Biaxial Orientation of Polyamide Films: Processability and Properties

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Summary: The production of biaxially oriented films can be performed with two techniques: the tenter frame and the double bubble process. The most important difference between the two processes is that in tubular orientation the MD and TD stretching are simultaneous. This event is very important specially in the case of biaxially oriented polyamide films to avoid hydrogen bonding which occur during the first stretching stage of tenter frame process and cause resistance to subsequent transverse direction orientation (1-4). Double bubble process consists in the stretching of a tubular film where the stretching ratios in the machine and transverse directions are determined by inside bubble pressure and the difference in roll speeds between the two sets of nips rolls that contain the bubble.
The work presented here reports some results about double bubble polyamide films realised with a laboratory scale system. The study concerns the processability (5-6) of two different polyamides: a nylon 6 (PA6) and a copolymer of the nylon 6 with isophthalic acid and isophorondiamine (PA6 – IPA.IPD) at 5% w/w of comonomer. Two main process arrangements where adopted differing for first bubble cooling technique: a water cooling and a air cooling. The films produced in both conditions were then characterised with a particular regard to mechanical and barrier performances. Morphological analyses were also carried out in order to correlate the process conditions to structure and properties of films.

Keywords: POLYAMIDES FILM BLOWING DOUBLE BUBBLE

1 Experimental Part

1.1 Materials

To produce our samples we have used a polyamide 6 (PA6 FL34) and a copolymer of the PA6 with isophthalic acid and isophorondiamine (PA6 – IPA.IPD) at 5% w/w of comonomer, supplied by SNIA (Italy). These materials were chosen as they are widely used for film packaging, due to their good mechanical and barrier performances. The copolymer used here has an improved processability for the blown film process, due to a more branched structure which acts as a bubble stabiliser during the process itself, as was verified in an our previous

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work (7) where the effect of different comonomer structures on properties of copolyamides was shown. Polymer chips, due to their hygroscopicity, were always dried for 12 h at 110°C in a vacuum oven before melt processing.

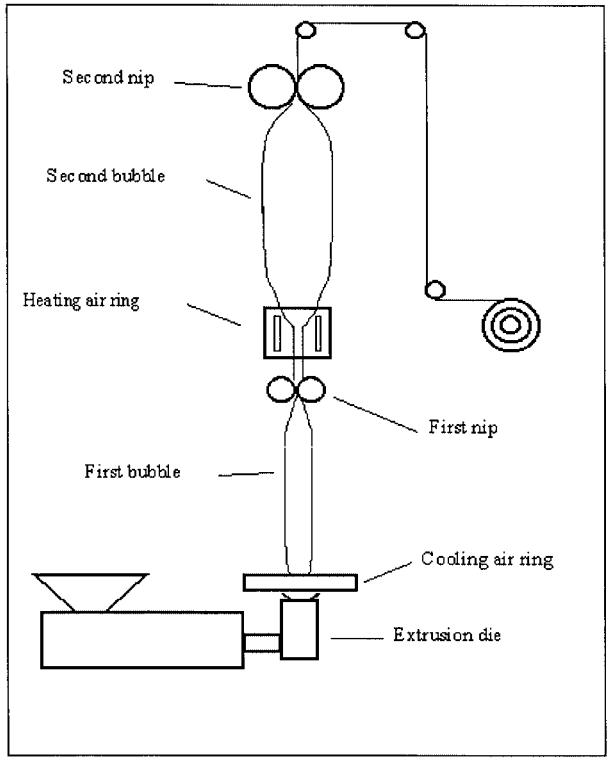

Figure 1. Double bubble apparatus scheme

1.2 Single and Double Bubble Apparatus

Single bubble films were prepared using a GIMAC mod. 12/24 single screw extruder with an anular die of 31 mm for the inner diameter and 32 mm of outer diameter. The single bubble take up frame used was a HAAKE mod. 002-4848.

