

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

MACROMOLECULAR DIVISION
COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

A COLLABORATIVE STUDY OF THE STRUCTURE AND RHEOLOGICAL PROPERTIES OF EVOH/SMA[†] BLENDS PRODUCED BY REACTIVE EXTRUSION

(Technical Report)

Prepared for publication by

P. S. HOPE¹, J. G. BONNER¹ and J. E. CURRY²

¹BP Chemicals Ltd., Applied Technology, P. O. Box 21, Bo'ness Road, Grangemouth, FK3 9XH, UK

²Werner & Pfleiderer Corporation, 663 East Crescent Avenue, Ramsey, NJ 07463, USA

*Membership of the Working Party during 1989–95 was as follows:

Chairman: H. M. Laun (Germany); *Secretary:* R. S. Bailey (UK); *Members:* G. Ajroldi (Italy); P. S. Allan (UK); V. Altstaedt (Germany); M. Bevis (UK); J. G. Bonner (UK); C. B. Bucknall (UK); A. Cervenka (Netherlands); D. Constantin (France); P. Covas (Portugal); J. E. Curry (USA); C. Dehennau (Belgium); M. J. Doyle (USA); A. Ghijssels (Netherlands); Y. Giraud (France); L. Glas (Belgium); W. Gleissle (Germany); A. Gray (UK); D. Groves (UK); B. Gunesin (USA); P. S. Hope (UK); M. Kozlowski (Poland); J. Lingaae-Jorgensen (Denmark); F. H. J. Maurer (Sweden); J. Meissner (Switzerland); G. Michler (Germany); D. R. Moore (UK); A. P. Plochocki (USA); S. Rober (Germany); J. C. Seferis (USA); S. S. Sternstein (USA); P. Szewczyk (Poland); S. Turner (UK); T. Vu-Khanh (Canada); J. L. White (USA); J. G. Williams (UK); H. G. Zachmann (Germany).

[†]EVOH = ethylene-vinyl alcohol copolymer; SMA = styrene-maleic anhydride copolymer

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference to the source along with use of the copyright symbol ©, the name IUPAC and the year of publication are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

A collaborative study of the structure and rheological properties of EVOH/SMA blends produced by reactive extrusion (Technical Report)

Synopsis

Blends of ethylene-vinyl alcohol copolymer (EVOH) and styrene-maleic anhydride copolymer (SMA) have been produced by reactive extrusion and characterised in terms of their rheology, phase morphology and the degree of covalent bonding interaction (ester linkages) between phases, as determined by FTIR.

Strongly synergistic behaviour in terms of viscosity and melt elasticity was seen in all blends, for low frequency dynamic and low shear rate capillary tests, the largest increases occurring in blends containing 50-60% EVOH. Finely dispersed droplet phase morphologies were seen in most of the blends, the minor phase forming the dispersed phase. However the blends containing 50-60% EVOH were co-continuous or partly co-continuous; it was also notable that the blends containing 60% EVOH exhibited a surprisingly low value of Melt Index. Evidence of covalent bonding was apparent in all blends, the highest interaction levels again being seen for the 50-60% EVOH blends, despite a very low anhydride/alcohol molar ratio (only 0.05). Increased mixer speed and vacuum venting during processing also improved reaction levels.

These findings suggest that the availability of reactive groups is restricted by the phase morphology of the blend during production. As a result, more reaction occurs at or near co-continuous phase compositions, where the surface area is maximised. The synergistic behaviour in viscosity and elasticity can be seen as consistent with the observed increased bonding levels, which causes more efficient stress transfer into the dispersed phase.

1. INTRODUCTION

The in-situ formation of covalent bonds between blend components during melt mixing, or reactive extrusion, is now well established as a technique for preparing novel materials, and a substantial body of literature exists. The driving force is usually the attainment of enhanced properties, which derive from the improved dispersion of, and adhesion to, a normally immiscible secondary blend component. Typical reactions include transesterification, and the products of amine-anhydride, amine-acid, oxazoline-acid and alcohol-isocyanate reactions.

Reactive processing involving bonding between anhydrides and amines has been extensively studied (references 1-8 for example). This is partly because this system forms the basis of commercial routes to toughening polyamides, but also because the imide linkage formed is readily identifiable using fourier transform infra red spectroscopy (FTIR). The present study focusses instead on reactive extrusion utilising bonding between anhydride and alcohol functionalities, which results in the formation of ester linkages. These are more difficult to quantify analytically, and the reaction is reported to be reversible at elevated temperatures.

Other workers (9-12) have found that the extent of reaction following reactive processing depends on the rheology of the blend components and on the mixer operating conditions. Furthermore, in reactive extrusion the phase morphology of the normally immiscible blend components and the extent to which the covalent bonding reaction occur are likely to be inter-related in a complex fashion. The particular objective of this work is to study this interdependence using a blend of commercially available polymers exhibiting anhydride and alcohol functionalities, namely styrene-maleic anhydride copolymers (SMA) and ethylene-vinyl alcohol copolymers (EVOH). Some aspects of this work have already been presented at IUPAC conferences (13,14).

A preliminary blending study was carried out by BP Chemicals using EVOH and maleic anhydride-grafted high density polyethylene (MAH-g-HDPE), in order to assess the feasibility of creating and

detecting ester linkages between phases. This is described in Section 2.4. All subsequent SMA/EVOH blends were prepared by Werner and Pfleiderer. Two types of mixer were used, a laboratory batch mixer and a laboratory twin screw compounder, and the effects both of blend composition and mixer operating conditions were explored. On-line rheological measurements were carried out during blend production. Capillary rheometry was carried out on the products by Enichem and Solvay, who also performed small strain dynamic frequency scans, and the stability of the products in oscillatory shear was assessed by Huls. The product microstructure was examined at Enichem and BP Chemicals using scanning electron microscopy (SEM). BP Chemicals also assessed the degree of chemical bonding using FTIR and solvent extraction techniques, and carried out melt index tests. ^{13}C NMR was performed by BASF.

2. EXPERIMENTS AND RESULTS

2.1 Materials

For the batch mixing experiments, and for the twin screw extrusion experiments to investigate effects of blend composition and operating conditions, SMA was supplied by Arco as Dylark 332 in the form water-clear pellets. This grade contained 14% (mole) maleic anhydride, and absorbs <0.1% water at ambient temperature. EVOH was supplied by DuPont as Selar OH3003, in the form of milky-white pellets; this grade contained 67% (mole) vinyl alcohol, and absorbs 6.7 - 8.6% water at ambient temperature.

Additional twin screw extrusion experiments were carried out to assess the effects of maleic anhydride functionality level and viscosity of the polystyrene phase, by diluting the blend components. The diluent polymers used for this were Sartomer 3000A, a low molecular weight SMA copolymer containing 20% (mole) maleic anhydride, which was supplied in powder form, and Arco Dylene 86, which is the (unfunctionalised) polystyrene precursor to Dylark 332.

All materials were pre-dried under vacuum at 90°C for a minimum of 2 hours before mixing and processing.

2.2 Production of preliminary blends in a batch mixer

Small samples were blended at Werner and Pfleiderer in a Haake M5000 torque rheometer with a Rheomix 600 mixing bowl and roller blades, in order to screen formulations and operating conditions. In most cases pre-mixed 60g samples were loaded directly to the bowl heated at 220°C and rotating at 100 rpm (*pre-mix*); however in some cases the SMA copolymer was added after the EVOH was already fluxed (*post-add*). The torque and temperature vs. time traces were recorded in order to observe reaction exotherms and any torque build due to crosslinking reactions. Mixtures were prepared with the loading ram down (*non vented*) and up (*vented*).

The findings for a series of blends containing up to 60 weight % EVOH are summarised in Table 1. The anhydride/alcohol molar ratio calculation is shown in the Appendix. For the pre-mixed blends, any reaction exotherm or torque was masked by melting of the blend components. Adding the SMA after the EVOH fluxed allowed the two melting peaks to be seen, followed by an exotherm and a strong torque build, corresponding to estimated viscosity increases of up to 370 Pa.s (15). The highest levels of reaction (as judged by torque increase) took place for the blends containing upwards of 50% EVOH, which had very low anhydride/alcohol molar ratios. High reaction also seemed to be favoured by post-addition of the SMA copolymer and by venting the mixer during the process. The blends showing strong reaction appeared to contain substantial gel which produced a cheesy look in pressed sheet.

Table 1 Summary of Haake batch mixing experiments on blends of SMA (Dylark 332) with EVOH (Selar OH 3003)

Weight % EVOH	Premix/ Post-add ?	Vented ?	anhydride/ alcohol molar ratio	Torque increase (mg)	Temp increase (°C)	Cycle time (min)	Product
2	Premix	Yes	3.83	0	0	12	Brittle
8	Premix	Yes	0.90	0	0	12	Brittle
20	Premix	Yes	0.31	0	0	12	Brittle
40	Premix	Yes	0.12	0	0	12	Rubbery
50	Premix	Yes	0.08	320	0	23	Cheesy
60	Premix	No	0.05	230	0	13	Cheesy
60	Post-add	Yes	0.05	1020	4	15	Cheesy
60	Post-add	Yes	0.05	1050	12	23	Cheesy

2.3 Production of blends in a continuous extruder

This was done at Werner and Pfeleiderer using a ZSK-30 co-rotating twin screw extruder, configured to vent gases and to measure melt viscosity on-line (Figure 1). Two series of runs were performed. In the first (6173) the effects of blend composition, operating conditions and vacuum venting were assessed, while in the second (6409) further samples were produced to investigate blend composition effects, and the effects of SMA anhydride level and viscosity. The samples distributed to programme participants for structural and rheological testing are summarised in Table 2.

