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THE EFFECT OF PIB MOLECULAR WEIGHT ON THE CLING CHARACTERISTICS OF POLYETHYLENE-PIB FILMS FOR STRETCH AND CLING FILM APPLICATIONS*

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ABSTRACT: The effect of molecular weight on the migratory characteristics of polyisobutylene (PIB) additive from the bulk to the surface of a range of monolayer and multilayer extruded polyethylene films has been analyzed by FTIR-ATR and peel cling analysis. Migration rates are shown to be higher for lower molecular weight PIB additive, and cling strength increases as the PIB molecular weight increases.

KEY WORDS: PIB, LLDPE, cling strength, blends, stretch films, metallocene, Z-N catalyst, coextrusion, FTIR, molecular weight.

INTRODUCTION

AN AUTOADHESIVE OR cling surface may be imparted to polyethylene film using coatings or coextrusion techniques and through the incorporation of cling agents blended into the polyethylene resin, which migrate to the film surface after extrusion by blown film or cast film techniques. The processes associated with the development of a cling

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or tack surface on polymer films employing migratory cling agents have not been widely reported in the published literature, although there are many patents by individual companies regarding the manufacture of such films [1–4].

The migration of cling additives may be compared to the migration of low molecular weight slip agents and stabilizers in films [5–7]. Factors influencing the migration rates of such additives from the bulk to the film surface have already been reported to include film morphology, compatibility of the polymer–additive mixture, extrusion processing variables (including co-extrusion systems), and film post extrusion conditioning. However, Jalbert et al. [8] reported that the concentration and the molecular characteristics of migratory additives could affect the surface segregation or migration process. Indeed, this migration process may relate to incompatibility arising from differences in the surface free energy of each component in the blend, and it has been reported that molecules with the lowest surface free energy will prefer the polymer–air interface, i.e., the film surface [5,8,9]. The difference in molecular weight between the additive and bulk resin may also influence the migration process.

The packaging industry trade literature and analysis of commercial films suggest that polyisobutylene (PIB) is the most predominant cling agent used in stretch–cling films. Polyisobutylenes can range from waxy solids to extremely viscous liquids depending on their molecular weight. The resins in the molecular weight range of 100–3000 g/mol (i.e., viscous liquids) are most suitable for cling agents and are the basis of most commercial cling films. The molecular weight of the resin determines the cling strength between adjacent films and will also influence such characteristics as unwinding noise, roll telescoping, and surface ‘feel’ of the film [10].

In our previous work [11,12], cling film was manufactured from both polyethylene and ethyl vinyl acetate (EVA) resins, blended with a single commercial PIB masterbatch (PW52), at a range of concentrations. The work showed that the surface cling development was affected by the morphological properties of the films, which were dependent on the extrusion process parameters and also on the molecular characteristics of the polyethylene or EVA resin. Another work [13] reported that Fourier Transform Infrared–Attenuated Total Reflection (FTIR–ATR) techniques could be used to determine the migration of PIB elements in polyethylene film and this could be correlated well to the cling strength of films.

This work investigates the modification of polyethylene film, to produce cling surfaces, using a range of PIB masterbatches, manufactured

from different molecular weight PIB resins. The analysis also examines the effect of PIB concentration in surface layers of coextruded films and highlights the possibility for significant reductions in overall PIB content compared to that needed for similar cling in monolayer films.

EXPERIMENTAL

Materials

The technical specifications of the various materials used in this investigation are detailed in Table 1. Initially, a range of films containing 10% PIB masterbatch (Polytechs SA) were manufactured from each PIB masterbatch sample, blended with the metallocene polyethylene ML2518FC.

The PIB masterbatches were manufactured from a range of PIB molecular weight resins blended $52 \pm 2\%$ in an LLDPE carrier resin (octene comonomer). The PIB molecular weight ranged from 100 to 2100. Due to the processing difficulties, masterbatch PW1778 contained a blend of PIB resins (M_w 300 and 2100) combined at a 1:1 ratio.

During coextrusion trials, metallocene LLDPE (octene comonomer) resin ML2518FC was extruded as a core layer $\approx 20 \mu\text{m}$ thick in a three-layer coextruded film. LLDPE resin NG5056E, blended with varying concentrations of PIB masterbatch PW52, was used as the skin layers $\approx 2.5 \mu\text{m}$ thick. Blends were produced containing 0, 5, 10, 15, and 20% PIB masterbatch PW52. All blends were mixed thoroughly prior to being fed directly into the feed hopper of the extruder.

