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Chain Extension and Foaming of Recycled PET in Extrusion Equipment

L. Di Maio, I. Coccorullo, S. Montesano, L. Incarnato*

Department of Chemical and Food Engineering, University of Salerno, Via Ponte Don Melillo, I-84084 Fisciano (SA), Italy

Summary: In this work industrial scraps of poly(ethylene terephthalate) (PET) were used for the production of foamed sheets. The process was performed by making use of a chemical blowing agent (CBA) in the extrusion process. Due to the low intrinsic viscosity of the recycled PET (IV=0.48dl/g), a chain extender was also used in order to increase the molecular weight of the polymer matrix. Pyromellitic dianhydride (PMDA) and Hydrocerol CT 534 were chosen as chain extender and CBA, respectively. The reactive extrusion and foaming were performed in a two step process, analyzing the feasibility regarding an eventual use in an industrial context. Rheological characterization was carried out on PET samples previously treated with PMDA, as well as the morphological study was performed to define the cellular structure of the foams produced. Moreover, in order to correlate the working conditions in the reactive and the foaming processes with the final morphology of the foams, a mathematical modelling of the foaming process was applied.

Keywords: chemical blowing agent; foaming; morphology; reactive extrusion

Introduction

In the last few years the production of poly(ethylene terephthalate) (PET) foamed items, particularly sheets for insulating applications, is encountering a rising interest. Moreover, by the contrast to the commonly used thermoplastic resins, extrusion foaming of recycled PET is creating several challenges as well as being the source for many recent studies.

Nevertheless, difficulties are mostly related to the rheological characteristics and the process stability of the resin at the required high processing temperatures. In particular, if recycled PET with a very low intrinsic viscosity is chosen, additional processing complications are met since this kind of material does not possess favourable melt rheology for use in the manifacture of foams. Actually, the insufficient extensional viscosity of recycled PET was reported to be a limiting factor during the foaming process as it results in the collapse of the foam structure during the stabilization phase of the cell growth, in particular under the high strain rates found in the extrusion/foaming process.

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Thus, to obtain a good quality foam, it is of the up most importance to take the mechanism of bubble growth in the polymer matrix into account[1-3]. In particular, an increase in the polymer viscosity, particularly the extensional one, is necessary by the time the foam rise is complete. On the other hand, one must consider that recycled material is subject to degradation due to the repeated processing operations previously performed and its molecular weight drops as well as its melt strength.

In order to overcome this drawback and to enhance the foamability of recycled PET, various techniques have been investigated, including chain extension by reactive extrusion[4-8].

In this work, starting from PET industrial scraps with a very low viscosity, a reactive extrusion process using pyromellitic dianhydride (PMDA) as chain extender was carried out in order to increase the molecular weight and modify the molecular weight distribution of the polymer matrix, leading to a suitable rheological behaviour. Subsequently, the modified PET resins have been used in extrusion foaming by chemical blowing agent (CBA) to produce high density foams.

Rheological characterization was performed on modified PET samples as well as a morphological study was carried out to define the cellular structure of the foams produced. Moreover, the mathematical modelling of foaming process was implemented in order to describe the gas bubble growth in the polymer matrix and to simulate the cellular structure of foam in relation to rheological properties of the melt. Experimental data were compared with theoretical results for a preliminary model validation.

Experimental

Materials

PET industrial scraps (PURE PET) of low intrinsic viscosity (I.V.), valuated as 0.48dl/g, coming from the fibre production of a national company (Montefibre, Italy) were used. A bottle grade PET (BG PET, I.V. = 0.74 dl/g), supplied by MG Group, was used as reference sample. The chain extender used in this work is the Pyromellitic dianhydride (PMDA) purchased by Aldrich. PMDA is a well known tetrafunctional reagent that can lead both to chain extension and branching of PET's[9-10]. The chemical modification, in the proportion required for the aim of extrusion foaming, is simply achieved with very low content of PMDA in PET; specifically two levels of PMDA contents were analysed: 0.50

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and 0.75 weight % which resulted to be the right compromise to tailor the required rheological modification and suitable foaming processability of PET.