For the first series (6173) feedstock was pre-dried before being fed with two gravimetric feed devices. The minor component (usually EVOH) was delivered by a Thayer PIC-168 II loss-in-weight vibratory feeder, while the major component (usually SMA) was fed from a K-Tron GF06 weigh belt feeder. The ZSK-30 extruder was configured at 38 diameters length with accommodation for downstream feeding of the SMA (so the hygroscopic EVOH could be vented before reaction), and for pre- and post-reaction zone vacuum venting of possible moisture by-products. In fact it was necessary to abandon downstream feeding of the SMA because of occasional feed port pluggage. The screw configuration gave a flow restricted plasticating zone and contained neutrally staggered discs in the reaction zone (Figure 2). In the second series (6409) pellet blends were mixed in a double cone blender prior to drying, and fed to the extruder using a K-Tron 4" loss-in-weight belt feeder. The Sartomer powder, when used, was not dried and was fed from a K-Tron T-20 loss-in-weight twin screw feeder. In this case the ZSK-30 extruder was configured as for series 6173, but was restricted to 35 diameters length (Figure 3) by shortening the discharge end by 1 barrel. In both series of runs barrel temperatures were in the region of 220°C, and screw speeds were in the range 150 - 180 rpm. Samples for testing were extruded as strands (2 hole die), water quenched and pelletised, and air dried.

The extruder was equipped with an on-line capillary rheometer (Göttfert Bypass Rheograph, capillary length 100 mm, diameter 5 mm). Figure 4 presents the steady shear viscosity of the blends at 13.5 s⁻¹ as a function of composition, combining results from both series. It is clear that a viscosity maximum is found at intermediate compositions. Estimates of the variance of shear viscosity (3 standard deviations) during steady operation gave low values similar to those for the base resins (<50 Pa.s) for all blends except the 50% EVOH blend, which gave 400 Pa.s. This material showed poor sample consistency, being locally very inhomogeneous and having a high gel content.

Table 2 Summary of ZSK-30 samples distributed to programme participants for structural and rheological testing

BLEND COMPOSITION	Series 1	Series 2	Comment
Effect of EVOH Level			
0 EVOH / 100 SMA(1)	6173/ 21	6409/ 1	
2 EVOH / 98 SMA(1)	6173/ 11		
8 EVOH / 92 SMA(1)	6173/ 10		
10 EVOH / 90 SMA(1)	6173/ 9		
20 EVOH / 80 SMA(1)	6173/ 8		
50 EVOH / 50 SMA(1)	6173/ 6	6409/ 6	
60 EVOH / 40 SMA(1)	6173/ 4	6409/ 4	
80 EVOH / 20 SMA(1)		6409/ 5	
90 EVOH / 10 SMA(1)		6409/ 7	
100 EVOH / 0 SMA(1)	6173/ 1	6409/ 3	
Effect of anhydride functionality (variable VR**)			
60 EVOH / 40 PS		6409/ 8	AAR* 0
60 EVOH / 40 SMA(1)		6409/ 4	AAR 0.05
60 EVOH / 40 SMA(2)		6409/ 11	AAR 0.07
Effect of PS Viscosity (AAR* constant = 0.05)			
60 EVOH / 28 SMA(2)/ 12 PS		6409/ 9	VR** 0.29
60 EVOH / 20 SMA(1)/ 14 SMA(2)/ 6 PS		6409/ 10	VR 0.90
60 EVOH / 40 SMA(1)		6409/ 4	VR 1.43

* AAR anhydride/alcohol molar ratio ** VR PS/EVOH viscosity ratio at 220°C, 13.5 s⁻¹

SMA(1) Dylark 332 SMA copolymer (14% mole anhydride)

SMA(2) Sartomer 3000A low MW SMA copolymer (20% mole anhydride)

PS Dylene 86 Polystyrene

EVOH Selar OH 3003 EVOH Copolymer (67% mole vinyl alcohol)

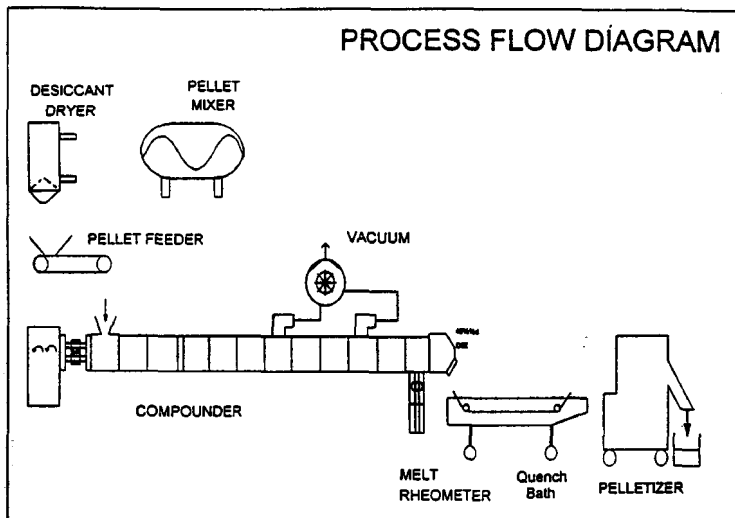
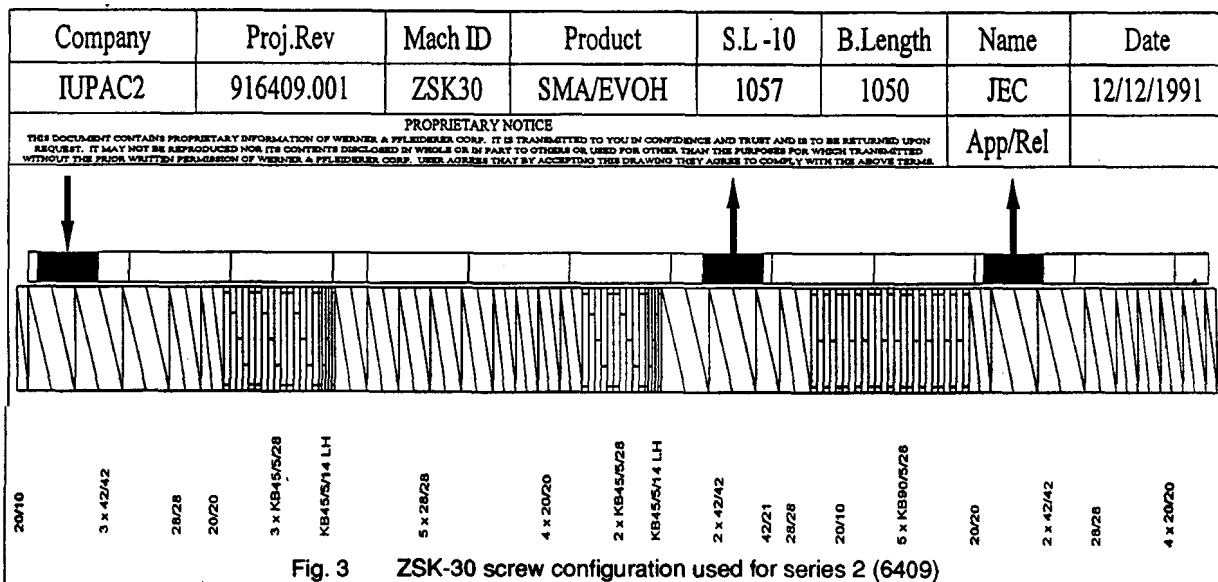
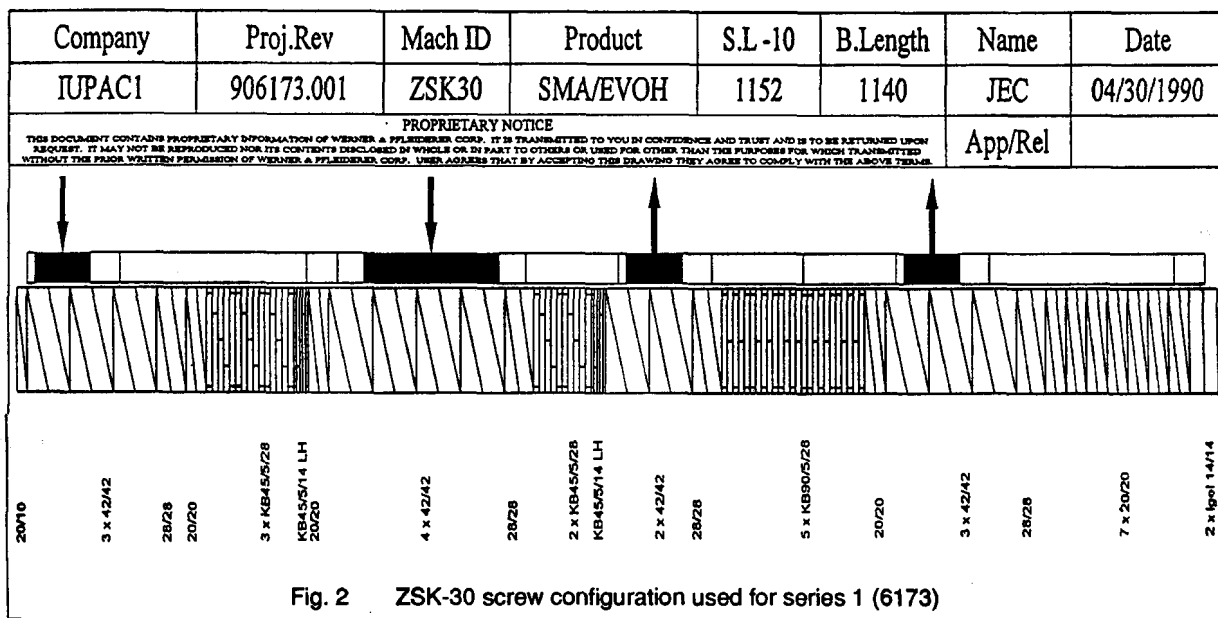