Table 1. Material characteristics.

Manufacturer	Grade	Density (g/cm ³)	PIB (M_w)	MFI (g/10 min)	Blend (polyethylene/PIB)	
					M_w	M_n
Polytechs SA	PW 52	0.892	–	>250	40,600	1510
	PW 1775	0.890	100	>250	34,500	590
	PW 1776	0.896	300	>250	37,000	930
	PW 1777	0.882	1200	>250	39,500	1480
	PW 1778	0.910	300+2100	>250	37,500	1380
Exxon	ML2518FC	0.918	–	2.5	88,000	36,000
Dow	NG5056E	0.919	–	1.1	129,500	32,700

Preparation of Films

For the initial trials, cast films were manufactured on a Killion cast film extrusion system, using a Killion-KN150 38 mm Extruder, with a general-purpose screw ($L/D = 30$, 3:1 compression ratio). The temperature profile was ramped from 200°C at the feed section to 220°C at the die. The extruder was fitted with a 600 mm flexible lip sheet die, with a die gap of 250 μm . Films were manufactured with an air gap setting of 100 mm and a chill roll temperature of 10°C. A rubber-coated roller was used to press the hot film extrudate onto the chill roll. The screw speed was held constant at 30 rpm. Haul-off ratio and nip roll speeds were adjusted to maintain a constant film thickness of 25 μm .

Coextruded cast films were manufactured on a Killion coextrusion system; using a KN150 38 mm Extruder for the mLLDPE (ML2518FC) and a KN100 25 mm Extruder for the LLDPE-PIB blends. The extruders were fitted to the 600 mm flexible lip sheet die. A feedback system attached to the die gave a film configuration of ABA ((LLDPE:PIB)/mLLDPE/(LLDPE:PIB)). The temperature profile of both extruders was ramped from 200°C at the feed section to 220°C at the die, and the screw speed was held constant at 15 rpm for the mLLDPE extruder and 12.5 rpm for the LLDPE-PIB blends. The downstream settings were the same as for the mono-layer film.

Film Cling Analysis

Film samples, 100 \times 250 mm, were laid in a double film ply, free from air pockets and film imperfections. Samples were placed between thin metal sheets and a 1-kg weight was applied to the samples for 24 h prior to cling analysis. The tack properties of the various films were recorded by measuring the force required to peel these apart at an angle of 180°, as shown in Figure 1. The tests were performed using an Instron 4411 Universal Tensile Tester at a crosshead speed of 250 mm/min and grip length of 50 mm, with a load cell of 0.1 kN. Samples were conditioned in an air-circulating oven at 25 and 45°C for up to 28 days prior to analysis in order to allow the development of tack. A range of samples were also refrigerated at -40°C, to determine the effect of low temperatures on the migration of different molecular weight PIB. Five specimens were analyzed for each film sample, typically the experimental error in results were within $\pm 5\%$.

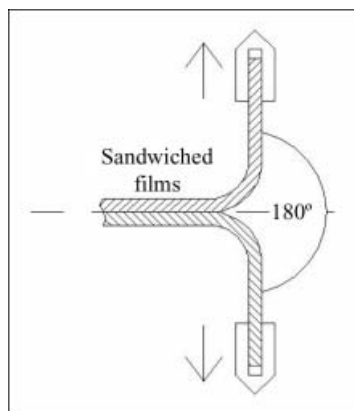


Figure 1. Tack strength analysis.

FTIR-ATR Analysis

Spectra were obtained using a Perkin-Elmer FTIR spectrometer (Spectrum 1000) fitted with an ATR diffusion cell. The equipment was positioned in a laboratory maintained at $25 \pm 1^\circ\text{C}$. A zinc selenide (ZnSe) ATR crystal having dimensions $50 \times 20 \times 2$ mm, an angle of incidence of 45° , and a refractive index of 2.4, was fitted to the spectrometer. The instrument operated with a resolution of 4 cm^{-1} , and 20 scans were collected for each sample. The IR absorbance scans were analyzed between 1350 and 1400 cm^{-1} , for changes in the intensity of PIB peaks. Throughout the analysis, a constant holding force was applied between the sample and the crystal to maintain consistency in readings. Scans used to differentiate between PIB absorbance were normalized to account for slight differences in the analysis parameters.