On the basis of the theory of the film orientation (8-9) we have designed and built in laboratory a double bubble tubular film blowing tower to produce the samples (10). The first phase of our process is a single bubble extrusion that we have carried out using the apparatus described above (HAAKE mod. 002-4848). Over the first pair of nip rolls is positioned an

heating apparatus constituted by an air ring, so that we could reach temperature up to 130 degrees. A second pair of nip rolls, that can be opened by two pneumatic pistons, are set over the oven at about the same distance between the first nip rolls and the extrusion die. In fig. 1 can be seen a scheme of the machinery. At the start of the process the film obtained from the single bubble apparatus, is reheated in the air ring and inflated again introducing air at the desired pressure opening the second pair of nip rolls. In this way the pressure of the air entrapped in the second bubble between the first and second pair of nip rolls induces the stretch for the orientation of the molecular chains in the Transverse Direction (TD), while the higher speed of the second pair of nip rolls ensures the orientation in the Machine Direction (MD).

1.3 Process Conditions

The process variables we have used to report the results achieved are, for the single bubble:

Draw Down Ratio: DR = S1nr/Se

where S1nr is the peripheral speed of the nip rolls and Se is the speed of exit of the polymer flow from the extrusion die;

Blow Up Ratio: BR = D1b/Da

where D1b is the diameter of the first bubble and Da is the outer diameter of the annular extrusion die.

For the second bubble:

Second Draw Down Ratio: SDR = S2nr/S1nr

where S1nr and S2nr are the peripheral speeds of the first and second pair of nip rolls;

Second Blow Up Ratio: SBR = D2b/D1b

where D1b and D2b are the diameter of the first and second bubble during the operation.

The condition used to produce film samples are:

Extrusion Temperature:	265°C;
Extrusion screw speed:	10 r.p.m.(corresponding to c.a.12 g/min) ;
DR:	10;
BR:	1;
SDR:	From 1 to 4.5;
SBR:	From 1 to 4;
Blowing up temperature:	From 170 to 230°C (measured at air ring).

1.4 Process Stability

A process stability analysis is reported to evaluate, for each material and operating condition, the range of the draw and blow up extent which allow a proper stable and continuous bubble for a good film production process.

1.5 Film Characterisation

The film samples produced in the conditions above mentioned, were characterised in order to correlate process conditions to film performances. Thermal properties of the film have been determined with a Mettler Differential Scanning Calorimeter DSC30.

Permeability measurements have been carried out with an isostatic gas-permeabilimeter Lyssy GPM 200. The barrier properties were thus evaluated respect to O_2, CO_2 and N_2.

Mechanical properties of the films have been determined with an Instron mod. 4301 testing the films in the two directions, the MD and the TD, with rectangular samples of 11.7 mm width and 110 mm length, the thickness depended on the process conditions while the grip distance was of 50 mm.

2 Results and Discussion

2.1 Range of Stability

The production of the samples was performed running various operating conditions in order to check processing limits (from the stability point of view). The parameters modified during the production of the samples were: extrusion rate, periphera l speed of the nip rolls, air pressure inside the first and second bubble. We present the results as functions of SDR and SBR.

The fields of stability for the process with second bubble temperature of 170, 200 and 230 °C are shown in the figures 2-4 on the right respectively from top to bottom. Each geometrical symbol