Fig. 1 Flow diagram for ZSK-30 extrusion compounding



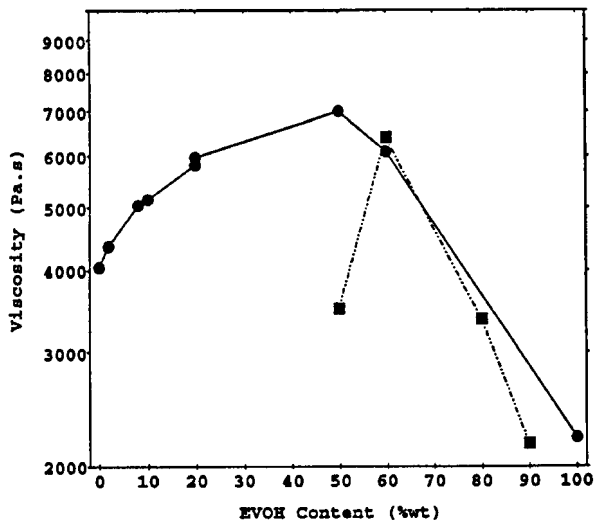


Fig. 4 On-line capillary rheometry results for EVOH/SMA blends produced on ZSK-30 twin screw extruder (shear rate 13.5 s^{-1} , temperature 200°C)
Legend: series 1 - circles; series 2 - squares

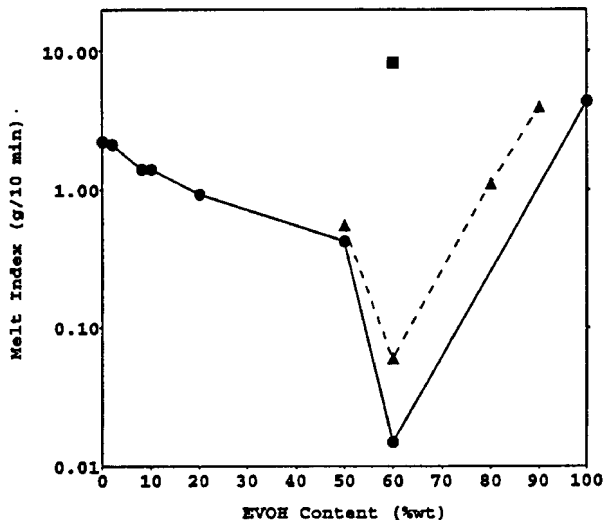


Fig. 5 Melt index measurements for blends produced on ZSK-30 twin screw extruder Legend: EVOH/SMA series 1 - circles; EVOH/SMA series 2 - triangles; EVOH/PS - square

Melt index measurements on the products (Figure 5) gave decreased values compared to the blend components. Values for the blend containing 60% EVOH were consistently surprisingly low; the reasons for this are not understood, although intractable gel, difficult to clear from the extruder, was formed at this composition. A blend of (unfunctionalised) polystyrene with 60% EVOH showed a much higher melt index, more in line with the blend component viscosities.

Figure 6 shows contour plots of on-line viscosity (η) against blend composition (%EVOH), vacuum level (VAC) and screw speed/throughput (RPBYRA), calculated using multiple regression on data from both series. These data suggest a strong second order effect of EVOH concentration, a negligible antagonistic effect of vacuum level, and a moderate synergistic effect of increasing screw speed or decreasing throughput.

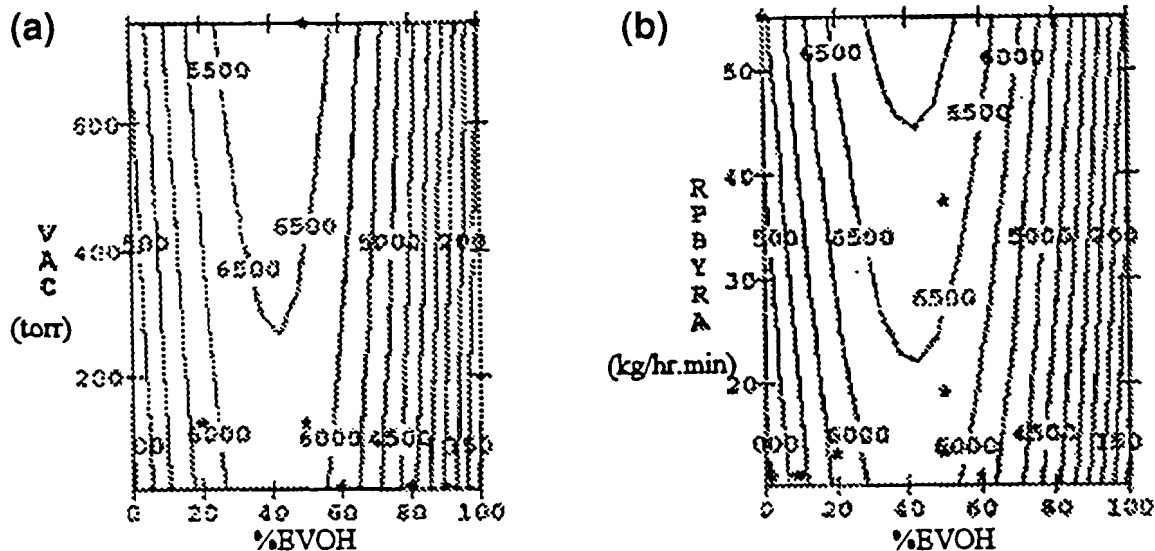


Fig. 6 On-line capillary rheometry contour plots, showing the effects of vacuum level and screw speed/throughput on viscosity (Pa.s) at various blend compositions (a) contours vs. %EVOH and applied vacuum (160 rpm, 9 kg/hr) (b) contours vs. %EVOH and rpm/rate (100 Torr, 100-450 rpm)

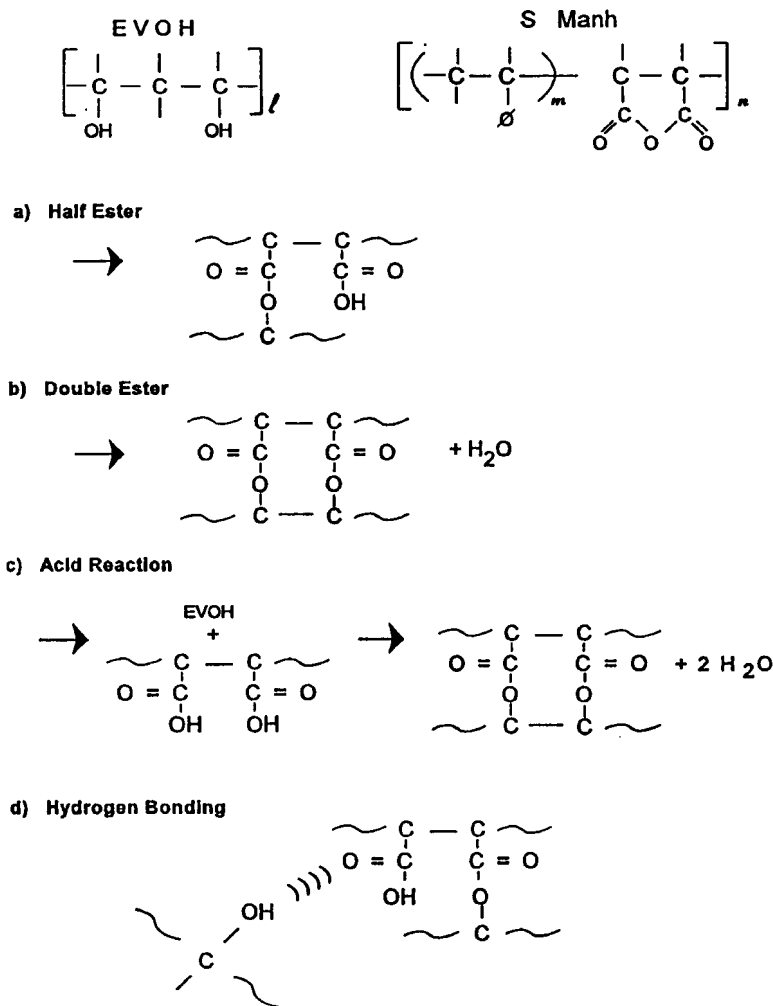


Fig. 7 Interfacial reactions between anhydrides and alcohols

2.4 Characterisation of chemical bonding interactions

During mixing EVOH and SMA, half ester/acid, double ester, and hydrogen bonding reactions are possible (Figure 7). The SMA can easily be hydrolysed to an acid by the presence of water, especially if absorbed in the EVOH feedstock. Acid-alcohol interfacial reactions are also possible by the condensation of water and formation of an ester crosslink. Sterically, the most probable reaction forms half ester/acid crosslinks.

To investigate the feasibility of reactive extrusion using an ester linkage, and of quantifying the level of bonding formed, a pilot study was performed by BP Chemicals in which an EVOH containing 56% (mole) vinyl alcohol was mixed in a Brabender Plasticorder with a maleic anhydride-grafted high density polyethylene (MAH-g-HDPE) containing less than 1% by weight maleic anhydride. A 50:50 mixture was mixed at 200°C for 10 minutes at 50 rpm under nitrogen. One possibility for this system is that carboxylic acid groups could be formed merely by hydrolysis of the anhydride. To check this a second set of samples was produced by heating both MAH-g-HDPE and the blend powder to 160°C for 4 hours under vacuum, to drive off any residual moisture and to regenerate any anhydrides which may have hydrolysed. Fourier transform infra-red (FTIR) spectroscopy was performed on thin films of these materials, and spectra are shown in Figure 8. Anhydride bands in the MAH-g-HDPE were much reduced in the blend, although bands attributed to carboxylic acid were present in both samples before heat treatment, suggesting that some hydrolysis had occurred. The acid carbonyl band in the MAH-g-HDPE was relatively narrow compared to the blend, suggesting increased hydrogen bonding in the blend. No ester carbonyl peak was seen (1735 cm⁻¹), but masking by the broad, overlapping carbonyl spectrum may have occurred. Judging by the much reduced acid carbonyl band in the MAH-g-HDPE after heat treatment, it seems that the anhydride was regenerated from any hydrolysed groups.