RESULTS AND DISCUSSION

Film Cling Strength

To evaluate the effect of post extrusion storage temperature on the surface migration of different molecular weight PIB masterbatches, the films were stored at -40 , 25 , and 45°C , prior to testing. The cling strength of the films is reported in Figures 2–6, and these results highlight the effect of PIB molecular weight and conditioning temperature on cling strength.

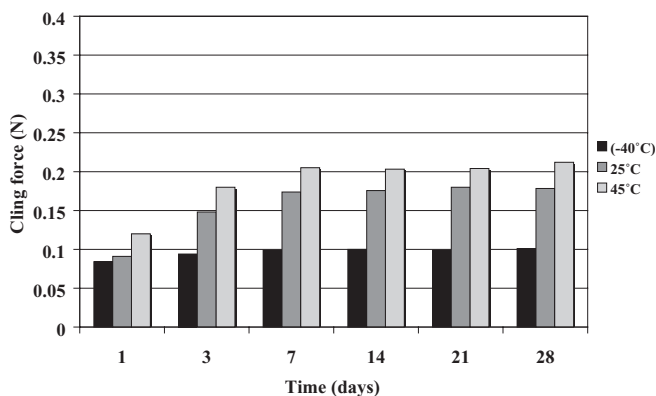


Figure 2. The effect of conditioning and aging on the cling strength of ML2518FC films containing PW 1775 (M_w 100).

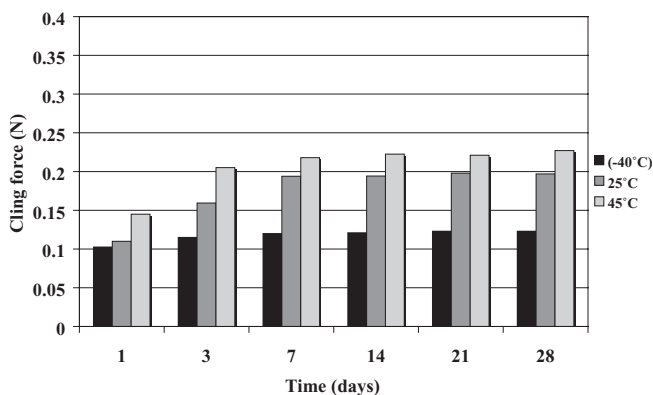


Figure 3. The effect of conditioning and aging on the cling strength of ML2518FC films containing PW 1776 (M_w 300).

In general, the cling strength was shown to increase significantly as the molecular weight of the PIB component increased from 100 to 1200 g/mol. For example, an increase in cling strength from 0.21 to 0.39 N was reported for PW 1775 (M_w 100) and PW 1777 (M_w 1200), respectively, after 28 days at 45°C. However, increasing the molecular weight also led to an increase in the time required for maximum cling strength development. In low molecular weight PW 1775 (M_w 100), maximum cling was developed between 7 and 14 days, whilst in PW 1777 the maximum cling strength had still not been reached in 28 days.

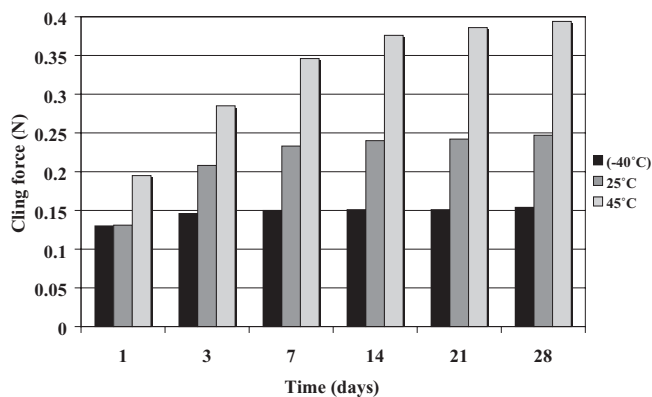


Figure 4. The effect of conditioning and aging on the cling strength of ML2518FC films containing PW 1777 (M_w 1200).

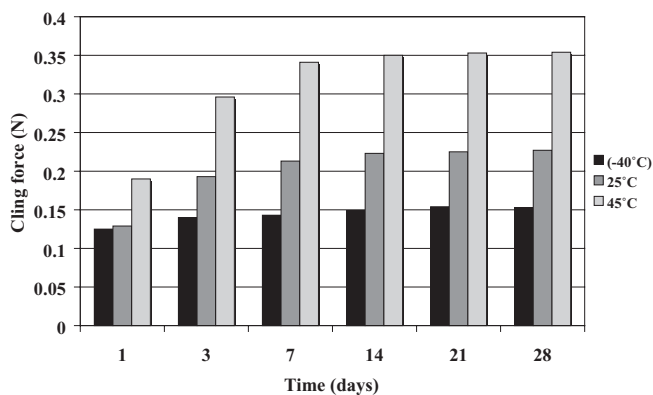


Figure 5. The effect of conditioning and aging on the cling strength of ML2518FC films containing PW 1778 (M_w 300 + 2100).

