



The Effect of Vinyl Acetate Content and Polyisobutylene Concentration on the Properties of Metallocene Polyethylene-Ethyl Vinyl Acetate Coextruded Film for Stretch and Cling Film Applications

G. M. McNally, C. M. Small, W. R. Murphy, G. Garrett

► To cite this version:

G. M. McNally, C. M. Small, W. R. Murphy, G. Garrett. The Effect of Vinyl Acetate Content and Polyisobutylene Concentration on the Properties of Metallocene Polyethylene-Ethyl Vinyl Acetate Coextruded Film for Stretch and Cling Film Applications. *Journal of Plastic Film and Sheeting*, 2005, 21 (1), pp.69-83. 10.1177/8756087905053791 . hal-00572058

HAL Id: hal-00572058

<https://hal.science/hal-00572058>

Submitted on 1 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THE EFFECT OF VINYL ACETATE CONTENT AND POLYISOBUTYLENE CONCENTRATION ON THE PROPERTIES OF METALLOCENE POLYETHYLENE–ETHYL VINYL ACETATE COEXTRUDED FILM FOR STRETCH AND CLING FILM APPLICATIONS*

G. M. McNally,[†] C. M. Small, W. R. Murphy and G. Garrett

*Polymer Processing Research Centre
Queen's University of Belfast
Ashby Building, Stranmillis Road
Belfast, BT9 5AH
North Ireland*

ABSTRACT: A range of EVA–mLLDPE–EVA coextruded films, with polyisobutylene (PIB) masterbatch content of 0–20% and vinyl acetate (VA) comonomer content of 6, 12, and 18%, is manufactured. The films are aged at 45°C for up to 28 days to enable tack (cling) development. The results show that film tack strength improves significantly with aging. Increased VA concentration in the surface layer also shows significant improvement in film tack strength. The film tensile strength, elongation, and tear properties in both machine direction (MD) and transverse direction (TD) are not significantly affected by increase in PIB concentration. Increased VA content shows slight improvement in MD mechanical performance of the films, although TD properties are relatively unaffected.

KEY WORDS: polyisobutylene, LLDPE, mLLDPE, octene, EVA, cast film, coextrusion, crystallinity, tensile properties, modulus, tear strength, peel strength, tack strength, DSC, stretch, cling.

*Note: This is an expansion of the paper presented at ANTEC 2003, the annual technical meeting of the Society of Plastics Engineers held in Nashville, Tennessee on May 4–8, 2003; copyright SPE.

[†]Author to whom correspondence should be addressed. E-mail: g.mcnally@qub.ac.uk

INTRODUCTION

THE PRINCIPLE OF stretch wrapping is that the film is stretched around the article to be wrapped and the residual tension gives a tight contour wrap. This is made possible by stretching the film within its elastic region and in this loaded state, the polymer molecules attempt to regain their original conformation and thus exert force on the article. The common problem associated with these stretch wrap films is optimization of the surface tack or cling properties, so that the film adheres to itself instantly and thus prevents film recovery or loss of the containment forces.

In the past, stretch wrap and cling films have been manufactured from low-density polyethylenes (LDPE), ethylene vinyl acetate (EVA), and polyvinyl chloride (PVC). Recently however, Lipsitt [1] has compared the mechanical performance of metallocene-catalyzed linear low-density polyethylenes (mLLDPE) with both EVA and flexible PVC. This work has shown that mLLDPEs exhibit higher tensile strength, elongation, and tear resistance than EVA or PVC films, and can be processed at a substantially lower thickness. Polyethylenes, however, require adhesive additives to develop significant tack strength for use in cling film applications. In contrast, EVA films are inherently tacky and the tack strength is dependent on the ratio of ethylene to vinyl acetate (VA) comonomer, the higher the VA content the stronger the tack performance.

