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Heat Melding of Voided Polyethylene Microstructures

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Abstract

This paper is concerned with the fabrication of voided polyethylene microstructures by heat melding of plastic microcapillary films (MCF) to form microcapillary monoliths (MCM), which are consolidated layers of MCFs forming in two dimensional arrays of microcapillaries. MCMs were manufactured by heat melding together multiple layers of low-voidage MCFs or high-voidage MCFs. The optimal conditions for interface adhesion of the MCFs to create MCMs without compromising capillary integrity and the influence of compatibility between MCFs on melt processing, was investigated.

The MCFs were processed from linear low-density polyethylene (LLDPE) and the melt rheology of the polymer was studied to provide rheological parameters that could be used both to gain an understanding of the character of the polymer and for modeling of the MCM forming process. In particular, the temperature dependent nature of the rheology was investigated. Recognizing the transition from viscous-dominated behavior to elastic-dominated behavior was important for the success of the melding process by which MCMs were formed. Modelling of the melding process provided some additional information and confirmed issues in relation to the thermal bonding temperatures and mechanisms.

INTRODUCTION

The voided polyethylene microstructures studied in this paper is referred to as a micro-capillary film (MCF), characterized by a parallel array of near uniform capillaries embedded within a thin linear low density polyethylene film as shown in Figure 1.

Hallmark and Mackley [1] initially addressed the manufacture of these novel flexible films. The film has affine properties to standard plastic film [2-4], closed-cell polymer foam [5, 6] and hollow fibres [7-9] embracing characteristics of these three. The manufacture of MCFs was attained by entraining air within the polyethylene from injection nozzles during the extrusion process at the point the molten polymer exits. Posterior extruding the molten polyethylene through air-entrained nozzles slit die, the molten film was drawn with a set of chill rollers to produce a solidified sheet, termed low-voidage MCF, which is characterized for having consistent thickness and capillary diameters along the film.

Subsequently different kinds of MCFs have been emerged, such as small diameter low-voidage MCF, high-voidage MCF and ultra-high voidage MCF [10]. Hydraulic capillary diameters on the MCFs range from 3.5 μm to 5000 μm . The MCFs can be classified according to their capillary diameter as small diameter low-voidage (with capillary of hydraulic diameter of order 3.5 μm), low-voidage (with capillary of hydraulic diameter of order 200 μm), high-voidage (with capillary of hydraulic diameter of order 800 μm).

Microcapillary monolith

A micro-capillary monolith (MCM) is a solid polymer block of MCFs, containing a two-dimensional array of capillaries. The monolith consists of two or more layers of MCFs permanently bonded together over their full length. This multi-layer structure is created by “hot pressing” at temperatures close the melting point of the polymer. This is a delicate process because the temperature, time and load need to be precisely controlled in order to meld the interfaces and to prevent collapse of the hollow capillaries.

The process of MCM formation relies on ‘polymer welding’, in which two molten or near molten interfaces are bonded together.

The most common processes for joining plastic components can be classified as: mechanical joining [11], adhesive bonding [12] and welding [13].

LLDPE MCF are heated during the welding process in order to create intimate contact between the interfaces enabling polymer chain diffusion across the interface allowing subsequent entanglements to achieve the join strength [13]. The welding process starts when the MCFs are at a temperature close to the melting point of the LLDPE.

At this temperature a reduction in the viscosity and entropy occurs, making the mobilization of polymer chains possible, and since pressure is applied this facilitates the intimate contact of the MCFs. It gives as a result interdiffusion of polymer chains, finishing with interfacial bonding [14].

The degree of welding and integrity of capillaries in the MCM formation are mainly the function of three factors, which are: the processing temperature, T , applied compression ratio and melding time.

