

An investigation of the potential of ethylene vinyl acetate/polyethylene blends for use in recyclable high voltage cable insulation systems

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Abstract Ethylene vinyl acetate (EVA) co-polymers can potentially provide novel materials for inclusion into extruded high voltage cable systems, providing a degree of electrical conductivity whilst avoiding the dispersion problems associated with conventional particulate fillers or conducting polymers. Although a degree of conductivity can decrease the electrical breakdown performance, it can help to suppress the development of space charge and increase the tree initiation voltage leading to enhanced dielectric properties. In addition, novel two phase morphologies can be formulated leading to the ability to control key thermal and mechanical properties and the ability to tailor these to suit the application. In addition, one of the problems with conventional cross-linked polyethylene (XLPE) is that it cannot easily be recycled; therefore, in this time of increasing environmental awareness, it is prudent to begin investigations into alternative recyclable materials to replace XLPE in extruded cables for the medium to long term. The current article focuses on the crystallisation behaviour, morphology, mechanical and dielectric properties of a range of polymeric insulation systems based on an EVA co-polymer together with a high density polyethylene (HDPE) component. The morphology was controlled by choosing co-polymers containing different vinyl acetate contents together with appropriate crystallisation routes. The relationships between the morphology and the mechanical and dielectric properties were explored. Blends containing a low vinyl acetate content co-polymer combined with HDPE have significant potential to replace XLPE in cable systems and have the

advantage of being easily recycled at the end of their service life.

Introduction

Ethylene vinyl acetate (EVA) co-polymers have been widely available for several decades and being technologically useful materials, they have received considerable attention in the literature. Early measurements [1] indicate an improved electrical breakdown performance at cryogenic temperatures is possible in EVA co-polymers high in vinyl acetate (VA) content. Despite their increased conductivity [2], the presence of an EVA co-polymer in blends with low density polyethylene (LDPE) reduces the number of deep traps and increases the number of shallow traps, this serves to reduce overall space charge accumulation leading to a useful increase in the tree initiation voltage [3]. This is supported by later work [4] where pulsed electro-acoustic measurements indicate that unusually, the dominant charge carriers in EVA co-polymers are positive holes; furthermore, accumulated space charge was reduced in the EVA material compared to the polyethylene (PE), whilst blends of PE with EVA had intermediate properties. Tanaka and Uchiumi [5] also reports improved space charge dissipation in a series of LDPE/EVA laminates, possibly resulting from increased conductivity wrought by the EVA component. Mobility of charge carriers was also considered [6] where for the first time charge ‘packets’ of positive carriers were observed directly. By contrast Guoxiong and Jianfei [7] indicates that the AC breakdown strength of EVA is reduced from that of PE but that of PE/EVA composites is significantly improved at cryogenic temperatures. The corresponding DC breakdown data (available only at cryogenic

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temperatures) also appear to indicate a lower breakdown strength is associated with EVA co-polymers. AC breakdown tests of EVA/linear low density (LLDPE) composites at higher temperatures [8] also indicate that EVA performs worse than LLDPE but that the poor breakdown performance of EVA can be significantly improved by blending with LLDPE.

Henderson [9] provides a useful review of the merits of EVA co-polymers; compared to conventional PE, EVA co-polymers offer improved elasticity, improved optical clarity, improved gas permeability and higher environmental stress crack resistance [10] at the expense of a reduced melting point. In addition, the polar VA group leads to better compatibility with polar polymers and fillers but with a higher dielectric loss factor [11]. The effect of VA content was studied [12] whilst VA content does not appear to affect the glass transition temperature, a reduction in melting point and crystallinity is reported as well as a loss of spherulitic structure at high VA contents, a result that concurs with other studies [13]. EVA co-polymers can be readily cross-linked by DCP (Dicumylperoxide) [14], however, it was reported that moderate cross-linking made less difference to the mechanical properties than varying the VA content.