To compensate for the physical and mechanical inadequacies of these materials in stretch or cling film applications, polymer blends and coextrusion techniques are being used increasingly to optimize the performance of these products. In coextrusion, the properties of each polymer is not sacrificed by the inclusion of the other, as each is a stand-alone entity in a composite sandwich type structure. This technique has been successfully developed to produce films with special properties for specific applications, by combining polymers with desirable properties, for example polyethylene and EVA, for stretch and cling films.

The majority of commercially available EVA contains 50% VA. EVAs used in film manufacture generally contain about 5% VA, with film toughness as well as tack strength increasing with increased VA concentration (up to 20% VA). However, there is a limit to the acceptable levels of VA in the films. High VA concentration can lead to film blocking during manufacture, and in cast film extrusion, adhesion to the chill roll increases line tension and can cause differential cooling characteristics leading to changes in mechanical performance.

The present work investigates the modification of mLLDPE stretch film, by using cast film coextrusion techniques, to produce stretch film exhibiting tacky or self-adhesive surfaces. The performance of 25- μm EVA–mLLDPE–EVA coextruded films and the effect of VA concentration (6–18% VA) on the mechanical, morphological, and tack behavior of the films are reported. The thin EVA surface layer (2.5 μm), with low VA concentration, provides inherent film tack strength. The incorporation of increasing concentrations of polyisobutylene (PIB) (0–20% masterbatch) into the EVA layers permits greater tack strength to develop by PIB surface diffusion after extrusion. This eliminates processing problems associated with extruding and collecting autoadhesive films.

Diffusion characteristics of PIB from the bulk to the surface of conventional LLDPE and mLLDPE films have been reported in our previous investigations [2,3]. These studies identified the morphology developed in the film and the post extrusion storage conditions as the main factors influencing PIB tack development. Studies by Marais et al. and Devallencourt et al. [4,5] have shown that the amorphous/crystalline ratio in EVA films increases significantly as the VA content is increased. However, it was also shown that surface polarity was modified and this could alter the diffusion characteristics of small molecules through EVA. This work also reports on the diffusion characteristics of PIB as the VA content is increased.

EXPERIMENTAL

Materials

The properties of the materials used in this investigation are detailed in Table 1. The metallocene LLDPE was extruded as a core layer $\approx 20\text{ }\mu\text{m}$

Table 1. Material characteristics.

Material type	Producer	Vinyl acetate (%)	Density (g/cm^3)	MFI ($\text{g}/10\text{ min}$)
mLLDPE	Exxon	n/a	0.918	2.5
EVA-6	Exxon	6.5 (w/w)	0.926	2.5
EVA-12	Exxon	12 (w/w)	0.934	2.5
EVA-18	Exxon	18 (w/w)	0.939	1.7
PIB	Polytechs	n/a	0.912	200–300
Masterbatch $52 \pm 2\%$ PIB in LLDPE				

thick in a three-layer coextruded film. The EVA was used as the skin layers, $\approx 2.5\ \mu\text{m}$ thick, with a range of VA concentrations (6–18%).

Blends were produced containing 0, 5, 10, 15, and 20% PIB masterbatch (Polytechs SA) in each EVA grade. The PIB masterbatch contained $52 \pm 2\%$ PIB in an LLDPE carrier resin (octene comonomer). The components were mixed thoroughly prior to being fed directly into the feed hopper of the extruder. All resins contained standard antioxidant and stabilizing additives.

Preparation of Films

Cast films were manufactured on a Killion coextrusion system, using a KN150 38-mm dia. extruder for mLLDPE (with a general purpose screw $L/D=30$, 3:1 compression ratio) and a KN100 25-mm dia. extruder for EVA (with a general purpose screw $L/D=30$, 3:1 compression ratio). The extruders were fitted to a 600 mm dia. flexible lip sheet die. A feedback system attached to the die gave a film configuration of ABA (EVA–mLLDPE–EVA). The temperature profile of the mLLDPE extruder was ramped from 225°C at the feed section to 230°C at the die, and the screw speed was held constant at 15 rpm. The EVA extruder was ramped from 180°C at the feed section to 200°C at the die, and the screw speed was held constant at 12.5 rpm. The chill roll temperature was maintained at 10°C, with an air gap of 100 mm. A rubber-coated roller was used to press the hot film extrudate onto the chill roll to ensure uniform cooling. Haul off ratio and nip roll speed were adjusted to maintain 25- μm thick film throughout the trials.