The welding, or healing, which consists of the diffusion of polymer chains across the interface, is dependent on temperature. The MCM melding process is carried out under isothermal conditions and can be modeled using the theory of reptation. The reptation theory, developed by De Gennes [15], which describes the motion of individual polymer molecules in the amorphous bulk is derived from a deduction by Edwards [16], who established a formula for the free energy of the polymer chains and a model where the chain is enclosed to a tube formed by surrounding chains.

The theory is suitable to define the back or forward movements of each polymer chain which is considered to be closely boxed in by the entanglements of contiguous chains. This model is well known and is illustrated in Figure 2, in relation to the MCF welding process. During the process it is assumed, that a perfect contact exists at the two MCF interfaces. At time $t = 0$ all the chains have zero diffusion through the other MCF, at later time ($t < t_R$), the chains are longer and have crossed the interface. When time is equal to the reptation time ($t = t_R$), both MCF polymer chains are totally interpenetrated creating entanglements, at this point the interface disappear becoming indistinguishable and the properties at the interface are the same as the ones at any point within the MCF. [17, 18].

The degree of healing is defined using the formula [14, 15, 19]

$$D_h(t) = \sigma / \sigma_\infty = x / x_\infty = (t/t_R)^{1/2}$$

Where σ is the bond strength which is related to the interpenetration distance defined as x , which in turn is proportional to the square root of the length l , σ_{∞} is the ultimate bond strength at values of x_{∞} and L .

In the case where the parts are brought together at temperatures close to or above the melting point, known as hot plate welding [20, 21], the time to achieve maximum bond strength is approximately the same value that it takes to reach intimate contact. As a result, the welding temperature has a profound effect on both the compression ratio and the matrix rheology and therefore on the quality of the fused interface [22].

EXPERIMENTAL

The linear low density polyethylene (LLDPE) used was a commercially available grade (Dowlex NG5056E, melt index 1.1 g/10 min, density 0.919 g/cm³).

Low-voidage MCFs were fabricated according to the method established by Hallmark and Mackley [1]. The heated extrusion line, shown schematically in Figure 3, used in the production of 19 capillary films consisted of a single-screw extruder connected to a gear pump. Pressure feedback control was present between the inlet of the gear pump and the motor drive to the extruder's screw. The polymer exited the extrusion line through a heated die with a convergent mid-section that contained air entrainment needles.

Upon exiting the extrusion die, the extrudate was taken through the chill rollers whose position relative to the die exit could be easily altered and act as a variable-speed haul-off device. The distance between the die exit and the chill rollers was termed the melt drawing length, L_D .

The air entrainment assembly was designed such that the tips of each nozzle were flush with the exit of the die. The die body and 19-injector assembly was attached to the extruder and the extrusion line. The extrusion line was operated at a constant polymer volumetric flow-rate, with the extrudate passing into the rollers and out to the haul-off device. For low-voidage MCFs the final voidage in the MCF film was close to that of the die injector voidage of 15%.

High-voidage MCF was fabricated using a similar process to the low-voidage-MCF, but with the difference of using two opposing high speed air jets, which were placed at the die

exit to quench the film [10] The cooling of the molten surface resulted in the internal voidage of the MCF increasing from the die voidage of 10% up to voidage of order 24-70%.

Low-voidage MCM formation process

The processing of the low-voidage MCM consisted of cutting 30 cm length of Microcapillary film, placing them on the top of each other and then heat welding them together to form a MCM. The thickness of the MCM would be a function of the number of bonded microcapillary films. The MCFs were placed in an adjustable custom-designed brass mould. The mould consisted of a brass top and an aluminium bottom plate, each 310 mm x 100 mm. The MCM thickness was controlled with brass spacer strips, which were 0.051 mm, 0.52 mm, 1 mm and 5mm thick. A heated press (Moore E1322) was used in order to obtain a controlled clamping load (Figure 4a). The following procedure was used: The multilayer stack of MCFs was prepared by layering the specific amount of MCFs on top of each other, the MCFs were held together using tape.