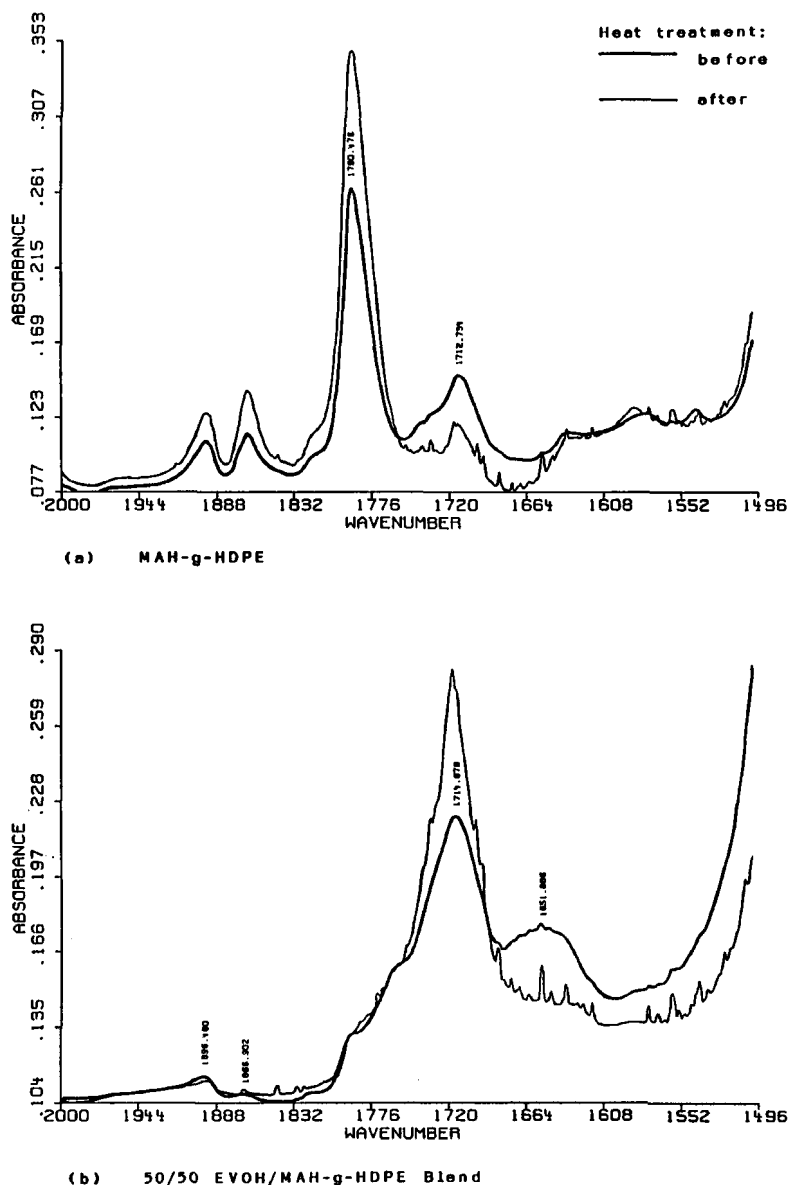


Fig. 8 FTIR spectra for (a) MAH-g-HDPE and (b) EVOH/MAH-g-HDPE blend, before and after heat treatment (4 hours at 160°C)

However no anhydride regeneration occurred for the blend after heat treatment; the acid carbonyl band appears strengthened, and no anhydride band was seen. It is unlikely that hydrogen bonding could have prevented anhydride regeneration, and so covalent ester bonding was assumed to have occurred in the blend.

FTIR was subsequently used to provide quantitative data on the level of bonding interaction in the SMA/EVOH blends. Samples were prepared by pressing at 220°C to give very thin films, and examined using a Nicolet 740 FTIR. The area of the carbonyl band at around 1720cm⁻¹ was measured, and a relative measure of the level of bonding interaction was obtained by dividing this area by the thickness of the film sample. The level of bonding as measured by FTIR is shown in Fig. 9. The bonding level passes through a maximum for blends containing in the region of 50 - 60% EVOH. No reaction was seen in a 60/40 EVOH/PS blend. The peak bonding level (at 60% EVOH) corresponds to an anhydride/alcohol molar ratio of around 0.05, whereas an anhydride/alcohol molar ratio of unity would correspond to a blend containing around 6% EVOH. This implies that the level of bonding achieved is primarily influenced by the mixing history and phase structure of the blends, rather than by stoichiometry considerations, and is quite consistent with the observation of higher viscosities noted earlier from the on-line rheometry measurements.

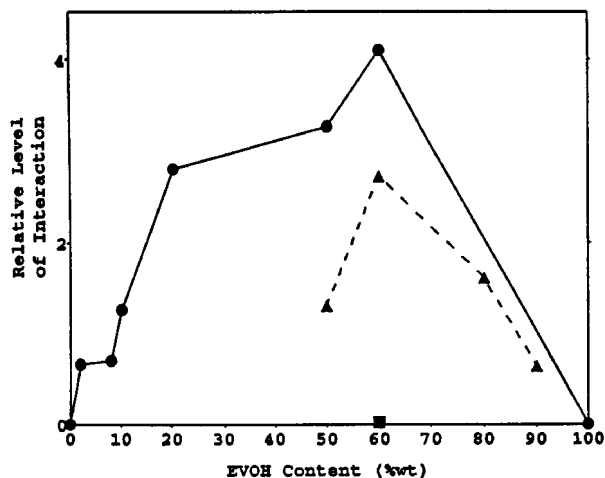


Table 3 Solvent extraction results on SMA/EVOH blends

Material	Weight % of total extracted	Weight % of PS/SMA extracted
EVOH	0	-
EVOH / SMA 50/50 (6409/6)	43	86
EVOH / SMA 60/40 (6409/4)	20	50
EVOH / SMA 80/20 (6409/5)	-1	-5
EVOH / SMA 90/10 (6409/7)	1	10
SMA	100	100
EVOH / PS 60/40 (6409/8)	40	100
PS	100	100

Fig. 9 Levels of ester bonding (by FTIR) in blends
 Legend: EVOH/SMA series 1 - circles; EVOH/SMA series 2 - triangles; EVOH/PS blend - square

To provide a second indicator of bonding level, a detailed investigation was carried out at BASF using ^{13}C solid state NMR on the blend components and on one blend (40% SMA + 60% EVOH). Spectra were recorded using "magic angle spinning" (5 kHz), dipolar decoupling (B_1 corresponding to 62.5 kHz) and in some cases cross polarisation. Measurements were run at 25 and 80°C on a Bruker CXP 300 and on a MSL 300 (^{13}C resonance at 75.47 MHz). ^1H ^{13}C NMR spectra are shown in Figure 10 for SMA, EVOH and a blend containing 60% by weight EVOH. The results are in agreement with previous literature data (17). The position, shape and intensity of the blend spectrum were a direct superposition of the components' spectra. Analysis of the blend spectrum gave no indication of chemical bonding between the alcohol and the anhydride, suggesting that much less than 1% of the alcohol groups could be taking part in esterification reactions. T_{rho} (H) relaxation times measured by the "proton prelock method" suggest that a large amount (around 50%) of the EVOH was situated at a distance of less than 1 nm from the SMA, and that the phase size of the EVOH was restricted.