As far as the foam production is concerned, the choice was directed to a chemical foaming agent based process. In particular Hydrocerol CT 534, kindly supplied by Clariant, was used as a chemical foaming agent. It was provided in form of powder, and is classified as an endothermic foaming agent, recommended for PET foaming, based on a mixture of both organic and inorganic foaming substances. The gas yielding during the process is reported as non toxic, presumably a blend of N_2, CO_2 with a very low level of water. As reported afterwards, the choice of the CBA was done mainly according to the processing conditions of PET, and to the decomposition products. The dosage of 0.30 and 0.50 weight %, was properly chosen to allow the production of high density cellular structure.

Blending and processing

The recycled PET (PURE PET), which is not suitable for the extrusion foaming process, was tailored by the chain extension reaction with the PMDA. The modified polymers were then used for the foam production. All the materials were vacuum dried overnight at 110 °C prior to any use and all processing steps were run under nitrogen blanket.

- *Reactive processing*

The reactive processing of PET with the PMDA and the foaming extrusion process were both performed with a Brabender single screw extruder (D = 20mm, L/D = 20). The operation was accomplished in two steps. In the first one, the polymer modification was realized by making use of the mentioned extruder equipped with a static mixer to allow the required residence time for the reaction between PET and PMDA. In a previous work[4] the chain extension of PET by reactive extrusion was studied in detail and optimized in order to improve the rheological and structural properties of recycled PET, with a particular regard to processes involving extensional deformation of melt (i.e. film blowing or foaming). On the basis of these studies, a screw rotation speed of 40 rpm was chosen in order to obtain the same average residence time, evaluated by means of some preliminary experiments performed at various extrusion speeds. The temperature profile used for the extrusion process was the following: extruder temperature (2 zones) 280°C; mixer temperature 290°C; die temperature 270°C.

- *Foaming*

The second step of processing consisted in the foam production by extruding the modified

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PET with the chemical blowing agent (CBA). Dry blends of treated PET and CBA powder were fed to the previously described extruder apparatus, which was operated without the static mixer. Since the process conditions for the polymer foaming operation depend on both the type of polymer and the type of foaming agent, preliminary extrusion tests were performed in order to make the proper settings, as described later on. In table 1 the working conditions for both the processes of chain extension and polymer foaming are reported.

Table 1. Operating conditions for chemical modification and foaming process.

Reactive extrusion process	
Extruder temperature (hopper, barrel) [°C]	280, 280
Static mixer temperature [°C]	290
Die temperature [°C]	270
Screw speed [Revolution per minute]	40

Foam extrusion process	
Extruder temperature (hopper, barrel) [°C]	270, 280
Die temperature [°C]	270
Screw speed [Revolution per minute]	40

Methods

- Rheological characterization

Rheological measurement in shear flow were performed using a Capillary Extrusion Rheometer (Bohlin Instruments) with a die radius of 1mm and a 16:1 length/diameter, equipped with a twin bore for the Bagley correction. Viscosity measurements were performed at 280°C within a shear rate range of 20÷10000 s^{-1}. As the shear rate at the wall is greater for pseudoplastic than for Newtonian fluids at a given volumetric flow rate, the Rabinowitsch corrections were applied in all cases.

Experimental runs in non-isothermal elongational flow were carried out with a capillary rheometer (Rheoscope 1000, CEAST) equipped with a tensile module. The measurements were performed using a 1 mm diameter capillary die (L/D = 20) with the tensile module situated about 20 cm from the extrusion die. An extrusion temperature of 280°C and a wall shear rate of $125s^{-1}$ were used. The tests allowed the determination of the melt strength (MS) and the breaking stretching ratio (BSR).

- Foams characterization

The PET foam densities were measured according to the standard ASTM D-1622.

A scanning electron microscopy analysis was carried out on cryogenically fractured

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specimens after gold coating, using a LEO ASSING 420 scanning electronic microscope (LEO Electron Microscopy, Ltd).