Film Tensile Analysis

All tensile samples were tested according to ASTM D882-95. Tests were performed using an Instron 4411 Universal Tensile Tester, with a load cell of 0.1 kN and a constant crosshead speed of 500 mm/min. Samples were tested in both transverse and machine axes of the film. Tensile strength at break and Young's modulus were recorded.

Tear Strength Analysis

All tear samples were tested according to ASTM D1938-94, single-tear method (trouser tear). Tests were performed using an Instron 4411 Universal Tensile Tester, with a load cell of 0.1 kN and a constant crosshead speed of 250 mm/min. Samples were tested in both transverse and machine axes of the film, and tear propagation strength was recorded.

Differential Scanning Calorimetry

Differential scanning calorimetry was used to investigate the effect of polymer type on the crystalline development of the film. Tests were performed on all samples using a Perkin Elmer DSC-6. Samples were heated from 40 to 140°C at a rate of 10°C/min. The latent heat of fusion, ΔH (J/g), was calculated for each sample.

Film Tack (Cling) Analysis

Film samples $100 \times 250 \text{ mm}^2$, were laid in a double film ply, free from air pockets and film imperfections. The samples were placed between thin metal sheets and a 1-kg weight was applied to the samples. The tack properties of various films were recorded by measuring the force required to peel these apart at an angle of 90°, 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 a grip length of 50 mm, with a load cell of 0.1 kN. Samples were conditioned in an air-circulating oven at 45°C for up to 28 days, prior to analysis, in order to allow development of the tack.

RESULTS AND DISCUSSION

Tensile Properties

The effect of VA content in the EVA layers and PIB content on the tensile strength of the coextruded cast films, in both the machine

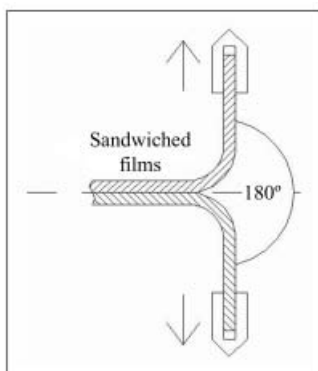


Figure 1. Tack strength analysis.

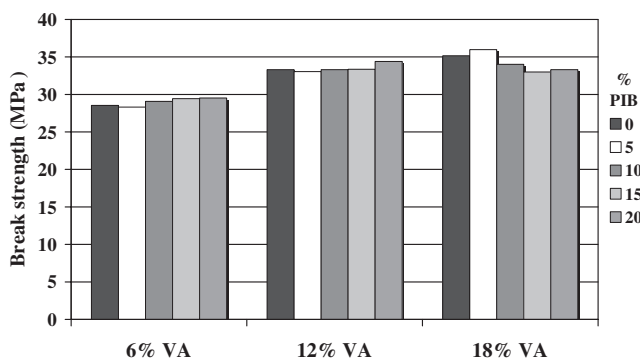


Figure 2. The effect of VA concentration and PIB content on MD break strength.