The thickness of the untreated stack (t_o) was measured and thickness of the mould (t_m) was also measured. A compression ratio was calculated from the difference of t_o minus t_m between t_m . The brass mould was adjusted to the resulting calculate thickness (t_c) as precisely as possible using the brass strips.

$$C_R = \frac{t_o - t_m}{t_m}$$

The untreated stack was loaded into the mould at room temperature. After that the mould was introduced into the hot press machine with no applied load, but in contact with the two plates, for six minutes to allow temperature equilibration (Figure 4b). Finally, after a melding time of 5 minutes at a constant temperature, and a load of 4 tonnes (Figure 4c) the pressure was released and the plates taken out of the press and allowed to cool down before opening the mould.

High-voidage MCM formation process

The manufacture of high-voidage MCMs was similar to the low-voidage MCM, with the difference of temperature, load and welding time parameters together with the use of a polymer film interlayer. Optimal parameters in order to avoid collapse or deformation of the capillaries were established.

Rheological characterization

Rheological characterisation experiments were carried out to obtain material parameters that describe the linear, non-linear visco-elastic response and temperature dependence of the base polymer.

The melt processing properties were investigated by performing shear rheometry. An Advanced Rheometric Expansion System rheometer (ARES-LC model 5450DT), was used to carry out these experiments. A stepper motor drives the lower plate in oscillation, while the upper plate is connected to a transducer, which measures torque and normal force (Figure 5a). In dynamic experiments, shear strain, resultant shear stress and the phase angle between these are resolved. As a result the elastic and viscous modulus can be calculated.

The ARES rheometer was configured with 25 mm diameter parallel plates and heated by an air-blast oven. For the solid samples a rectangular/torsion fixture was used as shown in Figure 5b. Rectangular samples (of dimensions $x = 1.5$ mm, $y = 12$ mm, $z = 30$ mm) were mechanically gripped and tested in a similar way to the melt.

Differential Scanning Calorimetry (DSC) was carried out on a Pyris 1 Perkin Elmer 300VA calorimeter with heating and cooling rates of $10^{\circ}\text{C}/\text{min}$ over the temperature range 0 – 200°C . The ramp rate of $10^{\circ}\text{C}/\text{min}$ was chosen to minimise structural reorganisation during heating whilst ensuring that reliable melting temperatures could be obtained [23]

The sensitivity of the DSC was 0.0001 mg. Samples with mass in the range 7.00 ± 0.50 mg were cut from the low-voidage MCF and HV-MCF samples.

In order to establish the capillary size, shape and interfacial bonding of the MCFs a visual characterization technique was used. An optical microscope Olympus BH-2 allowed effective detailed mapping of the MCFs capillaries size, shape and distribution along the film. A graticule was photographed and used to determine the film thickness and capillary size. These results were confirmed by JEOL 6340F Scanning electron microscopy (SEM) with an accelerating voltage of 5 kV.

RESULTS AND DISCUSSION

The rheology and DSC data are shown in figures 6 and 7 respectively. This data shows that for this polymer a melting transition occurs at around 114 °C and it is in this temperature region that melding experiments were carried out.

Low-voidage MCF melding

Figure 8 is an example of extreme melding conditions. If melding is carried out at 124 °C as shown in figure 8a there is complete collapse of the capillaries. By contrast if melding is carried out at 100 °C as shown in figure 8b, no interface bonding occurs. Clearly intermediate conditions are required and these are mapped out in Figure 9. The figure shows optical sections of MCM obtained for different compression ratios and melding temperature. All were taken for a 300 s melding time. The figure shows optimum interface formation whilst retaining capillary integrity of order $T = 114\text{--}120$ °C and $C_R = 0.26 - 6.82$ %. The diagonal cross hatched zone indicates two weak an interfacial bond and the horizontal hatched zone, partial capillary distortion. The optimum interface formation condition is close to the peak in the DSC trace and also at the cross over to the G' , G'' trace.