Results and Discussion

Rheological behaviour of the polymer matrix

A significant increase in viscosity due to the use of PMDA as chain extender in PET scraps (PURE PET) is evident from the flow curves reported in figure 1. These samples also exhibit a pronounced shear thinning behaviour particularly the blend PET + PMDA (0.75%).

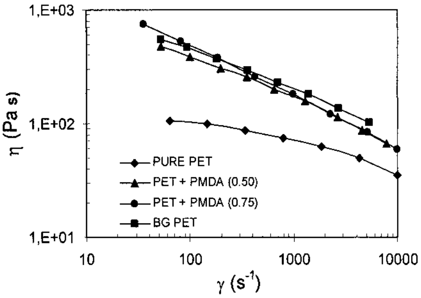

Figure 1. Curves of viscosity vs. shear rate for unmodified and modified PET samples.

Moreover, as results from the flow curves, at high shear rate, the viscosity of modified samples (in particular with a PMDA content of 0.75 %) become lower than that of bottle grade PET. This shear thinning behaviour, which is similar to commercial polymers used in film blowing or blow moulding, like LDPE characterized by long chain branching, can be attributed to the broadening of the material's weight distribution, (as confirmed by GPC analysis reported elsewhere[4]) and to the introduction of long chain branches in the PET molecules during the reactive extrusion with the PMDA.

In order to verify if the modified PET possesses melt properties suitable for foaming process, melt strength measurements were performed, the results being reported afterwords.

As it can be seen in table 2, a sharp increase in melt strength is encountered with increasing PMDA content (Table 2). Both the effects, the shear thinning behaviour and melt strength improvement, can be ascribed to the structural changes occurring during the chain extension process, i.e. the increase in Mw, the broadening of Mw/Mn and branching

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phenomena accomplished during the reactive extrusion[4]. As expected, although the bottle grade PET exhibits the best values of BSR and relatively high value of MS, the treated PET samples achieve good levels of both MS and BSR. Actually, too large values of the MS tend to inhibit the bubble growth during the foaming process. As reported later, the parameters so obtained allow in all cases the production of foams, although with some differences. However, the sample treated with 0.50 % of PMDA appears as the best accomplishment between the two parameters.

Table 2. Melt strength and BSR for PET and treated PET samples.

Samples	**Melt Strength (10^{-2} N)**	**BSR**
PURE PET	Not measurable	Not measurable
PET+PMDA(0.50%)	0.012	120
PET+PMDA(0.75%)	0.054	92
BG PET	0.010	320

Foaming

As far as the foaming process is concerned, the enhancement of processability of recycled PET is very significant being the operation governed basically by the above mentioned rheological properties of the system. Foam development was performed with both the treated materials and with the BG PET, while was not possible to produce foams with the PURE PET. In any case, processing presented some differences in term of conditions optimization. In order to regard the differences in foam properties due to variation in material melt behaviour, the work was carried out fixing the same operation parameters for all three materials tested. Attention was paid to the correct setting of temperature profile and extrusion speed; in particular, for the extrusion foaming process, the melt temperature has to be set at the same or higher value of the decomposition temperature of the foaming agent. On the other hand, the melt pressure, which is led by screw rotation once die geometry is fixed, has to be high enough to allow gas dissolution. These two parameters are strictly related each other: the higher the temperature the lower the melt pressure is. Efforts are thus needed in order to correctly set the temperature profile and screw speed. For the aim of the work, the decomposition temperature of the foaming agent was evaluated by a thermogravimetric analysis reported in figure 2. The weight loss starts at 220°C and keep on a constant gas yield up to ca. 300°C.

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The gas generated by CBA decomposition is kept dissolved in the melt by the pressure generated by screw rotation of the extruder. Bubble formation depends on the nucleation process which is believed to begin inside the shaping die where pressure profile is descendent. As the gas-laden melt emerges from the die, it undergoes a sudden pressure drop. This thermodynamic instability causes a phase separation. The escaping gas leads to expansion within the fluid matrix in such a manner that individual bubbles merge into cells and, through a subsequent solidification, stable expanded structures are produced[11]. The extrusion temperature profile, was thus fixed according to these data and is reported in table 1. During the foam extrusion, torque and die pressure measurements were performed in order to evaluate the effect of PMDA and CBA on processing parameters. These are reported in figure 3 as a function of the foaming agent content.