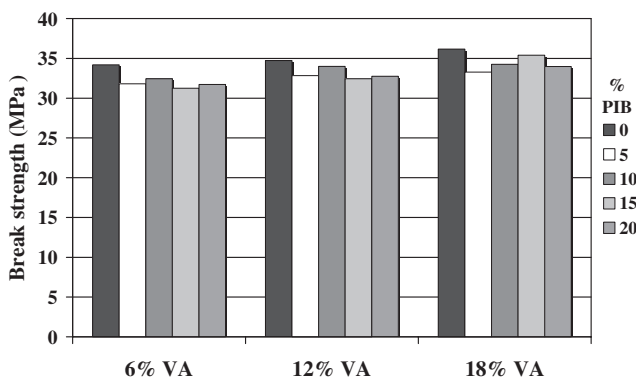


Figure 3. The effect of VA concentration and PIB content on TD break strength.

direction (MD) and the transverse direction (TD), is shown in Figures 2 and 3. The results show that the MD break strength increases progressively with increase in comonomer content in the EVA layers. However, increasing the VA content has little effect on TD strength. Increasing the PIB concentration shows no consistent increase in TD or MD break strength. The TD strength for most films is marginally higher than the MD strength.

The MD and TD elongation to break for the films is shown in Figures 4 and 5 and the results show a slight increase in MD elongation for films with increasing VA. However, the PIB had a significant effect on MD elongation, with elongation increasing progressively with increase in PIB concentration. In general, the values of TD elongation were similar for all films, with the VA and PIB concentrations having very little effect on TD elongation.

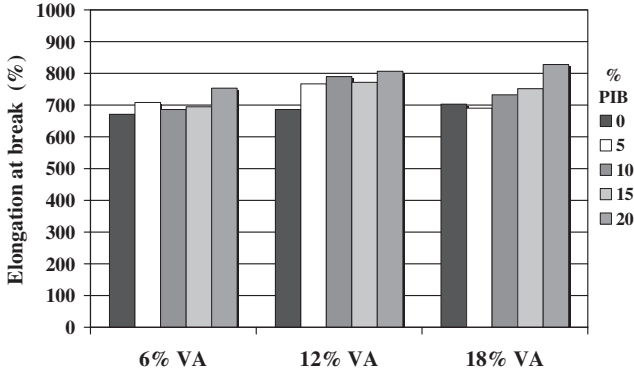


Figure 4. The effect of VA concentration and PIB content on MD elongation to break.

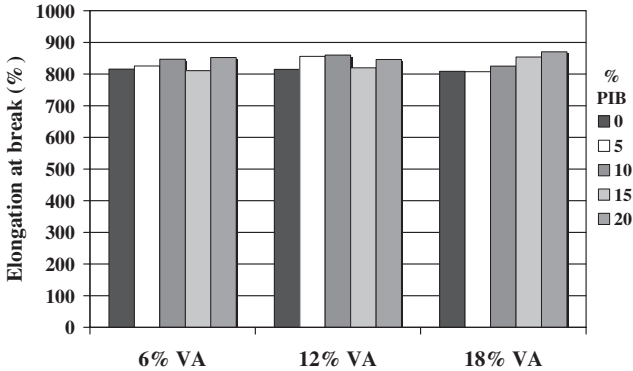


Figure 5. The effect of VA concentration and PIB content on TD elongation to break.

The effect of VA and PIB content on the Young’s moduli for all films is shown in Figures 6 and 7. The MD modulus is shown to decrease significantly with increasing VA and PIB concentrations. The TD modulus decreases more significantly with increased VA and PIB concentrations.

These results would tend to indicate that the PIB additive was exhibiting a plasticizing effect on the film microstructure, as shown by the progressive decrease in modulus and increase in elongation as the PIB concentrations increase. The increase in VA in the outer layers caused a significant decrease in tensile modulus and a slight increase in MD elongation, with no change in TD elongation. This indicates that film crystallinity decreased with increasing VA content.