High-voidage MCFs

By virtue of its greater voidage, the high voidage MCF is more susceptible to loads than the low-voidage MCF and in addition fundamental differences in interface bonding were discovered. Figure 10 shows a series of high voidage MCM sections for melding at similar conditions to the low-voidage examples. Two things are noticeable; the collapse of the capillaries as shown in Figure 11 and the poor interface bonding. Increasing the temperature or bonding time did not enable bonding to occur without capillary collapse.

It was suspected that the high voidage interface behave in a different way to the low-voidage interface and X-ray measurements shown in figure 12 indicated that the high voidage MCFs were oriented and the low-voidage were not. The DSC curve in Figure 7 also shows the high voidage MCF has a higher melting point. It appears that orientation reduces the melding ability at these intermediate temperatures and it was not found possible to form high-voidage MCMs in the same way as low-voidage MCMs were achieved.

An effective way of forming high-voidage MCMs was discovered; a plane film of LLDPE was used as an interlayer between adjacent MCFs. This is shown in Figure 13 where conditions were found for good interface bonding and also capillary integrity.

Modelling of MCM formation

A number of aspect for the low-voidage MCM bonding have been modelled including the development of the MCM, thermal profile, capillary distortion due to an uneven interface and reptative polymer diffusion across an interface. The modelling is far from complete but it does help to understanding some of the physical issues involved.

Thermal modelling

The heating temperature kinetics of the MCF stack was calculated and compared with the measure kinetic. A schematic of the geometry is shown in Figure 14 and the heat differential equation (1) given below was numerically solved.

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \equiv \frac{\rho C_p}{\lambda} \frac{\partial T}{\partial t} \quad (1)$$

where T is the temperature of the MCM at coordinate x and y at specific time t , ρ is the density, C_p the specific heat capacity and λ the thermal conductivity for the MCF.

The experimentally measured input surface oven plate was introduced as a boundary condition and the temperature rise kinetic of both mould plates and MCF stack established. The numerical results agree well with the experimental thermocouple temperature profile positioned at the centre of the stack as shown in Figure 15. The modeling showed that most of the thermal resistance came from the heating of the mould and not the MCF itself.

MCF Interface modeling

The surfaces of the MCFs were not perfectly flat and an essential part of the good interface bonding between adjacent MCF surfaces was to have a good contact. A minimum value of

compression ratio was necessary to achieve good contact, however if the compression ratio was too high distortion of the hollow capillaries occurred.

In an attempt to gain some insight into this process mechanical numerical modeling was carried out on an elastic MCF with smooth boundary conditions on one side and an irregular boundary on the other. The geometric section of MCF and boundary is shown in Figure 16.

The thermomechanical model was solved numerically assuming the young modulus $E = 2.5E5$ Pa and poisson ratio $\nu = 0.45$. Figure 17 shows the distortion of the capillaries for a compression ratio deformation of 5.9 %. The results show that if one of the surfaces is irregular, distortion of the capillary holes will occur. In general this was not seen experimentally except in the case of the high voidage MCM where capillary collapse occurred. In reality some plastic distortion almost certainly occurs at an uneven interface when a load is applied and this will need to be included in future modeling.

Interface bonding.

The modeling of the interfacial bonding is difficult unless the two surfaces are considered as molten polymers of unique molecular weight and that the surfaces are in perfect physical contact. The reality is that the surfaces are not necessarily in perfect contact, the polymer contains a distribution of molecular weights, the polymers themselves are not in the fully molten state and that partial crystallinity influences the bonding process. The fact that the oriented high voidage MCF had different bonding characteristics to the unoriented low-voidage MCF demonstrates that interfacial bonding in the temperature regime considered has considerable complexity.

