90° to 250° for 15-60 min, in both

conventional air oven and microwave furnace (a multimode cavity CEM MAS 7000 Incinerator, 2.45 GHz, 950). Temperature of the samples in the microwave treatments was determined by a thermocouple immediately after the turning off of the microwave irradiation.

The amorphous PET was prepared by melting PET chips in DSC analyser and quenched immediately in liquid nitrogen.

Methods

Differential scanning calorimetry experiments

DSC measurements were carried out in a Perkin Elmer DSC-4 calorimeter. Samples were heated from 30° to 300°C with a heating rate of 10 °C/min under a nitrogen atmosphere.

Solid state NMR studies

The CP-MAS ^{13}C NMR spectra at 75.4 MHz were recorded at room temperature with a Bruker ASX-300 spectrometer, using a 7mm ZrO_2 rotor. The cross polarisation (CP) contact time was 1,2 ms while the repetition time and the ^{1}H 90° pulse were from 4 to 20 s and 3.7 μs, respectively. The full width at half-height of the reference glycine was 27 Hz.

Chemical shifts were measured with respect to glycine as external reference set at 42 ppm from silyltrimethylpropionic acid sodium salt (TSP). For each spectrum 128-500 transients were accumulated with 1K data points. The spinning rate was 4.0 KHz, and the sweep width 360 ppm. The spectra were manually phased.

^{13}C T_1 relaxation times were measured by the Torchia sequence using CP T_1 experiments[1] where the magnetisation associated with each carbon atom is reduced to zero during longitudinal relaxation.

^{1}H spin-lattice relaxation measurements ($T_{1\rho}$) were used to quantify spin-diffusion via ^{13}C nucleous observation. The measurements were carried out under high resolution conditions to identify single phases where magnetisation propagation occurred.[2] The sequences have been described by Voekel.[3] Data were elaborated with both mono- and bi-exponential function, using xwin-NMR software by Bruker.

Results

Differential scanning calorimetry experiments

In order to focus the optimal conditions for any textiles thermosetting treatment it is necessary to know the morphology of the material on 1-50 nm scale, a region which can strongly influence the mechanical properties of the material.

In order to determine macroscopic phase transitions of PET after conventional or microwave annealing preliminary DSC measurements were performed. It is known that isothermal crystallization of isotropic PET samples is mainly controlled by the annealing temperature. [4,5]

Thermograms of the quenched PET and of the as received material are reported in Figure 1.

The variation of the base line before the 100°C is a clear image of the glass transition (Tg) temperature typical of non ordered areas, while the exothermic peak around 130°C is explainable through the crystallisation of the fold surface layers. Comparing the ΔH values of the quenched PET and of the as received one it is evident that the

industrial drying stage in vacuum at 105°C induces a partial reorganisation of the material.

The endothermic peak around 230°C is a clear image of melting as the transaction typical for the crystalline regions.

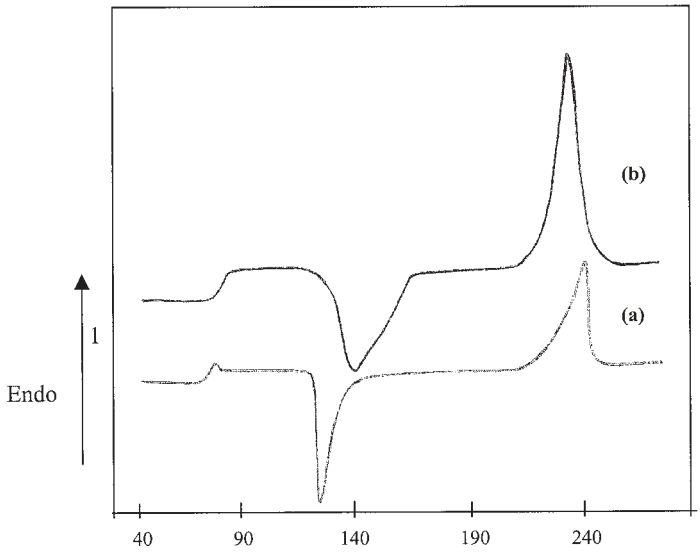

Figure 1 - DSC scanning of the as received (a) and quenched (b) PET samples.

The endothermic peak of cold crystallisation is not clearly visible any more already in the samples air annealed at 120°C (Figure 2), suggesting that when the system is brought towards a better mobility of the chains (T>Tg) the system has the tendency to reorganise in an ordered way when cooling down.