Both die pressure and screw torque of the BG PET present the higher values compared to those of treated PET. This behaviour was expected since the BG PET holds higher viscosity values (in particular in the region of shear rates relative to the rate of deformation achieved during the process). In all cases the presence of the foaming agent, which during the time it is dissolved in the polymer melt has a fluidisation action, causes the reduction of both pressure and torque. Nevertheless, a difference in this effect was observed and results from the experimental data of figure 3: die pressure and torque values reduction, due to the CBA content, is in fact less pronounced for the treated PET's compared to the BG PET. In particular, the PET modified with 0.75% of PMDA results less sensitive to the flowing promotion due to gas dissolved in the melt.

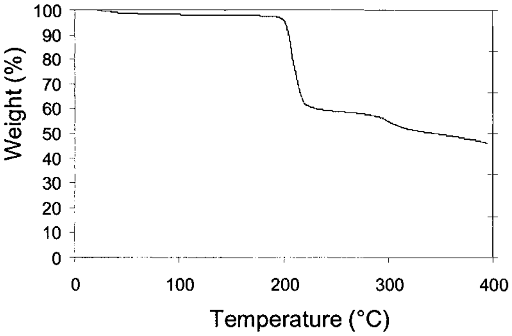

Figure 2. Weight loss of the chemical foaming agent versus temperature.

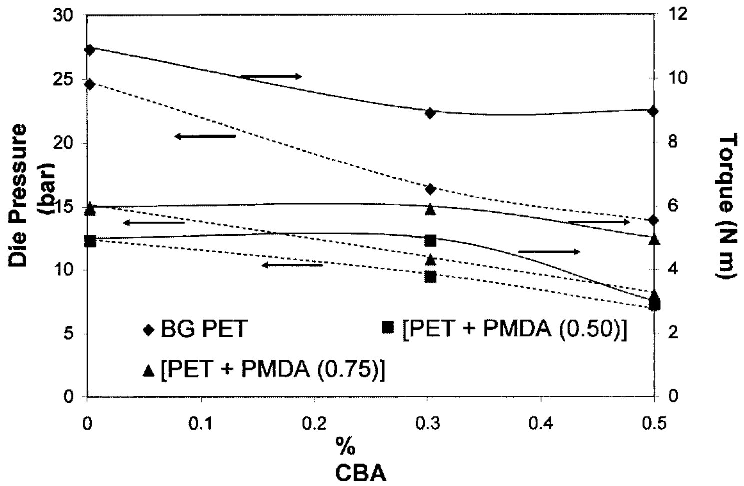

Figure 3. Torque (solid line) and die pressure (dashed line) readings of blends versus CBA content.

Cell morphology and structure

The foamed strips obtained have a closed-cell structure (see SEM micrographs in figure 6 and 7). Closed-cell foams are most suitable for thermal insulation and are produced when the cell membranes are sufficiently strong to withstand rupture at the maximum foam rise. The experimental conditions used in this work allowed to produce foams with densities which resulted to be relatively high, ranging between 800 and 1200 kg/m^3 (Table 3). As expected, the cell size and cell distribution, reported in table 4, are strongly dependent, during the foaming process, on the concentration of the chain extender and, consequently, on the high viscosity of the polymer matrix. With regard to the density values of table 3, the lowest density is reached with the system PET + PMDA (0.50 %) + CBA (0.50%). The blend of PET treated with the 0.75 % of PMDA and with the same content of blowing agent displays a slightly higher value of density. These results relate to the rheological and in particular to extensional properties of the molten polymer and confirm that more stable cell structures develop with branched polymers like the chain extended PET's are.

Table 3. Densities for modified PET and PET foam samples.