If a pure melt and perfect interface assumption is assumed, progress can be made in relation to modeling. The reptation concept of De Gennes [15], provides a framework for analysis [24]. The reptation diffusion, equation (2)

$$\frac{\partial P}{\partial t} \equiv D \frac{\partial^2 P}{\partial s^2} \quad (2)$$

can be solved, P is the probability density function, which is related to the position s of a chain segment at time t , D is the temperature dependant reptation diffusion constant, the diffusion constant depends of the length of the chain L by an equation (3) [19]

$$t_R(T_o) \equiv \frac{L^2}{2D_o} \quad (3)$$

where t_R is the reptation time, L is the total length of the chain and D_o is the isothermal reptation coefficient at temperature T_o .

After all, equation (4) shows the relationship between the minor chain length, the total chain length and the time of reptation [15, 18, 19]

$$\frac{l^2}{L^2} = \frac{t}{t_R} \quad (4)$$

Modelling the melding process at temperatures close to the melting point of the polymer is extremely difficult. This model requires knowledge of the reptation time for the polymer at the applied melding temperature. It is possible to obtain relaxation spectrum for the polymer used in this study at temperatures above the melting point. Figure 18 shows the frequency sweep at 140 °C, and using a software program RepTate [25], the longest relaxation modes can be identified as showed in Figure 19. This has been carried out for each temperature above the melting point and a plot is shown in Figure 20.

If this data is extrapolated to the melding temperature a τ_R of 2632 s is obtained. This almost certainly is an underestimate of the true reptation time at that temperature because the material is still partially crystalline.

The advancement of the diffusion of the chains to the interface, N , can be calculated with the following equation:

$$N = \frac{t}{t_R} \quad (4)$$

This defines the motion of the chain, when it goes out of the tube. A temperature of 114 °C, we get the advancement of the diffusion of the chains to the interface of 11 % when we maintain this temperature for 300 sec.

Full reptation is not necessary for complete melding plausible because the long modes correspond to highest molecular weights. Lower molecular weight polymer chains and parts of high molecular weight chains will be able to reptate across the interface with much shorter timescales and evidently give adequate bonding.

Conclusions

This paper has established melding conditions where plastic microcapillary film (MCF) can be bonded together to form a 2D microcapillary monolith (MCM). The problem is a delicate one as if too low temperature is applied the MCFs will not bound, however if too high a temperature is used the polymer melts and the hollow capillaries collapse. A reasonably wide processing window for low-voidage MCF was established in relation to moulding temperature, compression ratio and time.

High-voidage MCFs have intrinsic molecular orientation associated with the quench forming process and because of the orientation it was found difficult to establish a processing window where good interbonding could be achieved. The problem was partially overcome by using an unoriented plane film interlayer.

Rheological data for the LLDPE used to form the MCM has been presented over a temperature range that covers the materials solid and melt behaviour. In particular the region near the melting point brings particular difficulties in measurement, however it is in this region where the melding process occurs.

The formation of MCM was partially modeled by solving the transient heat transfer problem, analyzing the deformation of MCF under load and also examining interfacial reptation diffusion. Overall a picture emerges where a viable processing window can be identified in order that MCMs can be fabricated.

This may have future applications for MCFs when used for heat transfer, microreactors or other usage. The transition temperature behaviour of polyethylene presented in the paper has general relevance to polyethylene forming process at and around the melting range of the polymer.