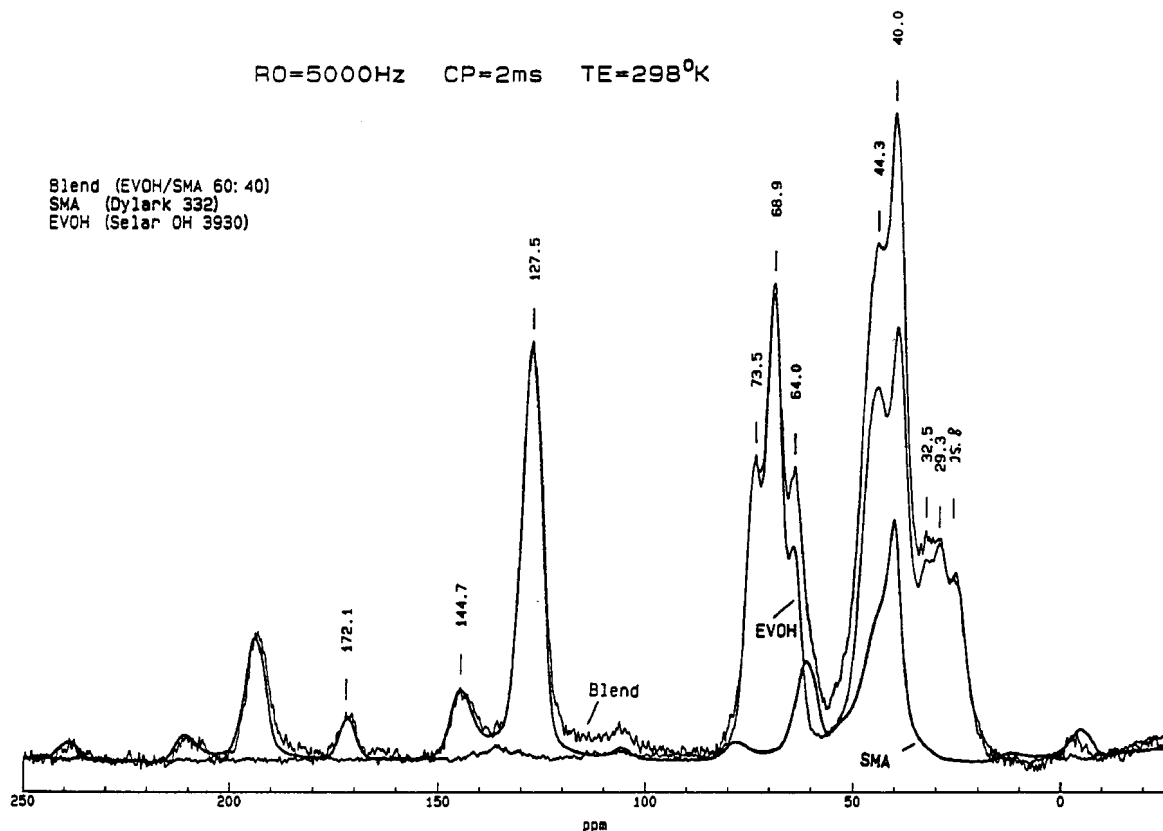


Fig. 10 ^{13}C NMR spectra of SMA, EVOH and blend containing 60% by weight EVOH

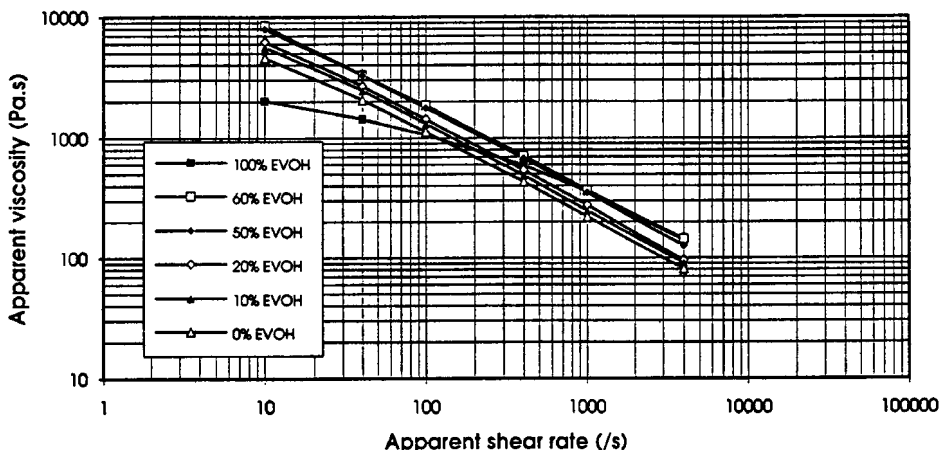


Fig. 11 Capillary rheometry data on SMA/EVOH blends: Effect of apparent shear rate on apparent viscosity

Finally, an indirect indication of bonding level was given by solvent extraction experiments on the blends, by refluxing in THF for 24 hours and recording the mass of material extracted (Table 3). For the EVOH/PS blend, all the PS was completely extracted even though it existed as discrete dispersed droplets (see phase morphology results below). In blends where SMA was in dispersed droplet form (80 and 90% EVOH) only small amounts were extracted, possibly as a result of bonding between the phases. However for the blends containing 50 and 60% EVOH, higher levels of SMA were extracted. This may reflect the increased access for solvent afforded by the co-continuous or partly co-continuous phase structures.

2.5 Rheological measurements

Capillary rheometry was carried out at Solvay and at Enichem. The Solvay data were measured at 220 °C on a Göttfert 2001, using a 12 mm diameter barrel and a flat entry die of radius 0.5 mm and L/R 40. No Bagley or Rabinowitsch correction was performed on these data, which are presented in Figure 11.

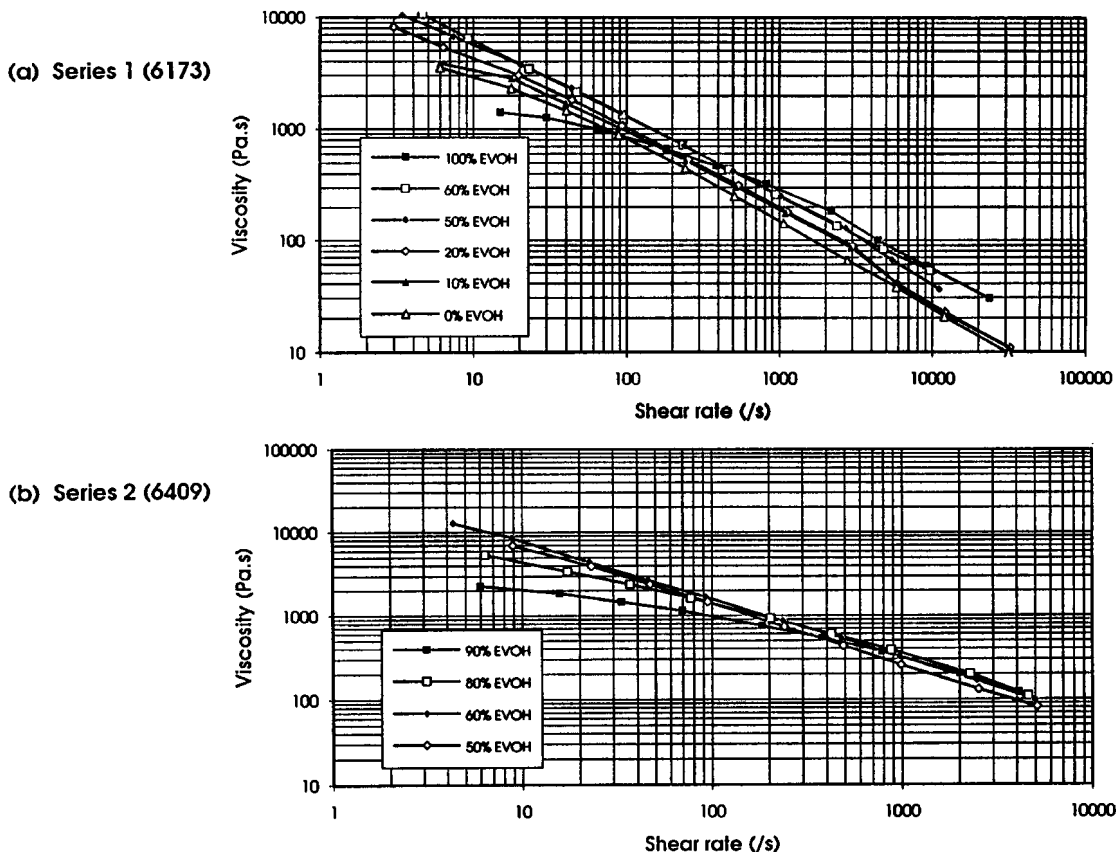


Fig. 12 Capillary rheometry data on SMA/EVOH blends: Effect of shear rate on viscosity (230°C)

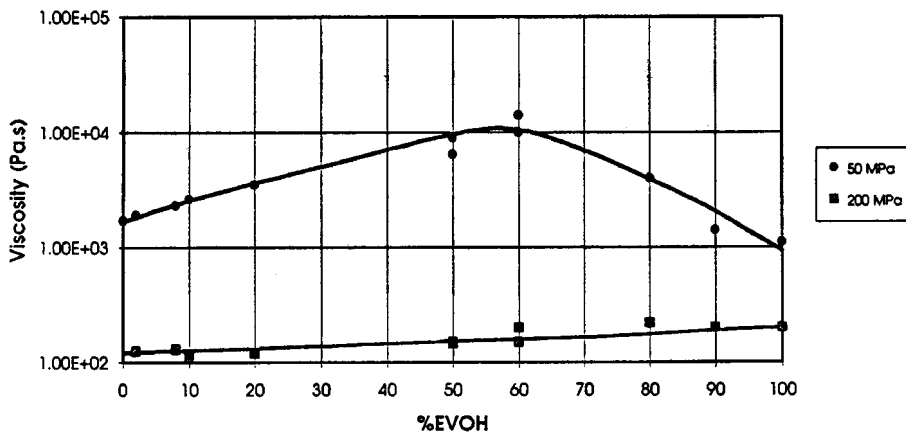
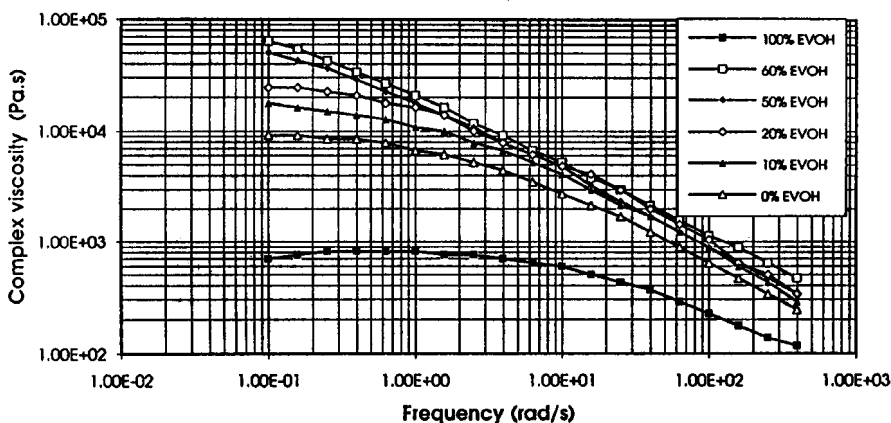


Fig. 13 Capillary rheometry data on SMA/EVOH blends: Effect of blend composition on viscosity at constant stress (230°C)

The Enichem data were obtained at 230°C using a Rosand twin-bore rheometer, using a flat entry die of radius 0.5 mm and L/R either 30 or 60. In this case a zero-length die was also used in the second barrel to directly measure die entry pressures, and data were both Bagley and Rabinowitsch corrected. Viscosity data are shown as functions of shear rate in Figure 12. The dependence of viscosity on blend composition, derived from the Enichem data, is shown at constant shear stress levels of 50 and 200 MPa in Figure 13. It is clear that while the viscosity obeys a linear mixing rule with blend composition at high stress levels, at low stress levels a significant increase in viscosity over and above that of either blend component is seen for intermediate compositions. The greatest viscosity synergy is seen for blends containing 50 - 60% EVOH. Comparisons at constant shear rate gave similar results. Although this was not specifically investigated, it is likely that the large rate dependence of viscosity for the blends is a result of melt structuring.