In the sample microwave annealed at 140 °C for 60 min the endothermic peak disappears faster than in the conventionally annealed sample indicating a prompter response of the material to thermal power. No differences in terms of ΔH_f (45-48 J/g) between air and microwave annealed samples were observed.

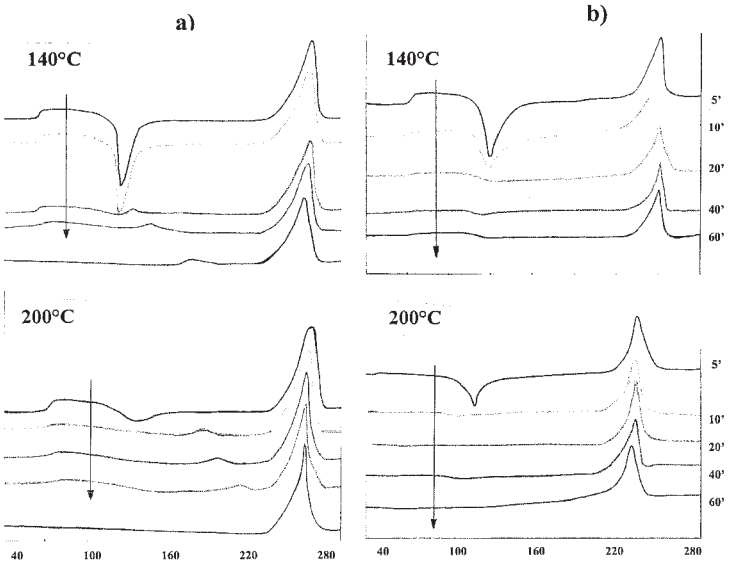

Figure 2 - DSC scans of the air (a) and microwave (b) annealed (140°-200°C) PET samples.

On the contrary by passing from 140° to 200°C a higher value of ΔH_f (80 J/g) was observed for the sample annealed in air in comparison to

the sample heated in microwave furnace (52 J/g) suggesting the presence of a bigger and/or more perfect crystals in the first case.

Thus the DSC data evidence a faster structural change of PET samples annealed by microwaves when the temperature is lower than 160°C but at higher temperature the conventional heating is more effective. The effects of the two types of annealing are comparable beyond 180°C.

For many samples an endothermic peak called "mobile peak"[6] appears whose position depends strongly on the annealing temperature and is generally located a couple of degrees higher that the annealing temperature and it goes to higher temperatures with increasing the treatment time.

The origin of the peak seems to be attributed to the formation of ordered small areas located in the fold surfaces layers of the crystalline blocks. The mobile peak appears always for both the annealing treatments performed.

^{13}C CPMAS NMR spectra

Solid State NMR Spectroscopy differently from other techniques as X-Rays diffractometry and vibrational spectrometry is well indicated both for studying local structures, in particular different conformational situations, as well as for defining polymer dynamics. In fact, through anisotropic nuclear-spin interaction and the resulting angle dependent NMR frequencies, the nuclei can act as local probes of segmental orientations. [7,8]

The CP MAS NMR spectrum of the PET samples show (Figure 3) three groups of signals typical of the material composition, centered in the region of 162, 130 and 61 ppm. In the as received sample the

signals are quite broad suggesting a dominant unordered structure contribution.