Although, the cling strength of PW 1778 was lower than that of PW 1777, the cling developed faster in PW 1778, and this was most probably due to the low molecular weight component present in this PIB blend. After 3 days at 45°C, the cling strength of PW1778 was 0.3 N, compared to 0.29 N for PW 1777. These results are quite significant to commercial cling film manufacture since conditioning of the film for any more than 3 to 4 days at the elevated conditioning temperatures is not cost effective. Therefore, a film blend that produces greatest cling strength within this short time period is more beneficial.

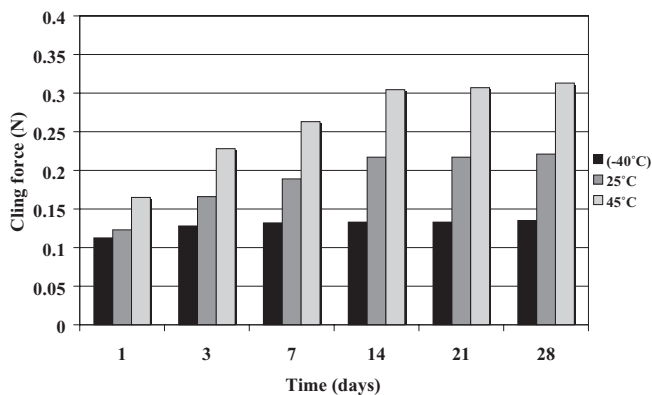


Figure 6. The effect of conditioning and aging on the cling strength of ML2518FC films containing PW 52 (M_w : not known).

The effect of conditioning temperature on the rate and magnitude of cling development is also shown in Figures 2–6. In general, films stored at -40°C showed no significant increase in cling strength throughout the duration of the analysis. At this temperature, the cling strength of the film was shown to be dependent on the quantity of PIB present at the film surface immediately after processing. As the conditioning temperature increased, the rate of cling development increased considerably and it might be suggested that the higher conditioning temperature permits the migration of higher molecular weight PIB species within the bulk of the film, resulting in higher surface cling strength. This is confirmed by a significant increase in cling strength between 25 and 45°C for the higher molecular weight PIB blends PW 1777 and PW 1778.

FTIR-ATR Analysis

Fourier transform infrared spectroscopy in the attenuated total reflectance mode was employed to evaluate the surface compositions of films containing PIB, over the 28-day test. This technique enabled the study of PIB accumulation at or near the film surface as a function of time, with the objective of investigating the differences in cling characteristics determined in the previous section.

Figure 7 illustrates the effect of the molecular weight of PIB on the surface spectra of polyethylene-PIB films after 14 days of conditioning at 45°C . In general, the intensity of IR absorbance decreased progressively with increasing PIB molecular weight, with the spectra

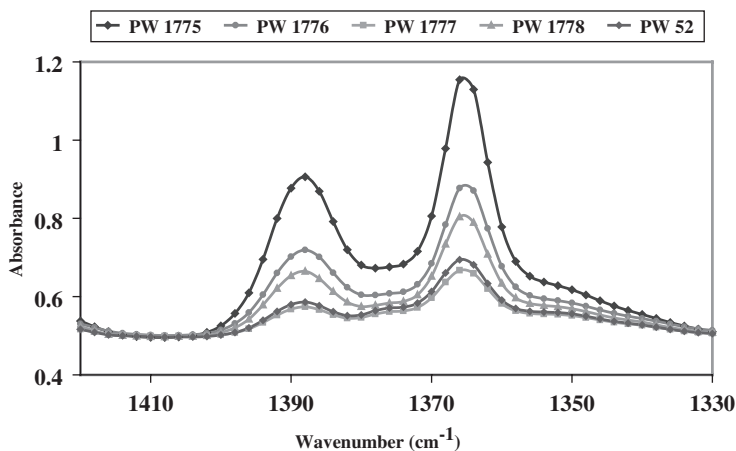


Figure 7. The effect of PIB molecular weight on the the FTIR-ATR spectra of film surface after 14 days.