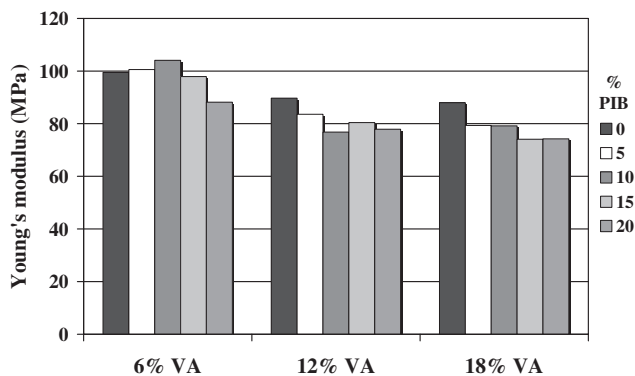


Figure 6. The effect of VA concentration and PIB content on MD tensile modulus.

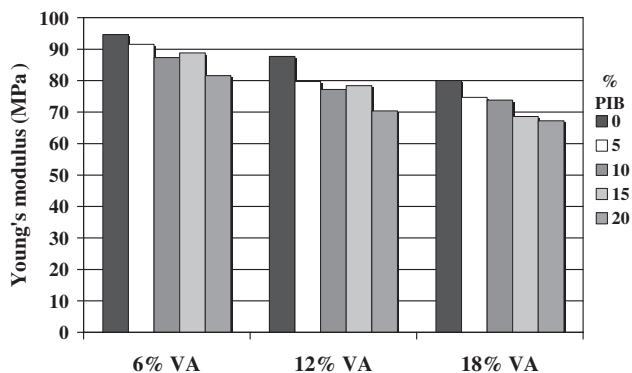


Figure 7. The effect of VA concentration and PIB content on TD tensile modulus.

Crystallinity

In order to investigate the effect of VA on the crystallinity of the EVA, DSC analysis was carried out on all the films. The thermograms in Figure 8 show the individual melting endotherms of the EVAs, mLLDPE, and PIB masterbatch. These results show that the area under the EVA melt endotherm decreases significantly, as did the melting temperature, with increasing VA. The same trend is shown for the endotherm of EVA-mLLDPE-EVA (2.5/20/2.5 μ) coextruded films in Figure 9. These results suggest the formation of smaller crystalline structures, with lower overall crystallinity, as VA is increased. Marais et al. [4,5] have reported that increase in VA content creates disorder

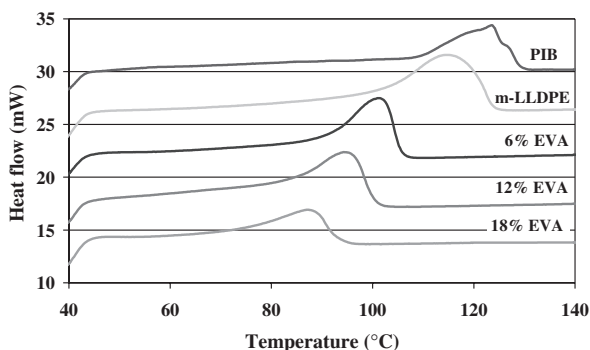


Figure 8. The effect of VA concentration on DSC thermogram of EVA pellets.

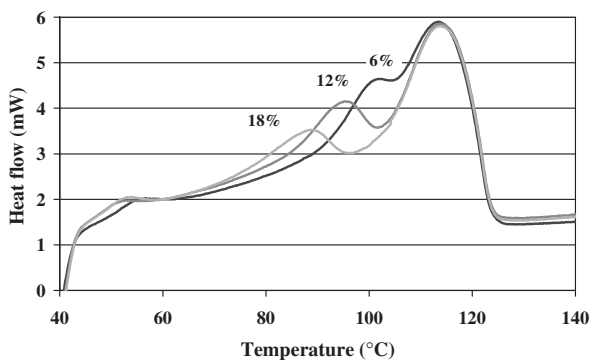


Figure 9. The effect of VA concentration on DSC thermogram of coextruded films.

within the EVA structure, limiting the ability of PE to crystallize, effectively reducing the crystallinity of the EVA.