Sample	**Density (Kg/m^3)**
PURE PET	1410
PET + PMDA (0.50 %)	1425
PET + PMDA (0.50 %) + CBA (0.30%)	1085
PET + PMDA (0.50 %) + CBA (0.50%)	835
PET + PMDA (0.75 %)	1435
PET + PMDA (0.75 %) + CBA (0.30%)	1165
PET + PMDA (0.75 %) + CBA (0.50%)	900
BG PET	1430
BG PET + CBA (0.30%)	1337
BG PET + CBA (0.50%)	1172

Table 4. Cell diameter and distribution for modified PET and PET foam samples.

Samples	**Cell diameter (μm)**	**Cell distribution (n/mm^2)**
PET PURE	Not measurable	Not measurable
PET+PMDA(0.50%) + CBA (0.50%)	270 ± 30	38
PET+PMDA(0.75%) + CBA (0.30%)	100 ± 10	28
PET+PMDA(0.75%) + CBA (0.50%)	200 ± 15	42
PET BG + CBA (0.50%)	50 ± 10	104

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Modelling

In order to correlate the working conditions in the reactive and foaming processes, the polymer and gas properties with the final morphology of the foam, a mathematical modelling of foaming process was implemented as follows.

Consider a polymer melt that has a dissolved gas concentration c_0 in equilibrium with the gas at some elevated pressure P_B. With the release of pressure at t=0, the solution becomes supersaturated, and nucleation and bubble growth begin. As the bubble growth proceeds, the pressure inside the bubble and the dissolved gas concentration at the bubble surface decrease. With time, gas diffuses into the bubble and a concentration gradient propagates radially in the polymer melt. A schematic of the bubble growth is shown in figure 4. The radius and the dissolved gas concentration are denoted by R(t) and c(r, t).

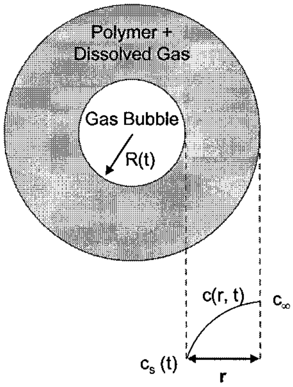

Figure 4. Schematic of single bubble growth.

Governing Equations for Single Bubble Growth[12-13]

A differential mass balance in a binary system assuming spherical symmetry, constant density and diffusion coefficient (D) is of the form:

$$\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)\right] \tag{1}$$

where c is the molar concentration of the volatile solvent in the liquid. The boundary and initial conditions for equation 1 are:

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$$c = c_S(t) \quad a \quad r = R(t)$$
$$c = c_\infty \quad a \quad r = \infty \qquad (2)$$
$$c = c_\infty \quad a \quad t = 0$$

If only the volatile solvent is present within the bubble, which is in chemical equilibrium with the liquid at the bubble surface, then we may apply Henry's law:

$$c_S = H \cdot P_B \qquad (3)$$

where K is Henry's constant (molar base). In order to solve the problem another boundary condition is required.

The Navier-Stokes equation in the radial direction assuming creeping flow and spherical symmetry may be combined with the radial velocity of the liquid and a force balance at the surface of the bubble to give:

$$P_B - P_\infty - \frac{2\sigma}{R} = \frac{4\eta}{R}\left(\frac{dR}{dt}\right) \qquad (4)$$

where $P_B(t)$ is the pressure in the bubble, P_∞ is the ambient pressure, σ is the surface tension and ρ is the liquid viscosity. The initial condition for the last equation is:

$$R = R_0 \qquad @ \qquad t = 0 \qquad (5)$$

Model formulation

In analyzing the bubbles growth process, the following assumptions can be made:

1. The bubble is spherically symmetric when it nucleates and remains so for the entire period of growth.
2. There are no chemical reactions during bubble growth.
3. Gravitational effects can be neglected.
4. Latent heat of solution is neglected.
5. Inertial effects are neglected and the fluid is assumed to be incompressible and Newtonian.
6. The gas within the bubble obeys the ideal gas law.
7. The interfacial tension at the gas-liquid interface has a constant value σ.
8. The bubble growth is controlled by viscous forces.