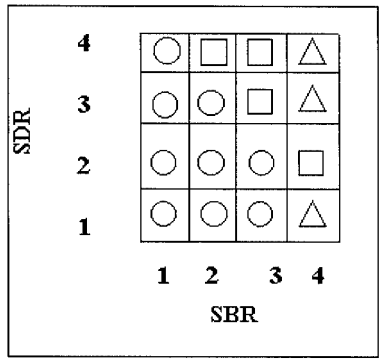

Figure 2. Stability at 170 °C

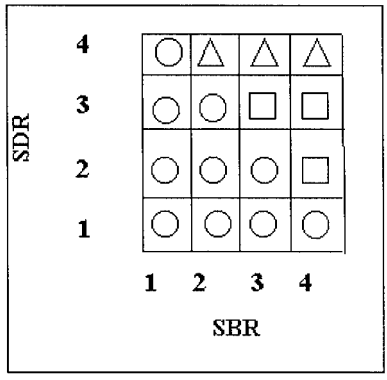

Figure 3. Stability at 200 °C

represents the process stability or instability as follow: O=stable process; =continuous but unstable process; Δ=dis-continuous process. A large number of conditions were tested, but for the sake of brevity here are reported only the most significant. As reported in the figures the bubble stability is strictly dependent on the temperature of the second bubble, which strongly affect also the final properties of the film.

The results have shown that, heating of the second bubble at 200°C, more conditions of stability are possible, in particular higher blow up ratios (SBR) are reached.

In the case of water cooling of first bubble (which ensures a more amorphous material to stretch in the second bubble) the results are similar in terms of SBR and SDR but the temperatures of second bubble can be quite lower. It has to be noted that for the production of double bubble samples it has been necessary to work with a very stable first bubble because every little irregularity in the thickness or in the radius have a negative effect on the blowing and stability of the second bubble. We have thus used a BR = 1 (Blow Ratio of the first bubble) to reach the best results in the blowing of the second bubble so to obtain the best orientation of molecular chains in TD and to ensure the lowest degree of crystallinity of the film from the first bubble at the moment of the blowing of the second bubble.

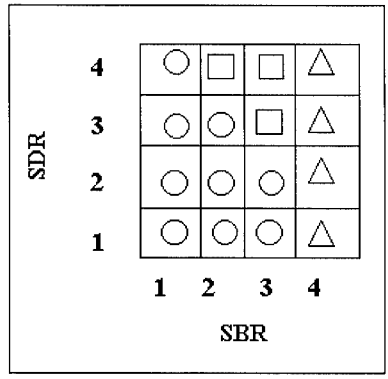

Figure 4. Stability at 230 °C

2.2 WAXS Analysis

In order to verify the effectiveness of the process used in producing biaxially oriented films, X-ray diffraction analysis was performed on samples with different SDR and SBR values, obtained from a first bubble completely amorphous and unoriented. In figure 5 is reported as example the WAXD pattern for a film with SBR and SDR both equal to 3 from a second bubble blown up at 200°C. The arrow states the machine direction of the film. The figure clearly

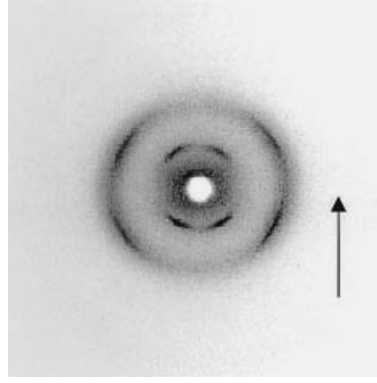

Figure 5. Example of WAXD pattern

shows that this sample is biaxially oriented in MD and TD. Similar results were obtained also analysing film samples having different SDR and SBR values.

2.3 Permeability Tests

Since the gas barrier behaviour of polymeric films is correlated to morphology (orientation, crystallinity) developed during the process, permeability tests were executed for CO_2, O_2 and N_2 with particular regard to operating conditions effect. The results are reported in table 1 for some of the process conditions tested. The permeability is expressed in $cm^3(STP)\cdot cm/cm^2\cdot Pa\cdot s$. Comparing the permeability data measured for different values of stretch ratios and blowing up temperatures, it appears that the lowest permeability results are obtained for the sample E produced at T=200°C. Moreover the SDR and SBR values corresponding to films with lower permeability depend on temperature used for the second bubble. In fact, it is well known (11) that the orientation effect (and so the developed film morphology) of a stretching process is related to the stretching temperature, from which depend the relaxation times of the polymer. As a consequence, both stretching ratios and second bubble blow up temperature have to be optimised to increase the gas barrier performance of the films.