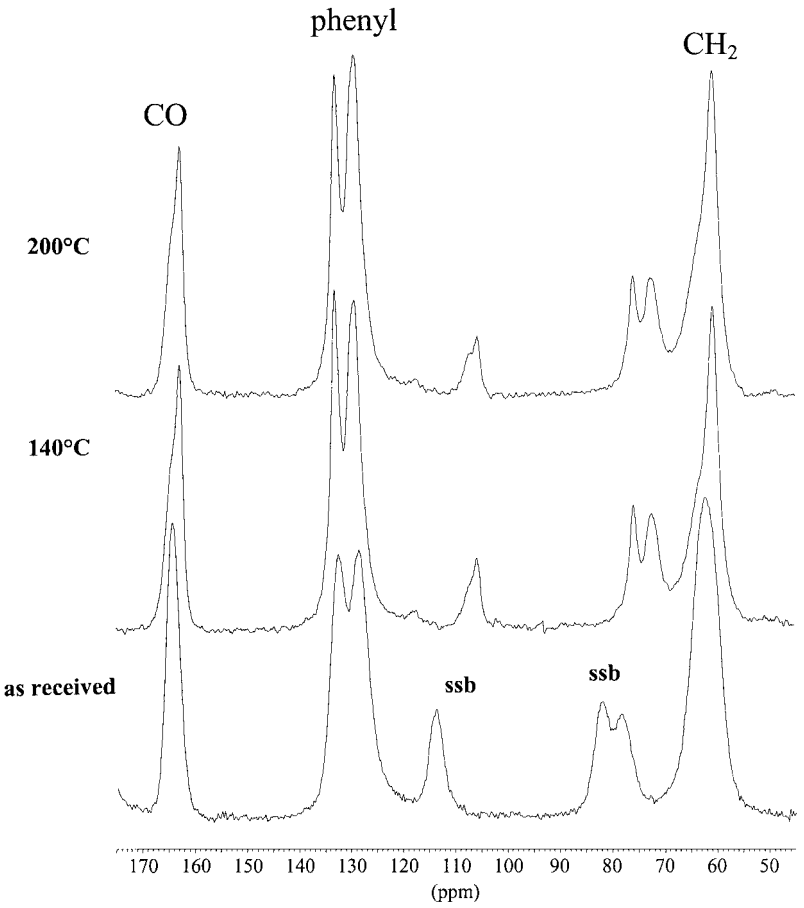

Figure 3 - CP MAS spectra of PET samples as received and at various air annealing temperatures.

Sample annealing both in air and in a microwave oven above glass transition temperature (Tg) induces a segment mobility of PET that brings to the formation of structures that seem more ordered, as evidenced from the narrowing of the signal and change in chemical shifts of the signals.

In fact, when passing from as received sample to the air annealed at 140° and 200°C for 60 min, a progressive reduction of the broadening of the signal of the samples is observed together with the co-existence of two components in the signals of the C=O (162.5 and 160 ppm) and CH_2 (60.5 and 60 ppm) groups.

Microwave annealing of the samples in the same experimental conditions of the conventional treatment brings to similar results, but less effective In fact, it is peculiar to point out the presence of two components in the C=O signal already for the sample treated at 140°C, but a slower kinetic in the structural change of the two termosetting treatments (Figure 4).

Even thought we do not expect large differences in the chemical shifts between the gauche and trans conformations of PET because the interactions with the substitutents in a γ position are small, nevertheless they are sufficient for making a distinction between the two PET conformations, the reduced mobility of the chain and the reduction in the broadening of the signals.

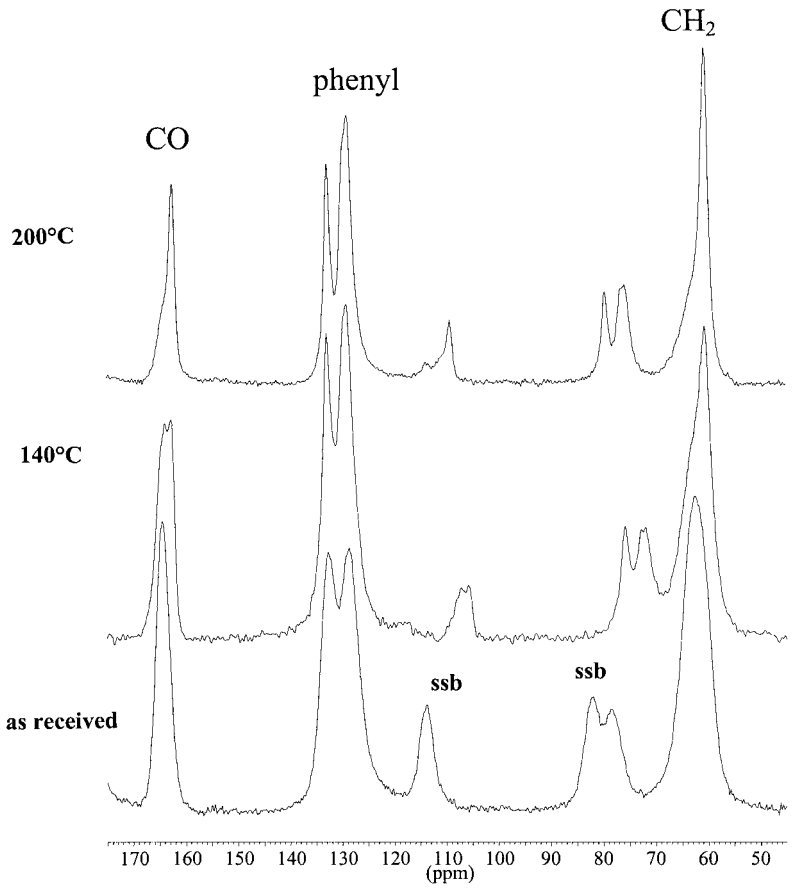

Figure 4- ^{13}CP MAS spectra of PET samples as received and at 140°-200°C microwave annealing temperatures.