showing a significant decrease in the absorbance for both CH_3 vibrations (1366 and 1386 cm^{-1}) as the PIB molecular weight or the combined molecular weights of PIB blends increased. These two principal spectral peaks are representative of the presence of PIB on the film surface. The only other CH_3 component in the films is associated with polyethylene elements, the concentration of which was not sufficient to produce such absorbance peaks. PW 1778 shows a considerably higher presence of PIB on the film surface after 14 days compared to PW 1777. The masterbatch PW 1778 is a blend of two PIB resins with average molecular weights 300 and 2100 g/mol . It might be suggested that the low molecular weight component in this blend can migrate more freely than higher weight components and therefore a higher PIB surface composition has been detected. The analysis would tend to suggest PW 52 is of a molecular weight similar to PW 1777. However, this may also contain minor concentrations of slightly lower molecular weight PIB resin. This would confirm the slightly lower cling strength reported for PW 52 in the previous section.

In Figures 8–10, the effect of conditioning temperature and aging on the peak height absorbance recorded from the FTIR-ATR analysis at wavenumber 1366 cm^{-1} for the range of PIB samples are reported. These data illustrate the effect temperature and aging has upon PIB surface accumulation and thus on the migration rates of PIB from the bulk of the film.

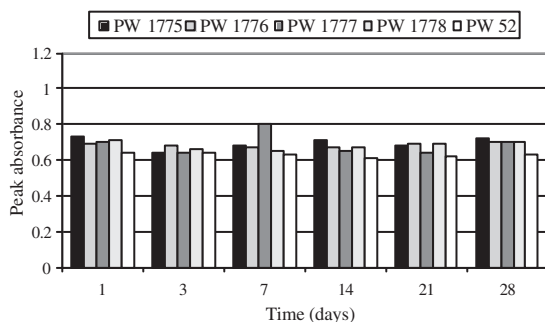


Figure 8. The effect of aging on ATR spectra (1366 cm^{-1}) of PIB-based films at -40°C .

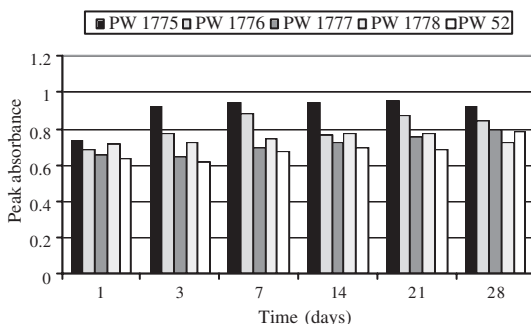


Figure 9. The effect of aging on ATR spectra (1366 cm^{-1}) of PIB-based films at 25°C .

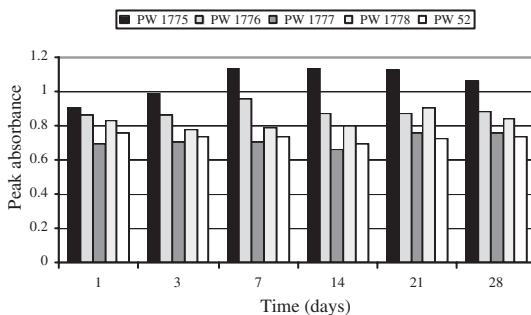


Figure 10. The effect of aging on ATR spectra (1366 cm^{-1}) of PIB-based films at 45°C .

In general, conditioning films at -40°C essentially halts the migration of PIB from the bulk to the surface. It might be suggested that at this low temperature, the mobility of both the polyethylene segments in the amorphous and partially ordered crystalline interface, and the PIB molecules, are so limited that the molecular motions, which are

necessary to facilitate the migration of PIB molecules through the bulk polyethylene, are very low.

Coextruded Films

The effect of increasing PIB concentration on the cling characteristics of the coextruded cast films is reported in Figures 11 and 12. The results show the effect of aging on the cling strength of samples conditioned at 45°C for up to 28 days. They also show a progressive increase in cling strength as the PIB concentration of the surface layers was increased. The cling strength was shown to increase dramatically within the first 3–7 days, compared to monolayer PIB films [11]. The higher cling strengths recorded for these coextruded cast films reflect the higher concentration of PIB at or close to the film surface. The fact that the longest distance PIB must migrate to reach the film surface is 2.5 μm , results in higher cling strength being developed in the early period of the analysis.