(a) Series 1 (6173)



(b) Series 2 (6409)

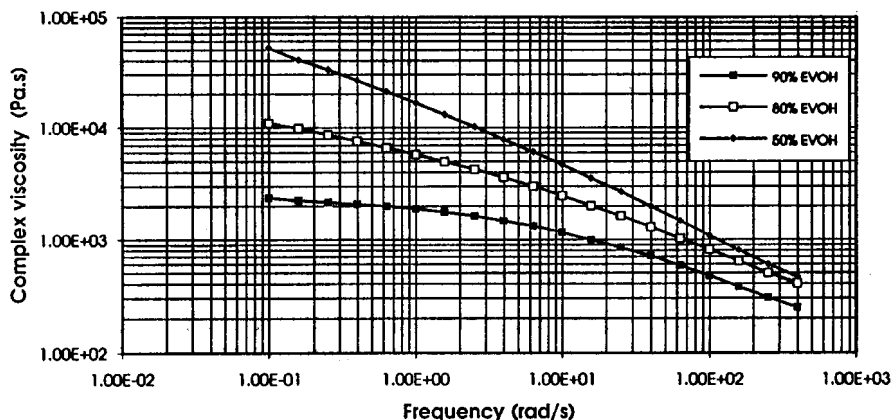


Fig. 14 Dynamic rheometry on SMA/EVOH blends: Effect of frequency on complex viscosity (220°C)

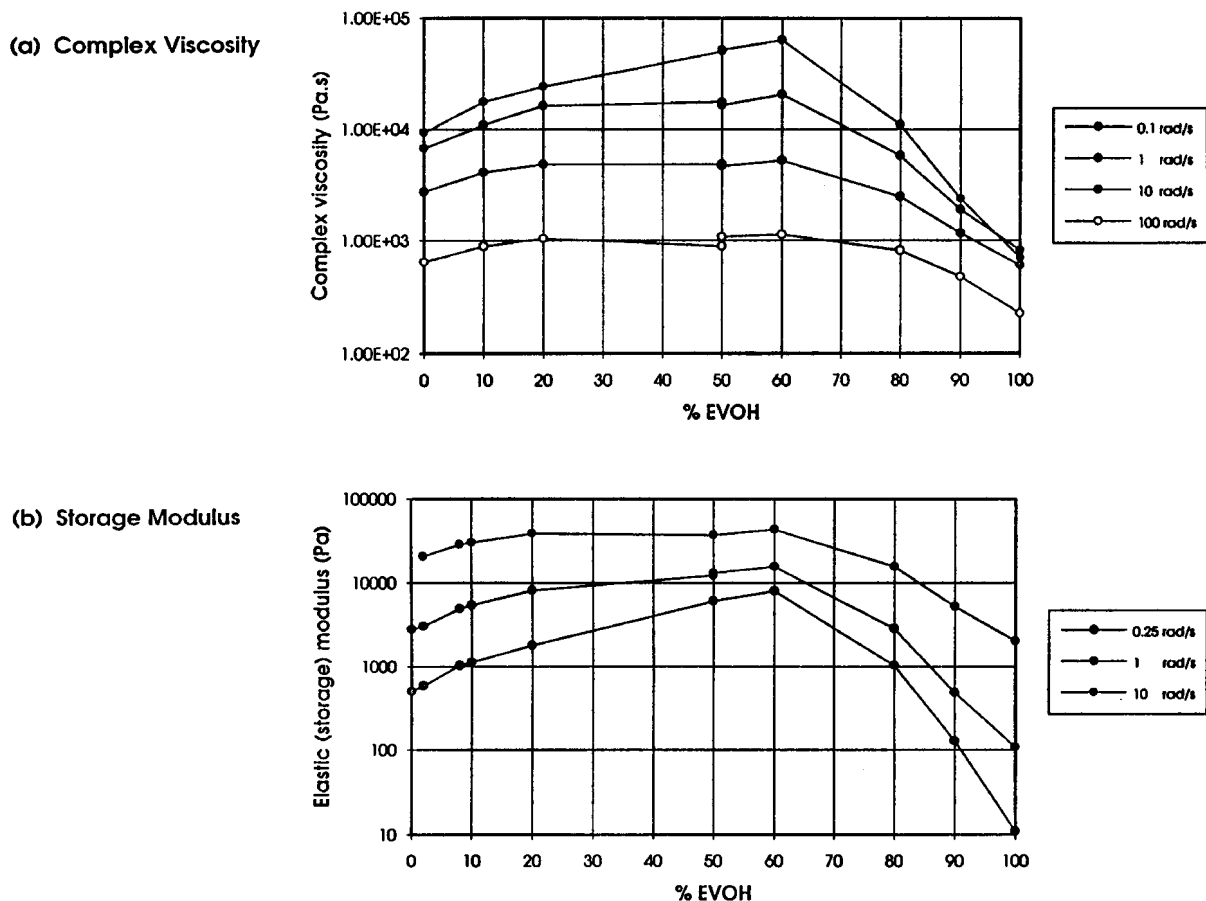


Fig. 15 Dynamic rheometry on SMA/EVOH blends: Effect of blend composition on complex viscosity and storage modulus (220°C)

Dynamic rheometry was carried out by Solvay, using sheet samples compression moulded at 210°C. Dynamic frequency scans were performed at 220°C on a Rheometrics-RDS system, using a 50mm diameter parallel plate geometry. A frequency range of 0.1 to 500 rad/s was covered at strains below 20%. Complex viscosity data are presented in Figure 14. Figure 15 shows the dependence of complex viscosity and storage modulus, measured at constant frequency, on blend composition. As in the capillary results, viscosity synergy is also seen with the greatest increases occurring for blends containing 50 - 60% EVOH. The same effect is also seen for storage modulus. In both cases the viscosity or modulus increases are greatest at low frequencies, suggesting that this synergistic behaviour probably best describes the equilibrium properties of the blends.

Measurements were also made by Hüls of the time dependence of the viscosities of the blend components and selected blends. This was done using a Rheometrics Mechanical Spectrometer RMS 800 using a 25mm diameter cone-and-plate geometry. All samples were dried for 8 hours at 70°C under vacuum and then measured at 220°C. The results are shown in Figure 16. A repetition of the frequency sweep after 30 minutes (Figure 16(a)) yielded an increase in viscosity for the EVOH (SELAR) and for the 60/40 blend, but not for the pure SMA (DYLARK). In a time sweep at constant frequency (Figure 16(b)) all EVOH-rich blends show a distinct increase in viscosity with time.

2.6 Characterisation of phase morphology

Scanning electron microscopy (SEM) was carried out on each blend to study their phase morphologies at BP Chemicals and Enichem. At BP Chemicals the samples were prepared by polishing using a microtome at ambient temperature; subsequently some of the samples were etched in either methanol or tetrahydrofuran (THF) for about 1 hour before being gold coated. At Enichem the samples were prepared by fracture in liquid nitrogen before gold coating.

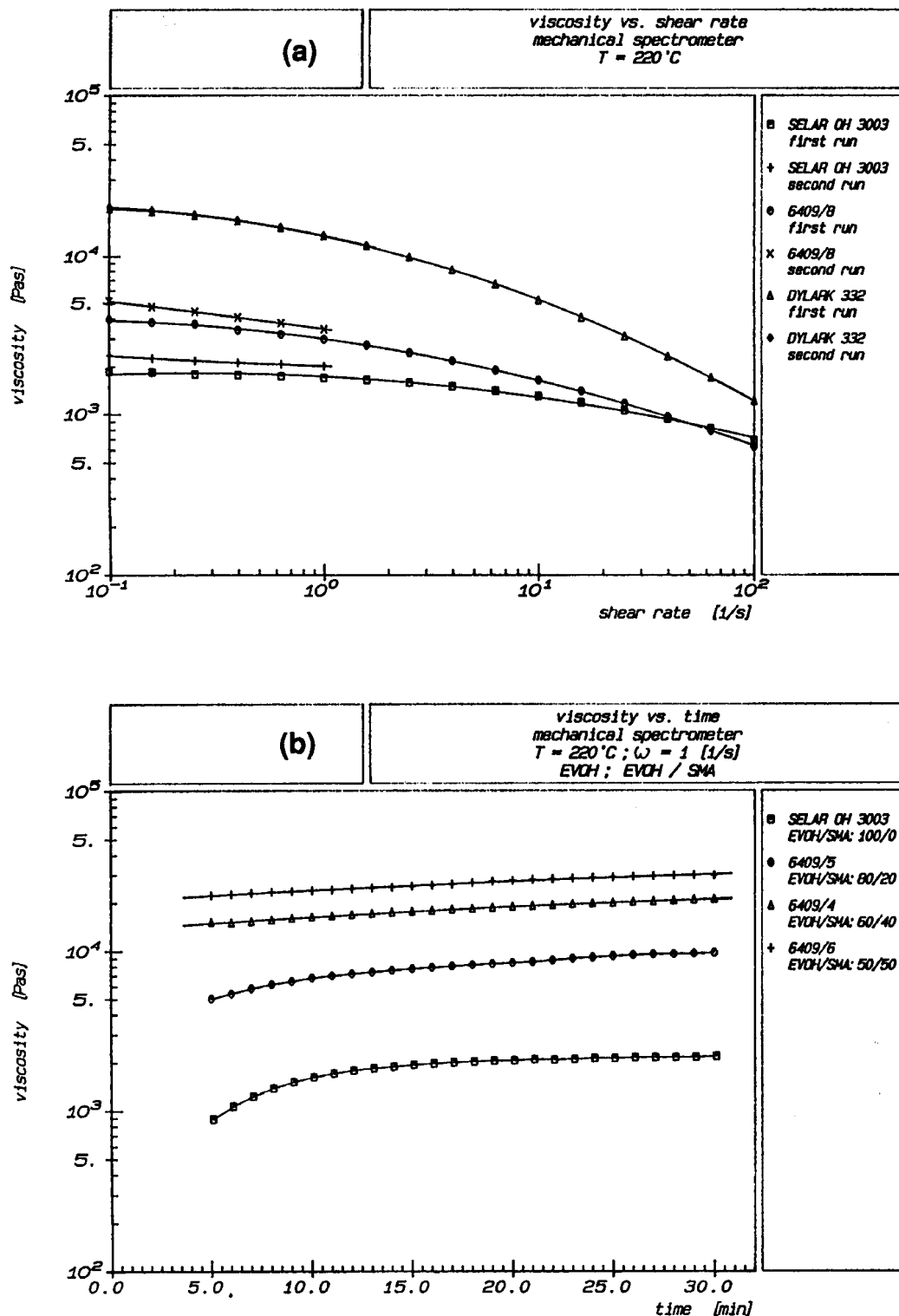
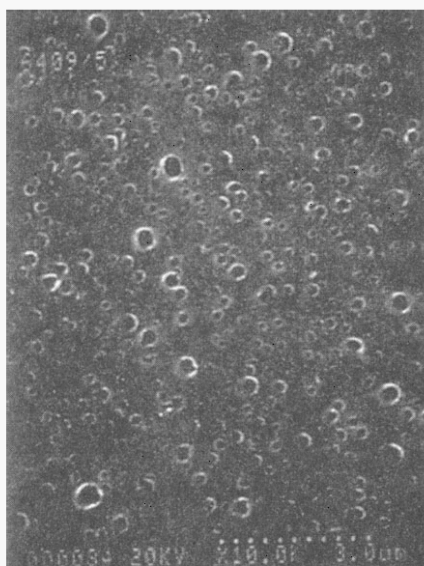
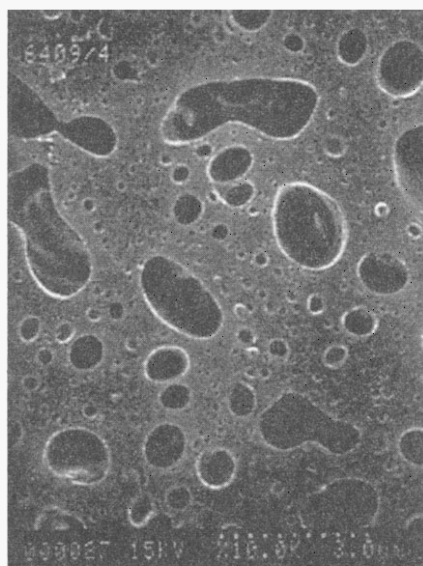