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REFERENCES

1. Hallmark, B., F. Gadala-Maria, and M.R. Mackley, *The melt processing of polymer microcapillary film (MCF)*. Journal of Non-Newtonian Fluid Mechanics, 2005. **128**(2-3): p. 83-98.
2. Briston, J.H. and L.L. Katan, *Plastics films*. 1st ed. 1974, London: The Plastics Institute. (Part 2).
3. Han, C.D., *Rheology in Polymer Processing*. 1 ed. 1976, New York: Academic Press Inc 366.
4. Zatloukal, M. and J. Vlcek, *Application of variational principles in modeling of the film blowing process for high stalk bubbles*. Journal of Non-Newtonian Fluid Mechanics, 2006. **133**(1): p. 63-72.
5. Mills, N.J. and H.X. Zhu, *The high strain compression of closed-cell polymer foams*. Journal of the Mechanics and Physics of Solids, 1999. **47**(3): p. 669-695.
6. Zhu, H.X., N.J. Mills, and J.F. Knott, *Analysis of the high strain compression of open-cell foams*. Journal of the Mechanics and Physics of Solids, 1997. **45**(11-12): p. 1875-1904.
7. Dees, J.R. and J.E. Spruiell, *Structure Development During Melt Spinning of Linear Polyethylene Fibers*. Journal of Applied Polymer Science, 1974. **18**(4): p. 1053-1078.
8. White, J. and M. Cakmak, *Orientation development and crystallization in melt spinning of fibers*. Advances in Polymer Technology, 1986. **6**(3): p. 295-337.
9. Syang-Peng, R., *Formation of hollow fibers in the melt-spinning process*. Journal of Applied Polymer Science, 2001. **82**(12): p. 2896-2902.
10. Medina, D., B. Hallmark, T. Lord, and M. Mackley, *The development of voidage and capillary size within extruded plastic films*. Journal of Materials Science.
11. Gao, S.M. and L. Budde, *Mechanism of Mechanical Press Joining*. International Journal of Machine Tools & Manufacture, 1994. **34**(5): p. 641-657.
12. Morris, C.E.M., *Adhesive Bonding of Polyethylene*. Journal of Applied Polymer Science, 1970. **14**(9): p. 2171-&.
13. Grewell, D. and A. Benatar, *Welding of plastics: Fundamentals and new developments*. International Polymer Processing, 2007. **22**(1): p. 43-60.
14. Prager, S. and M. Tirrell, *The Healing-Process at Polymer-Polymer Interfaces*. Journal of Chemical Physics, 1981. **75**(10): p. 5194-5198.

15. Degennes, P.G., *Reptation of a Polymer Chain in Presence of Fixed Obstacles*. Journal of Chemical Physics, 1971. **55**(2): p. 572-&.
16. Edwards, S.F., *The statistical mechanics of polymerized material*. Proceedings of the Physical Society, 1967. **92**: p. 9-16.
17. Kim, Y.H. and R.P. Wool, *A Theory of Healing at a Polymer Polymer Interface*. Macromolecules, 1983. **16**(7): p. 1115-1120.
18. Wool, R.P., B.L. Yuan, and O.J. McGarel, *Welding of Polymer Interfaces*. Polymer Engineering and Science, 1989. **29**(19): p. 1340-1367.
19. Yang, F. and R. Pitchumani, *Healing of thermoplastic polymers at an interface under nonisothermal conditions*. Macromolecules, 2002. **35**(8): p. 3213-3224.
20. Jenn-Yeu Nieh, L.J.L., *Hot plate welding of polypropylene. Part I: Crystallization kinetics*. Polymer Engineering & Science, 1998. **38**(7): p. 1121-1132.
21. M. N. Watson, M.G.M., *Recent developments in hot plate welding of thermoplastics*. Polymer Engineering and Science, 1989. **29**(19): p. 1382-1386.
22. Bastien, L.J. and J.W. Gillespie, *A Nonisothermal Healing Model for Strength and Toughness of Fusion Bonded Joints of Amorphous Thermoplastics*. Polymer Engineering and Science, 1991. **31**(24): p. 1720-1730.
23. Wunderlich, B. and G. Czornyj, *Study of Equilibrium Melting of Polyethylene*. Macromolecules, 1977. **10**(5): p. 906-913.
24. Gao, P. and M.R. Mackley, *The Structure and Rheology of Molten Ultra-High-Molecular-Mass Polyethylene*. Polymer, 1994. **35**(24): p. 5210-5216.
25. Ramirez, J. and A. Likhtman, *RepTate -Rheology of Entangled Polymers Toolkit for the Analysis of Theory and Experiments*. 2008, muPP2 project.