The cling strength of the 5–15% coextruded samples was equivalent to monolayer films [14] containing 4–6% PIB masterbatch throughout the bulk of the film. The 20% PIB coextruded film had a maximum cling strength of 0.39 N, which was higher than the 0.26 N cling strength recorded for the monolayer film containing 8% PIB [11]. The weight of PIB blended in the 20% coextruded film was equivalent to the weight of 4% PIB in a monolayer film. Therefore, coextrusion may potentially reduce the overall PIB content in the film by up to 50% without any deterioration in cling performance. However, large throughput rates would be necessary for the savings on PIB consumption to outweigh the increased expense of the coextrusion system required.

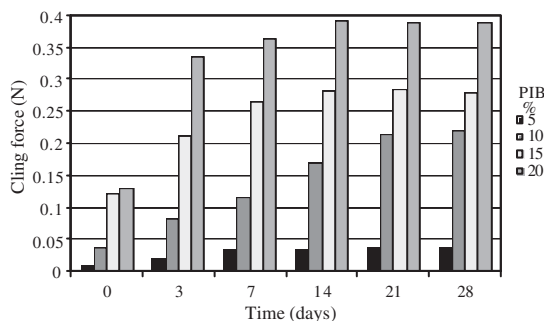


Figure 11. The effect of PIB concentration (expressed as %PIB masterbatch) on cling strength of coextruded films with 45°C conditioning.

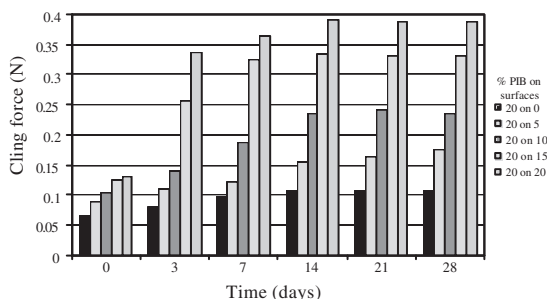


Figure 12. The cling strength of coextruded films containing 20% PIB masterbatch in one surface layer and a range of PIB masterbatch concentrations in the other.

Figure 12 also highlights that high concentrations of PIB are not necessary on both film surfaces to achieve significant cling strengths.

CONCLUSIONS

FTIR-ATR analysis reported higher accumulation of the lower molecular weight PIB at the film surfaces after 28 days; this however, did not equate to higher cling strength. The cling strength developed in polyethylene/PIB blends was shown to increase with higher molecular weight of the PIB additive; and the rate of cling development was shown to decrease as the molecular weight of the PIB decreased. Low molecular weight PW 1775 (M_w 100) developed maximum cling strength within 7–14 days. The cling strength of higher molecular weight PW 1777 (M_w 1200) had not reached equilibrium by 28 days.

Cling strength increased considerably with increase in conditioning temperature, greater surface cling strength was developed at higher temperatures and was shown to develop much faster.

The results also show that cling performance may be improved through the use of coextrusion techniques with surface cling strengths, comparable to monolayer films being achieved using lower overall PIB consumption.

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BIOGRAPHIES

Gerry McNally

Gerry McNally is a Senior Lecturer in Engineering Materials in the School of Chemical Engineering at the Queen's University of Belfast.

He has 12 years industrial experience at the senior management level in polymer extrusion. He is a founder member of the Polymer Processing Research Centre (PPRC) and was made its Director in 2004. His expertise is in various areas of processing of polymers and their additives. He has been, or is, the lead academic supervisor in 15 polymer-related TCS Programmes, one of which was awarded Best TCP in 1999. He has authored over 175 papers.

Christopher Small

Christopher Small was awarded a B.Eng (Honours) degree in Mechanical Engineering and a M.Sc. (with distinction) in Polymer Engineering, both from the Queen's University of Belfast. He went on to complete a PhD in investigating the effects of manufacturing variables on the properties and performance of polyethylene stretch and cling films.

William R. Murphy

William Murphy is Professor of Chemical Engineering at the Queen's University of Belfast, where he was the Head of the Department of Chemical Engineering (1987–1997) and was Director of the Polymer Processing Centre from 1997 to 2004. He has been active in the research and development of materials processing, including polymers, for over 20 years. He has authored two books and written over 100 papers.

Alan Clarke

Alan Clarke obtained his BSME and then spent 10 years working in extrusion-based industries involved with packaging production before joining the Polymer Processing Research Centre at the Queen's University of Belfast, where he is now the Extrusion Manager.