The overall crystallinity of the range of coextruded films is shown in Figure 10. Crystallinity is shown to decrease significantly with increasing VA. The results also show a slight reduction in crystallinity with increasing PIB content for films with 6 and 12% VA. The crystallinity of the 18% VA films is shown to increase slightly as PIB content is increased from 5 to 20%. It is suggested that the LLDPE carrier in the PIB masterbatch may be responsible for this increase in crystallinity. The crystallinity of the LLDPE reduces the amorphous/crystalline ratio in the EVA layers and thus the overall crystallinity increases. This was confirmed by DSC analysis, which showed an increase in the area of the higher temperature peak as the PIB concentration was increased in 18% VA films.

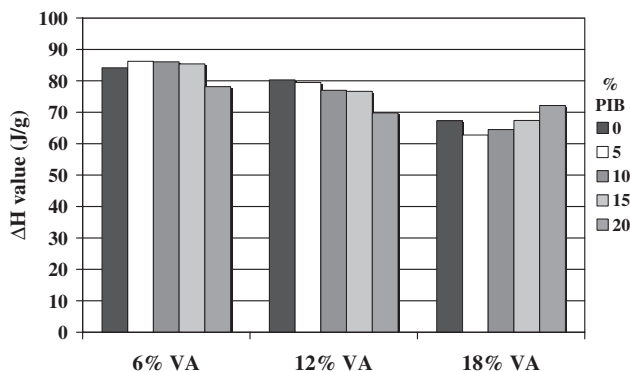


Figure 10. The effect of VA concentration and PIB content on crystallinity.

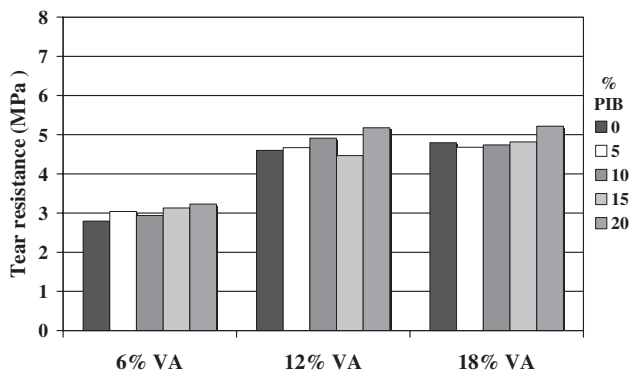


Figure 11. The effect of VA concentration and PIB content on MD tear stress.

Tear Properties

The effect of VA and PIB content on the tear propagation resistance of all films is shown in Figures 11 and 12. Film tear strength is higher in the TD compared to the MD. The MD axis shows increasing tear strength for all films with increasing VA and only a slight increase in tear strength with increasing PIB concentration. TD tear strength is found to decrease slightly with increasing VA; and increased PIB concentration has only a varied effect on tear strength.

Tack Strength

The migration of PIB from the EVA layer to the surface of the films was characterized by measuring the tack strength as a function of time,

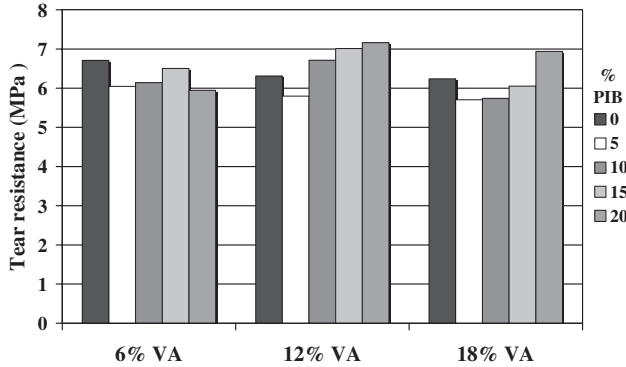


Figure 12. The effect of VA concentration and PIB content on TD tear stress.