Moreover, as for thermoplastic foam extrusion, growth occurs in the molten-to-solid transition state. The polymer is cooled from 280°C (die temperature) to 25°C (ambient

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temperature). Rheological property variation certainly changes the isothermal growth scenario and hence, a transient heat transfer problem is considered here.

Under these assumptions the Navier-Stokes equation (4) in the radial direction can be used to calculate the evolution of the bubble growth rate:

$$\left(\frac{dR}{dt}\right)_{t(i)} = \frac{R_{t(i-1)}\left(P_B - P_\infty\right) - 2\sigma}{4\eta\left[T(t(i))\right]} \tag{6}$$

where $P_B(t)$ is the pressure in the bubble, P_∞ is the ambient pressure (a constant in this work), σ is the surface tension and ρ is the liquid viscosity.

The initial condition for the last equation is:

$$R = R_0 \qquad @ \qquad t = 0 \tag{7}$$

Viscosity is related to temperature by an Arrhenius expression and its variation with thermal profile is:

$$\ln\frac{\eta_{0T}}{\eta_{0T_r}} = \frac{E_a}{R_g}\left(\frac{1}{T} - \frac{1}{T_r}\right) \tag{8}$$

Where E_a is an activation energy for viscous flow, η_0 and η_{0Tr} are the zero shear viscosity corresponding to T and T_r, respectively.

As foam sheet emerges from a die, we assume the one-dimensional heat conduction becomes the main heat transfer mechanism. The temperature variation across the thickness at different times can be described as[14]:

$$\frac{T_1 - T(y,t)}{T_1 - T_0} = 2\cdot\sum_{n=0}^{\infty}\frac{(-1)^n}{\pi\left(n+\frac{1}{2}\right)}\cdot\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2\frac{\alpha t}{b^2}\right]\cdot\cos\left[\left(n+\frac{1}{2}\right)\frac{\pi y}{b}\right] \tag{9}$$

where y is the thickness direction and α is the thermal diffusivity, ($\alpha = k/\rho C_p$). The subscripts “1” and “0” denote “surrounding” and “initial”, respectively (25 and 270°C in this work).

Temperature distribution is minimized when thickness is reduced. It is therefore reasonable to assume an averaged flat profile foam for thin sheet[15].

Since the polymer matrix was produced by a chain extension process, we considered the viscosity changing with the chain extender content using a polynomial fittings curve to interpolate the experimental data of η_0 vs % PMDA:

$$\eta_0\,(\%\text{PMDA}) = 6577\,(\%\text{PMDA})^2 - 742.64\,(\%\text{PMDA}) + 160 \tag{10}$$

Bubbles distribution per unit of volume (N_B) is given by:

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$$N_B = \frac{\dfrac{gas\ volume}{volume\ of\ blend}}{volume\ of\ one\ bubble} = \left[\frac{bubbles\ number}{volume\ unit\ of\ blend}\right] = \frac{w_L\, c_{CBA}\, \rho_P \dfrac{R_g\, T}{P_B\, Mw}}{\dfrac{4}{3}\pi R^3} \tag{11}$$

in which ρ_P is polymer density, c_{CBA} blowing agent concentration, M_W molecular weight of the gas (N_2), w_L blowing agent weight loss.

The blowing agent weight loss w_L was evaluated by means of thermogravimetric measurements and is about 54%.

Main physical properties of the analysed system used in the model are reported in table 5.

Table 5. Physical properties used in the model[16].

Physical Properties	
PET density ρ_P	1.34×10^{-3} kg/cm^3
R_g	82.06 cm^3 atm/(mol K)
Nitrogen molecular weight M_w	28 g/mol
Surface tension σ	44.6 mN/m
Activation energy for viscous flow E_a	94000 J/mol
PET specific heat Cp	1130 J/(kg K)
Thermal Conductivity K	2.18×10^{-3} W/(cm K)

The model above described was implemented in a simulation code developed in Labview 6.0i (Laboratory Virtual Instrument Engineering Workbench - National Instruments). The simulation code starting from material properties and working conditions calculates the evolution of the bubbles size and number for unit volume in the foam sheet. After that, the computer code builds the corresponding image which can be compared with SEM images.