Fig. 16 Dynamic rheometry on SMA/EVOH blends: Time stability of complex viscosity (220°C) (a) repetition of frequency sweep after 30 minutes (b) time dependence of viscosity at $\omega=1$ rad/s

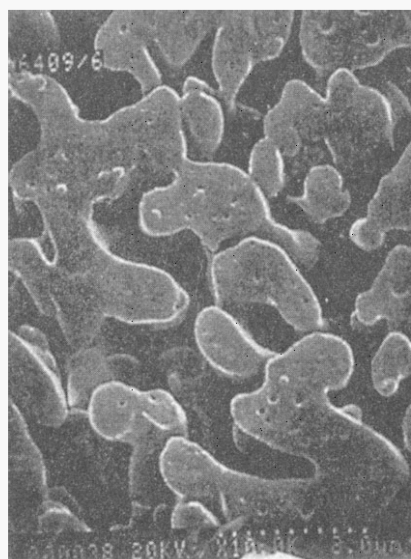
SEM micrographs revealed that the phase dispersion in the EVOH/SMA blends was very fine, and for all blends except those containing 50 or 60% EVOH the minor phase existed as dispersed droplets generally less than $2\mu\text{m}$ in diameter. However, the blends containing 50 and 60% EVOH both showed evidence of co-continuous (interpenetrating) phases (see SEM micrographs in Fig. 17). The blend containing 60% EVOH is compared with a blend in which the SMA has been replaced by PS in Fig. 18; the EVOH/PS blend was clearly coarser and did not show co-continuity.



(a)



(b)

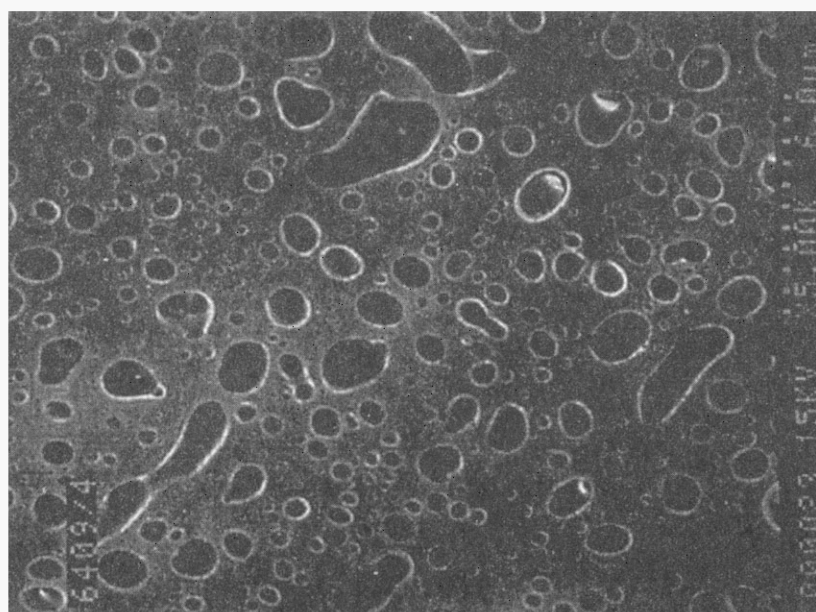


(c)

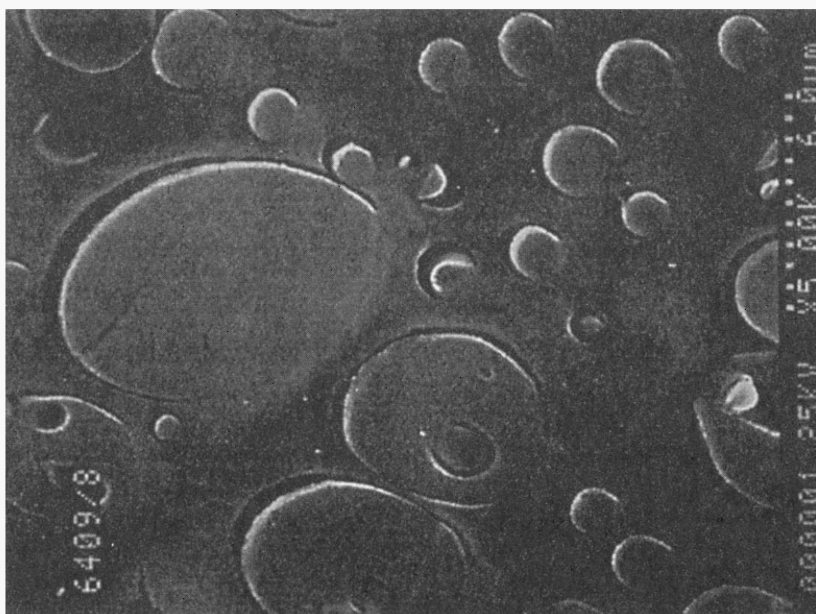
Fig. 17 SEM micrographs of SMA/EVOH blends
(a) 80% EVOH (b) 60% EVOH (c) 50% EVOH

3. DISCUSSION

Most previous studies of reactive processing involving anhydrides have focussed on blends with amines, where the imide linkage formed is readily identifiable using FTIR. For example, Scott and Macosko (5) solution blended SMA copolymers with amine-terminated butadiene-acrylonitrile copolymers and with nylon 11, both having amine functionality, and demonstrated the formation of cyclic imides, detected by infra red bands at 1771 and 1701 cm^{-1} . They also looked at interfacial reactions in bi-layer films. The kinetics of the reaction were shown to be strongly affected by molecular weight and temperature. Bourland et al. (7) studied reactions between SMA copolymers and C_{18} primary amines by solution mixing and by melt blending, and concluded that half amide/acid structures were rapidly formed, but that imide ring closure took longer (several minutes at 220°C). Venting to remove the water by-product was found to be advantageous. However, melt mixing diamine-terminated polybutadiene with SMA copolymer at 210°C caused crosslinking of the SMA copolymer, suggesting limited utility for difunctional reactants.