When using the deconvolution of the signal at 60.5 ppm and integrating the two components it has been possible to determine the percentage of the trans and gauche conformation.[9,10] As an example, in Figure 5 is reported the CH_2 signal deconvolution of

the air annealed (160°C) PET sample and its reconstructed profile.

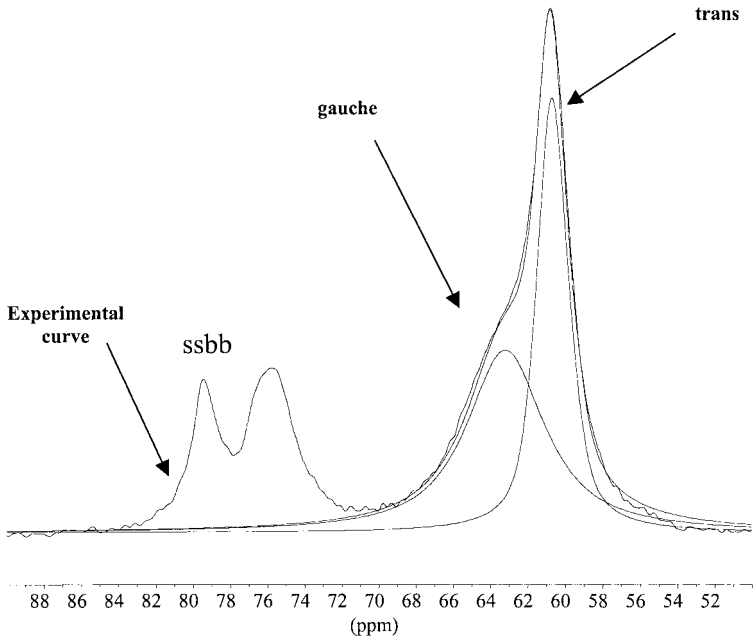

Figure 5 – Deconvolution of the methylen carbon CP-MAS resonance peak of PET (Gaussian and Lorentzian combination). The fitted curve is practically overlapping the experimental one.

In table 1 are reported the percentage of trans and gauche conformers obtained by deconvolution procedure for all samples.

Table 1 - Conformer distribution of methylen carbons.

sample	Air annealing temperature (60 min)	Trans (%)	Gauche (%)
PET	as received	3.5	96.5
	140°C	39.5	60.5
	160°C	37.0	63.0
	180°C	70.0	30.0
	200°C	>75	<25

sample	Microwave annealing temperature (60 min)	Trans (%)	Gauche (%)
PET	as received	3.5	96.5
	140°C	47.0	53.0
	160°C	43.0	57.0
	180°C	61.5	38.5
	200°C	>60	<40

The values of the trans conformation are stabilised after the treatment at 180°C.

The Magic Angle Spinning spectra (MAS) are sufficiently to point out the most mobile components of the system (Figure 6).[11]

The resonance of various groups, even though the MAS technique induces the loses of the more rigid components of the system, becomes narrower with increasing the temperature of treatment up to 160°C. Therefore, in spite a considerable number of scans, may be worthwhile to notice the presence of a limited amount of mobile parts in the as received sample that remains present till reaching the temperature of 160°C in the treatment.