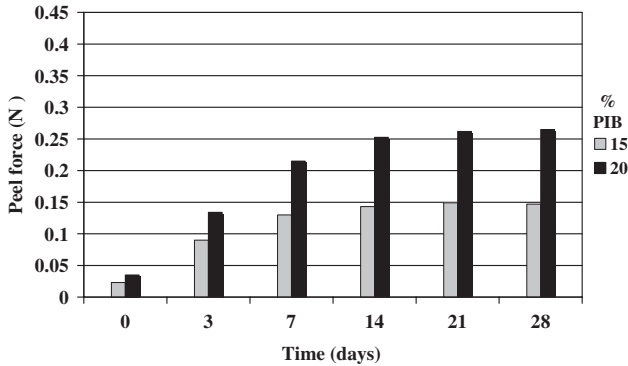


Figure 13. The effect of PIB content on peel strength of 6% EVA films (conditioned at 45°C).

as shown in Figures 13–15. The results show the effect of VA and PIB content on the surface tack strength of films conditioned at 45°C. In general, an increase in tack strength was recorded for all films with progressive increase in PIB concentration. In the 12 and 18% VA films, an increase in PIB content from 5 to 15% caused an increase in tack strength of 300%. Increasing the PIB content to 20% had a lesser effect with only a 7–8% increase in tack strength.

Tack strength also increased significantly with increasing VA content. Increasing VA from 12 to 18% caused a progressive increase in the tack strength of 0% PIB films. However, as PIB concentration was increased the effect of VA was very small, producing only a slight increase in tack strength.

Tack strength was shown to improve slightly with aging. Films containing high PIB concentrations (15 and 20%) and stored at 45°C,

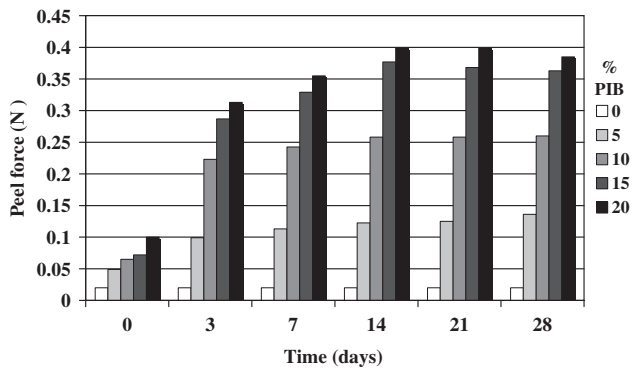


Figure 14. The effect of PIB content on peel strength of 12% EVA films (conditioned at 45°C).

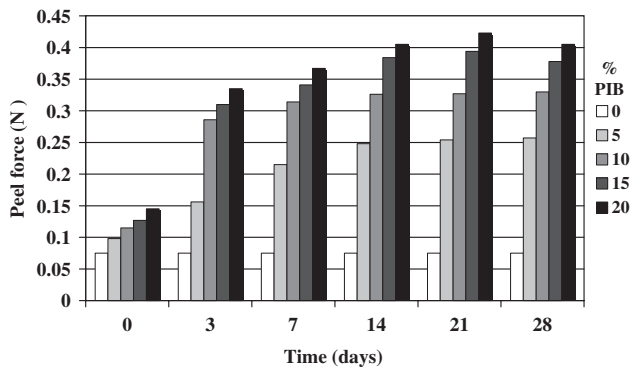


Figure 15. The effect of PIB content on peel strength of 18% EVA films (conditioned at 45°C).

developed maximum tack strength between 14 and 21 days; however, beyond this time the tack strength decreased slightly. These same trends were reported earlier for PIB diffusion in LLDPE film [2].

The diffusion rate of PIB in 6% VA films was significantly lower than that for higher VA content and no tack was measurable for films with PIB content <15%. Since the crystallinity of these films was relatively high, it would reduce diffusion of the PIB to the surface.