Table 1. Permeability values

Sample	*Stretching ratios*	*Permeability x 10^{14}*			*Second bubble blow up temperature (°C)*
		CO_2	*O_2*	*N_2*	
A	SDR=2 SBR=3	0.94	0.30	0.12	170
B	SDR=2 SBR=2	1.54	0.87	0.62	170
C	SDR=3 SBR=2	0.61	0.19	0.083	170
D	SDR=2 SBR=3	1.04	0.25	0.048	200
E	SDR=2 SBR=2	0.51	0.10	0.024	200
F	SDR=3 SBR=2	2.36	1.26	0.85	200
G	SDR=2 SBR=3	0.53	0.12	0.036	230
H	SDR=2 SBR=2	1.63	1.29	1.00	230
I	SDR=3 SBR=2	1.03	0.27	0.061	230

Mechanical tensile performances of the films were measured both in the machine and transverse directions. As expected, modulus, stress at break and elongation at break are dependent on the extent of film stretching and orientation. In the diagrams below (figures 6 and 7) are reported the modulus and stress at break values for the two stretching directions as a function of the SDR/SBR ratio, which is the measure of the extent of film orientation.

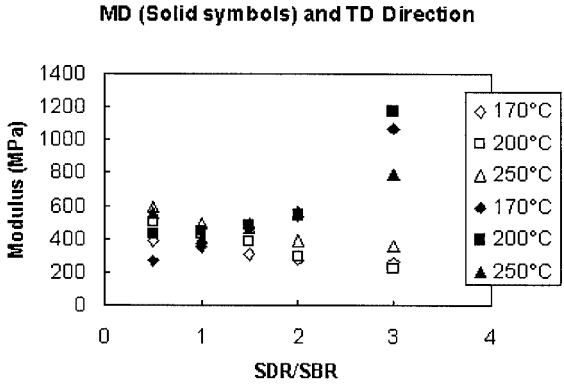

Figure 6. Tensile elastic modulus

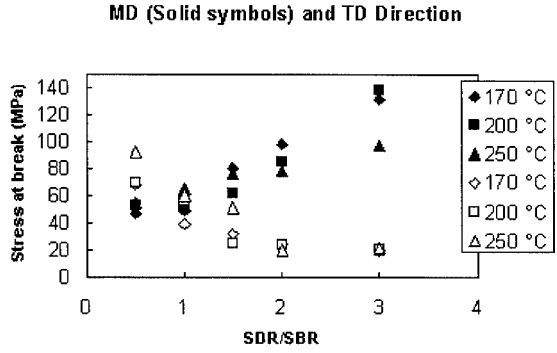

Figure 7. Tensile stress at break

At higher values of this ratio correspond higher modulus and stress at break in the MD. Opposite behaviour was displayed for the same parameters in the TD. Moreover, at SDR/SBR=3, where the differences in the mechanical parameters are consistent, it is evident

that also in the case of tensile properties the best performances are shown by film obtained using a temperature of 200°C for blowing up the second bubble.

Conclusions

The production of biaxially oriented PA films was performed in laboratory on an experimental apparatus. The system allowed to test several process conditions and a particular attention was paid to stretching ratios and blowing up temperature of the second bubble. From them, in fact, depend the extent of orientation in MD and TD and the morphology of the samples, that in turn influence the mechanical and barrier properties of the films.

Regarding to the fields of stability for the process, the experiments have shown that, heating the second bubble at 200°C, more conditions of stability are possible and higher SBR values can be reached. Moreover, in terms of performances the films produced at this temperature show also the best barrier properties and mechanical resistance in machine direction. In particular, the film E exhibits the lowest permeability to gases and comparable mechanical resistance values in MD and TD.

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