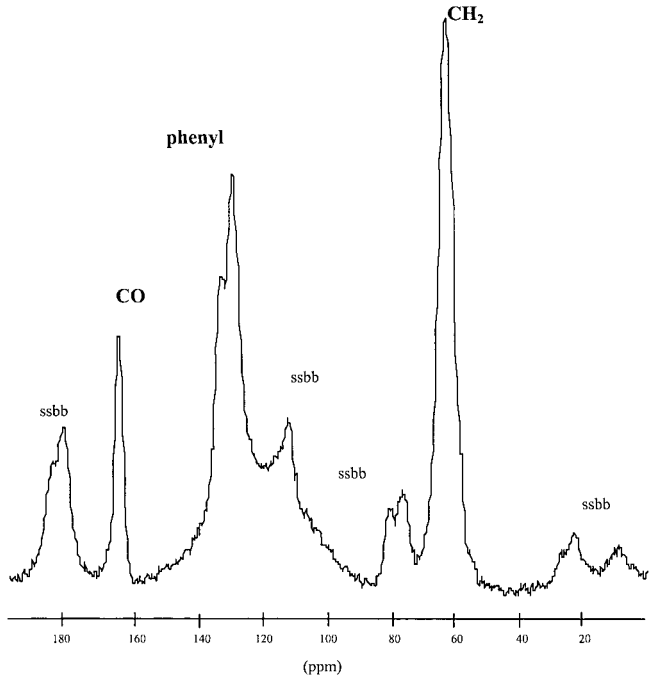

Figure 6 - Solid state NMR MAS spectra of PET.

Obviously in the quenched PET the mobile parts are much more numerous, indicating differently from what is shown in the XRD spectrum a significant crystallisation kinetic also in simple drying conditions for the material. This stresses out the importance of an NMR analysis to give direct information on local level without involving any result extrapolation.

Spin lattice relaxation times T_1 and $T_{1\rho}$

In order to study in detail the structure of the annealed PET materials we performed experiments of spin lattice relaxation times T_1 (Torchia) of the samples (Table 2).

Table 2- a) Single fitting of T_1-Torchia values (s)

PET sample		as received	140 °C	200 °C
ppm	162.5	14.3	63.9	158.1
	132.7	13.7	43.5	102.4
	129.9	12.0	37.1	76.5
	60.5	8.3	26.5	71.3

b) Double fitting of T_1-Torchia values (s)

PET sample				
ppm		as received	140 °C	200 °C
	162.5	23.9	79.3	437.7
		-	0.6	18.3
	132.7	24.2	70.4	227.0
		-	1.1	17.5
	129.9	19.6	54.8	143.4
		-	1.6	11.6
	60.5	12.7	48.3	119.6
		-	1.6	5.3

As evident from the table, T_1 shows extremely different values from the as received sample with respect to the sample treated for 60 minutes at 140°C. Resolving the decay curves of this last sample with a binomial function a significant improvement in the standard deviation is evidenced, as well as the appearance of two values for T_1

explainable respectively by the existence of a rigid and of an amorphous structure.

Clearer information in order to investigate PET materials can be obtained also through spin diffusion measurements obtained trough spin-exchange term in the Hamilton Integral describing the body proton-proton dipolar coupling. In the PET case spin diffusion measurements are easier because of the fact that they are of at least two orders of magnitude bigger of those performed in order to reach the equilibrium and therefor magnetisation remains constant together with the fact that the diffusion coefficients in the different regions of the material are extremely similar.Table 3 shows the $T_{1\rho}$ values for the samples heated for 60 min.

Table 3 - $T_{1\rho}$ of the PET samples (ms)

Air annealed PET					
ppm	as received	140 °C	160 °C	180 °C	200 °C
162.5	5.0	14.3	14.6	17.8	19.5
132.7	5.1	12.6	12.3	15.5	16.7
129.9	5.7	14.6	14.7	17.8	19.1
60.5	5.9	16.3	16.0	19.8	22.3
Microwaves annealed PET					
ppm		140°C	160 °C	180 °C	200°C
162.5		6.2	14.1	13.9	14.4
132.7		9.7	12.5	12.5	12.9
129.9		10.9	14.2	14.5	14.4
60.5		12.5	15.9	16.0	16.0

From the spin diffusion values the increment of the intensity of the signal at 60.5 ppm with increasing the annealing temperature in the

conventional treatment a clear increment of the dimension of the ordered phase is pointed out.

Comparing the $T_{1\rho}$ values for the single signal of the spectrum of the as received product the expected equivalence of the values is observed, typical of homogeneous systems, suggesting the presence of a phase of little dimensions. In the remaining annealed samples on the contrary, variations – particularly evident in the signal of the aromatic groups at 132.7 ppm - suggest significant dishomogeneities in the structure of materials.

Concluding remarks

In order to achieve innovation as a strategic element of product diversification and of processes competition, the present research allowed us to verify that PET textiles can be thermosetted by microwaves.

The effectiveness of the treatment depends on the operative conditions chosen, particularly on temperature and annealing time.

Microwave thermosetting seems to be less effective than the conventional one, but the use of single mode furnaces should ensure a better power density and therefore increase the effectivness of the treatment.

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