Comparison of Monolayer and Coextruded mLLDPE Films

Comparing Figures 2–15 with the data in Table 2 shows that reducing the thickness of the mLLDPE layer in coextruded films with EVA

Table 2. Typical properties of a monolayer mLLDPE film.

	Tensile strength (MPa)		Elongation (%)		Young's modulus (MPa)		Tear strength (MPa)		Tack strength (N)	Crystallinity ΔH (J/g)
	MD	TD	MD	TD	MD	TD	MD	TD		
0% PIB	36	35.5	810	750	99	93	5.4	5.9	n/a	91.35
**8% PIB	34.5	32.8	800	730	102	91	5.75	5.6	0.0265	83.45

**PIB additive dispersed throughout the film thickness (25 μm).

surface layers caused only a slight decrease in the tensile strength of these films. Increasing the VA content in the EVA layer to 18% produced a film with strength and elongation quite similar to a monolayer mLLDPE. The coextruded film exhibited much higher tack strength; however, the tensile modulus and overall crystallinity was significantly reduced as a consequence of the VA molecules hindering crystalline development in the EVA layer. Due to the lower crystallinity of the EVA layer and the high concentration of PIB, the diffusion and tack development in the coextruded film is much greater, with the overall mechanical performance of the film being maintained by the LLDPE in the core layer.

CONCLUSIONS

This study reports on the effect of VA concentration and PIB content on the mechanical performance, morphology, and tack characteristics of coextruded EVA–mLLDPE–EVA films manufactured by the cast film extrusion process. The results show that the tack strength and mechanical properties for 12 and 18% VA films with 15 and 20% PIB are relatively similar, although 12% VA has fewer processing problems. EVA content at these levels is shown to have little effect on the overall mechanical performance of the film compared to monolayer mLLDPE film. EVA–mLLDPE coextrusion produces very good instantaneous tack strength and with PIB only in the surface layer, this reduces the overall material costs.

REFERENCES

1. Lipsitt, B. (Sept/Oct 1998). Performance Properties of Metallocene Polyethylene, EVA and Flexible PVC films, *Medical Plastics and Biomaterials*.

2. Small, C.M., McNally, G.M., Marks, A. and Murphy, W.R. (2002). The Effect of Extrusion Processing Conditions and Polyisobutylene Concentration on the Properties of Polyethylene for Stretch and Cling film Applications, *Jrl. Plastic Film & Sheetting*, **18**: 245.
3. Small, C.M., McNally, G.M., Marks, A. and Murphy, W.R. (2002). The Use of FTIR/ATR to Investigate the Migration of Polyisobutylene in Polyethylene for Cling Film Applications, In: *ANTEC 2002 Proceedings*, pp. 2882–2886.
4. Marais, S., Saiter, J.M., Devallencourt, C., Nguyen, Q.T. and Metayer, M. (2002). Study of Transport of Small Molecules Through Ethylene Vinyl Acetate Copolymers Films, Part B: CO₂ and O₂ Gases, *Polymer Testing*, **21**: 425–431.
5. Devallencourt, C., Marais, S., Saiter, J.M., Labbe, M. and Metayer, M. (2002). Study of Transport of Small Molecules through Ethylene Vinyl Acetate Copolymers Films, Part A: Water Molecules, *Polymer Testing*, **21**: 253–262.

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 Programs, one of which was awarded Best TCP in 1999. He has published over 175 papers and international conference proceedings.

Christopher Small

Christopher Small was awarded a BEng (Honours) degree in Mechanical Engineering and a MSc (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 a 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 the Director of the Polymer Processing Centre from 1997 to 2004. He has been active in the research and development of materials processing for over 20 years. He has authored two books and written over 100 papers.

Graham Garrett

Graham Garrett spent over 20 years working in the textile industry before joining the Extrusion Centre at the Polymer Processing Research Centre at the Queen's University of Belfast, where he is now a Process Technician.