In an attempt to improve the intrinsic properties of EVA co-polymers and to provide useful electrically insulating composites, blends with a wide range of other polymers have also been studied. In blends of EVA with nitrile rubber [15], the minority component is dispersed within broadly spherical domains in a matrix of the majority component with a co-continuous morphology reported in 40–60% blends. The mechanical properties are reported to take intermediate values between those of the components. In blends of EVA with paraffin wax [16], it was found that the VA content controlled strongly the degree of phase separation; blends with an EVA co-polymer containing 3% VA content were miscible, whereas others exhibited increasing degrees of phase separation with increasing VA content. Blends with polypropylene (PP) are considered by Maciel et al. [17] and similar two phase morphologies are reported, the mechanical modulus increases with PP content (the more rigid component in this case). A more rigorous study of PP/EVA blends by Ramirez-Vargas et al. [18] revealed spherulites of iPP could form in a matrix of EVA (28% VA content) provided that the EVA content was not too high and demonstrated that mechanical properties could be controlled by suitable PP/EVA ratio. Similar two phase textures in LDPE/EVA blends are also reported by Suh et al. [4], Na et al. [19], Faker et al. [20] and in LLDPE/EVA blends by Wu et al. [21], the latter three publications indicate that control of mechanical properties is obtainable in the blend systems. Recently Li et al. [22] showed that the phase separation between the

LDPE and EVA phase could be increased by extended annealing in the melt phase.

An analogous mechanical and morphological behaviour has also been reported in high density polyethylene (HDPE) blends [23–25]. Despite the general similarities between LDPE/EVA and HDPE/EVA systems in terms of mechanical and morphological behaviour, Khonakdar et al. [26] demonstrated that LDPE rather than HDPE offered better compatibility with EVA co-polymers and smaller domain sizes were reported in the former system. Blends with polystyrene were considered by Prochazka et al. [27] and two phase morphologies were reported, again it was possible to control the mechanical properties of the resulting blends. Blends with polyamide were considered by Bhattacharyya et al. [28] and control of mechanical properties by appropriate blend ratio was again demonstrated; for small EVA contents dispersed ‘particles’ of EVA were reported, whereas larger domains giving way to a co-continuous morphology were reported for higher EVA contents. Finally, the role of nanofillers has also been investigated [29], the addition of small amounts of clay (2–8 wt%) has been reported to enhance the mechanical, thermal and swelling properties and improve the fire retardancy of the blends.

In all of the above studies two phase morphologies are the usual result of blending EVA co-polymers with conventional, non-polar semi-crystalline polymers. Nevertheless, Cassagnau and Michel [30] demonstrate improved dispersion is possible by controlling the temperature and mechanical shear during the mixing phase. Single phase morphologies are possible either by using EVA as a compatibiliser between two incompatible polymers [31, 32] or by blending with compatible resins. In a series of ‘Novalac’ (phenol–formaldehyde resin)/EVA blends [33] single phase morphologies were obtainable over a wide compositional range, this was attributed to the carbonyl groups of EVA bonding with the hydroxyl groups in the resin.

Ethylene vinyl acetate co-polymers have also been found useful to prepare conducting composites, either by use of a filler or a conducting polymer, we will only consider a few examples here. In blends with carbon black [34], it was found that the mechanical properties and conductivity could be changed by altering the carbon black content or the molecular weight of the EVA co-polymer. Similar results were reported in tertiary blends by Katada et al. [35], such systems, by virtue of the polar EVA component, offer improved control of conductivity compared to conventional carbon black filled polymer blends. Polyaniline/EVA blends were considered by Barra et al. [36, 37] and control of electrical conductivity was possible by varying the blend ratio, VA content (higher VA gave better dispersion of the polyaniline) and

through appropriate treatment good dispersion of the conducting ‘inclusions’ in the EVA matrix was possible. Tertiary blends of Pani/EVA/LDPE were considered by Zhang et al. [38] and again control of conductivity of the resulting blends was demonstrated; such blends could find practical use in electrostatic shielding applications [39].