In the following figures (5 and 6) simulated images are compared with SEM micrographs. Simulation code describes satisfactorily experimental data, better results can be attained assuming that not only viscous force but also mass transfer control the bubble growth.

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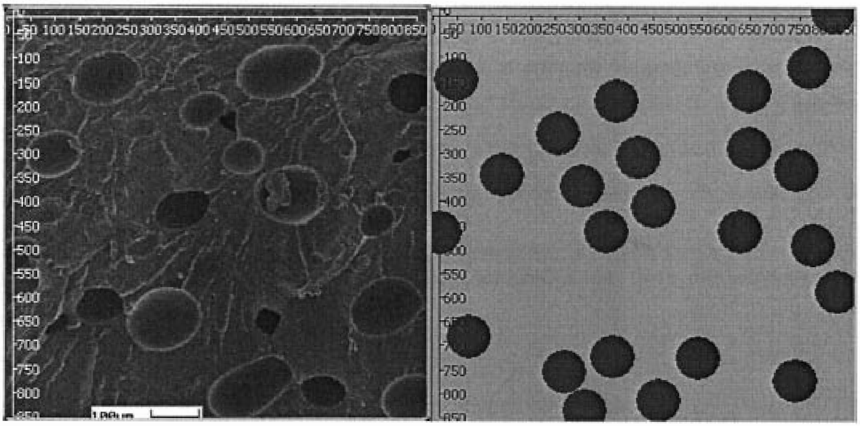
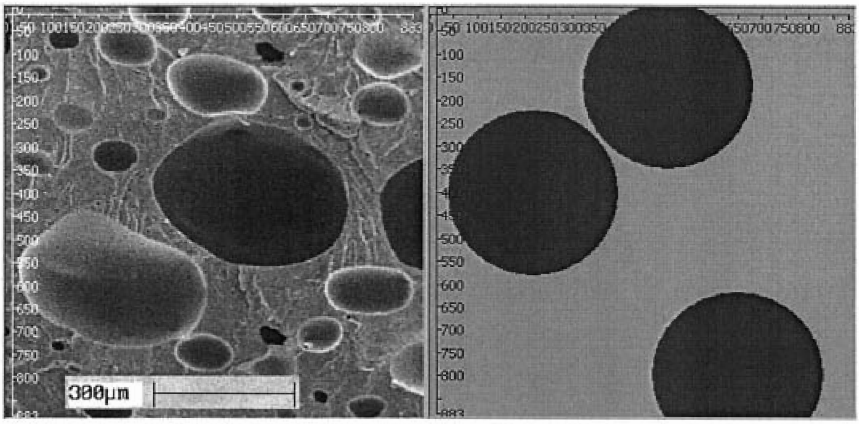


SEM SIMULATION

Figure 5. PET+ PMDA (0.75)+ CBA (0.3).



SEM SIMULATION

Figure 6. PET+ PMDA (0.75)+ CBA (0.5).

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Conclusions

The results presented above show that it is possible to produce a foam from a chain extended recycled PET with a two steps process (a chain extension and a foaming process). Due to the relatively high values of melt strength and the low percentages of chemical foaming agent used, the foam structure resulted to be a closed cell one. As expected, densities of foams were strictly dependent on the level of molecular modification/ branching of the recycled PET. The modelling of foaming process was realized by making use of fundamental transport equations and the results were in a quite good accordance with the experimental results. In particular the hypothesis of bubble growth governed essentially by viscous forces was verified.

Future improvements will depend on a better understanding of the mechanisms involved in a single step operation of chain extension/foam extrusion process. Work is underway to optimise process parameters, with particular regard to the type of CBA, to its concentration level and to evaluate product potential performances of PET foams.

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