(b)



(a)

Fig. 18 SEM micrographs of 60% EVOH blends with (a) PS (b) SMA

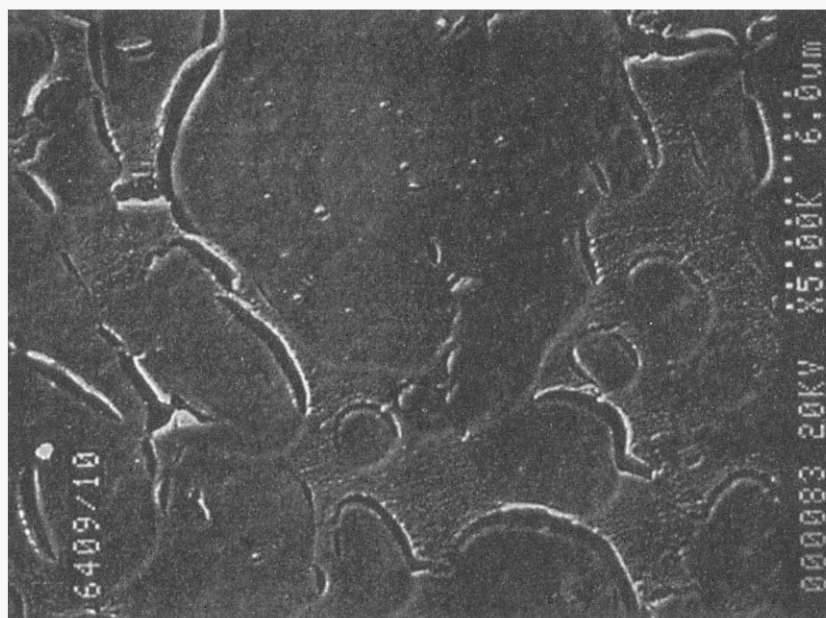
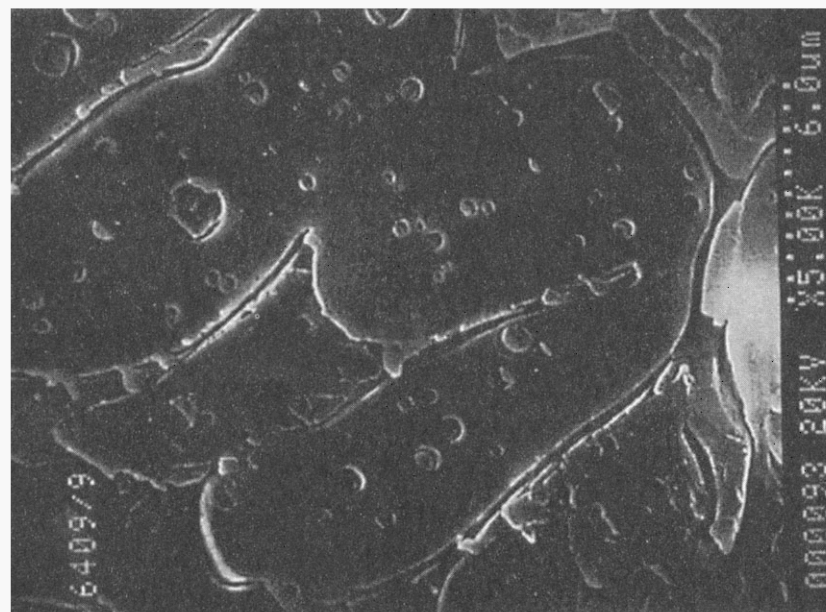
**(b)****(a)**

Fig. 19 SEM micrographs of multicomponent blends (a) 60% EVOH / 20% SMA(2) / 20% PS (b) 60% EVOH / 20% SMA(1) / 14% SMA(2) / 6% PS

Bourland also investigated esterification reactions, in which melt blends of an oligomeric polyTHF diol with SMA copolymer gave ready formation of half ester/acid structures at low reaction temperatures. Although no adverse crosslinking reactions were found, the half acid/ester structures reverted to anhydride during extrusion at elevated temperatures, again restricting utility for reactive processing applications. This reversibility has also been claimed in preceding patents. However, melt blending studies by Lambla et al. (16) have shown that stable irreversible ester linkages can be formed from mixtures of SMA copolymers and oligomeric mono or polyhydroxylic reagents. In the current study on SMA/EVOH blends it appears from the FTIR evidence that the ester linkages formed were stable and irreversible. This may reflect the relative inaccessibility of the ester linkage sites to moisture ingress, in comparison to the situation in more mobile solution-formed blends.

Taking into account the strong synergistic effects in melt viscosity and elasticity, the existence of co-continuous phase morphologies in blends containing 50 - 60% EVOH, and the relatively high levels of bonding seen in blends of intermediate composition, it seems likely that the microstructure and the bonding levels are related strongly to the rheology and the dynamics of the mixing process. The availability of reactive groups appears to be restricted by the phase morphology of the blend during production, resulting in the occurrence of more reaction at or near co-continuous phase compositions, where the surface area is maximised.

Some experiments were specifically performed to investigate effects of changing functionality level and viscosity ratio of blend components, based on a composition containing 60 % by weight EVOH, is summarised in Table 2. The anhydride level was varied by using different SMA grades and a PS control, although it is clear that the viscosity of the PS/SMA component also varied somewhat. To vary the viscosity ratio of the blend components the viscosity of the PS/SMA phase was adjusted, maintaining the anhydride functionality level, by using 3 and 4 component blends. Blend viscosities* and relative levels of bonding are summarised in Tables 4 and 5. Apart from the blend containing PS alone as the second component (6409/8), which of course gave no interaction, the rest of the results suggest that both the viscosity of the blend and the level of interaction are dominated by the viscosity of the SMA phase rather than by the level of MAH functionality. This is consistent with the view that the phase morphology governs the level of bonding in the blends, and not *vice versa*. However caution is needed in view of the complex phase structures of the multi-component blends (Figure 19).

Table 4 Effect of anhydride functionality level on blend viscosity and interfacial bonding level for 60% EVOH blends

Blend	Anhydride/alcohol molar ratio	Blend viscosity at 230°C, 20 s ⁻¹ (Pa.s)	Relative level of interaction (FTIR)
6409/ 8	0	1000	0
6409/ 4	0.05	6000	4.2
6409/ 11	0.07	700	1.3

Table 5 Effect of component viscosity ratio on blend viscosity and interfacial bonding level for 60% EVOH blends

Blend	(SMA/PS)/EVOH viscosity ratio at 220°C, 13.5 s ⁻¹	Blend viscosity at 230°C, 20 s ⁻¹ (Pa.s)	Relative level of interaction (FTIR)
6409/ 9	0.29	1300	1.2
6409/ 10	0.90	3000	2.7
6409/ 4	1.43	6000	4.2

4. CONCLUSIONS

1. At intermediate compositions, SMA/EVOH blends show strong synergy in equilibrium viscosity and modulus.
2. The blends exhibit finely dispersed droplet morphologies, which coarsen and show evidence of co-continuity at compositions containing 50 - 60% EVOH.

3. Covalent bonding was detected by FTIR spectroscopy in all blends, with the highest levels seen for the 50 - 60% EVOH blends, despite very low anhydride/alcohol molar ratios (around 0.05) at these compositions. This suggests that the availability of reactive groups during blend production is restricted by the mixture state of the developing blend morphology, and that this rather than the overall molar ratio of reactive groups determines the degree of bonding achieved.
4. Highly reacted product is also favoured by the use of high mixer shaft speeds and the application of vacuum to remove reaction products during blend preparation.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the contributions of the other participants in this study, namely C. Dehennau (Solvay, capillary and dynamic rheometry), D. Constantin (Enichem, capillary rheometry and microscopy), R. Voelkel (BASF, ¹³C NMR), and S. Rober (Huls, dynamic rheometry).

6. REFERENCES

1. R.W. Rees, *Polymer Preprints*, **14**, 796 (1973).
2. M. Raetzsch and V. Phien, *Faserforsch Textiltech*, **27**, 357 (1976).
3. S. Cartasegna and W. Heider, *Gummi, Fasern, Kunststoffe*, **41**, 110 (1988).
4. J.C. Angola, Y. Fujita, T. Sakai and T. Inoue, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 807 (1988).
5. C.E. Scott and C.W. Macosko, *Polymer Preprints*, **29**, 561 (1988).
6. S.D. Sjoerdsma, *Polymer communications*, **30**, 106 (1989).
7. L.G. Bourland, M.E. London and T.A. Cooper, *Seminar on Reactive Processing - Practice and Possibilities*, RAPRA, UK, 1989.
8. B.K. Kim and S.J. Park, *J. Appl. Polym. Sci.*, **43**, 357 (1991).
9. O. Chang, S.P. McCarthy and N.R. Schott, *Proc. SPE ANTEC '89*, 1824 (1989).
10. J. Curry and P. Anderson, *Proc. SPE ANTEC '90*, 1938 (1990).
11. G. Serpe, J. Jarrin and F. Dawans, *Polymer Eng. Sci.*, **30**, 553 (1990).
12. C. Maier, M. Lambla and D. Bigio, *Proc. SPE ANTEC '94*, 123 (1994).
13. P.S. Hope, J.G. Bonner and J. Curry, *Proc. 34th IUPAC International Symposium on Macromolecules*, Prague (1992).
14. P.S. Hope, J.G. Bonner and J.E. Curry, *Proc. 35th IUPAC International Symposium on Macromolecules*, Akron (1994).
15. J. Goodrich and R.S. Porter, *Polym. Eng. Sci.* **7**, 45 (1967).
16. M. Lambla, A. Killis and H. Magnin, *Europ. Polym. J.*, **15**, 489 (1979).
17. H. Ketels, J. deHaan, A. Aerdtts and G. van der Velden, *Polymer*, **31**, 1419 (1990).

Appendix: Calculation of Reactant Molar Ratios

Dylark 332 SMA contains 14% (mole) maleic anhydride of molar mass 98g, and 86% (mole) styrene of molar mass 104g, giving a molar mass of $14 \times 98 + 86 \times 104 = 10316\text{g}$ per 100 repeat units. Weight fraction maleic anhydride in Dylark 332 is therefore $14 \times 98 / 10316 = 0.133$.

Selar OH 3003 EVOH contains 68% (mole) vinyl alcohol of molar mass 44g, and 32% (mole) ethylene of molar mass 28g, giving a molar mass of $68 \times 44 + 32 \times 28 = 3888\text{g}$ per 100 repeat units. Weight fraction vinyl alcohol in Selar OH 3003 is therefore $68 \times 44 / 3888 = 0.770$.

For a 100g blend containing weight fraction Φ of Selar OH 3003, the weight fraction maleic anhydride is $0.133 \times (1 - \Phi)$, giving $0.133 \times (1 - \Phi) / 98$ moles. Similarly the blend will contain $0.770 \times \Phi / 44$ moles of vinyl alcohol. The anhydride /alcohol molar ratio is therefore

$$[0.133 \times (1 - \Phi) \times 44] / [0.770 \times \Phi \times 98]$$

or $0.078 \times (1 - \Phi) / \Phi$