Whilst the technological applications of EVA co-polymers are clearly vast and diverse, EVA co-polymers can provide novel new ways of formulating cable insulation systems with the potential to reduce incipient space charge formation leading to increased treeing resistance. This, coupled with their biodegradability [40], makes them potential candidates for new, enhanced recyclable cable insulation systems. In addition, blending offers a means whereby the electrical, thermal and mechanical properties can be precisely controlled and designed for the application.

With this application in mind, a number of studies have recently been performed to assess the suitability of EVA-based systems for cable applications. Gherbaz and coworkers [41] considered tertiary HDPE/LDPE/EVA blends rich in the PE component and demonstrated two phase morphologies, crucially, the presence of a minor amount of EVA did not significantly degrade the electrical properties. Nevertheless, in order to provide for enhanced treeing resistance a high VA content is preferred [1, 3], in blends this translates to systems rich in the EVA component. With this in mind, tertiary systems with high EVA content have also been considered [42] but unfortunately it was noted that the presence of the EVA degrades the electrical breakdown strength of the composite as reported elsewhere [7, 8]. Nevertheless it has been shown earlier in a series of LDPE/HDPE blends that HDPE can be used to give enhanced electrical breakdown performance given appropriate crystallisation and sufficient levels of HDPE [43]. In a later study, this was also found to apply over a variety of electrically ‘weak’ matrix materials [44] and blending EVA with HDPE might thereby provide a way to mitigate the observed deleterious effects of EVA in blends rich in this component [8].

In this publication, we continue our investigations of blends rich in EVA content with a view to designing materials for future enhanced recyclable cable systems. First, we consider the thermal, morphological, mechanical and electrical properties of a range of EVA co-polymers with varying VA content. Using these materials, a range of HDPE/EVA blends were then prepared and the ability of HDPE to improve the properties of the blends was considered. Finally, the properties of the blends were considered and compared to those of conventional cross-linked polyethylene (XLPE) and their merits and drawbacks were discussed.

Experimental

Materials and blending

Six starting materials were used in these investigations as summarised in Table 1, the GPC data shown being the average of two tests, a commercial LDPE (Exxon LD100BW), a commercial HDPE (BP, Rigidex HD5813) and four EVA co-polymers ranging in VA content from 9 to 40 mol.%. For convenience, the shortened designations shown in Table 1 will be used throughout.

From these materials, five blends with a fixed 20/80 HDPE/LDPE composition were prepared as summarised in Table 2; this composition was chosen in order to maximise any enhancing effect of the HDPE component [43]. All five blends were prepared by solution blending [41–44] as follows. The required amounts of the two blend components were carefully weighed out using a digital balance (accuracy ± 0.01 g) to a total mass of 5 g. This material was then placed into 200 mL of xylene (99% mixed isomers, Sigma–Aldrich Chem. Co.) in a round bottom flask attached to a water filled condenser. The mixture was then boiled under constant stirring. Meanwhile ~ 300 mL of methanol was placed into a large beaker and cooled to ~ 4 °C in a refrigerator. After 20 min of boiling, the xylene/polymer mixture was immediately stirred into the methanol inducing immediate precipitation. After cooling, the mixture was filtered over

Table 1 Base materials used in these investigations

Designation	Trade name	Mw (g/mol)	Mn (g/mol)	Mw/ Mn
LDPE	Exxon LD100BW	178,000	20,800	8.6
EVA09	DuPont Elvax 750	204,500	16,150	12.7
EVA20	DuPont Elvax 450	104,000	15,900	6.5
EVA33	Unknown ^a	66,800	18,150	3.7
EVA40	DuPont Elvax 40W	63,900	17,050	3.7
HDPE	BP Rigidex HD5813	55,700	15,900	3.5

^a This material was sourced from Sigma–Aldrich Chemical company under their stock code 346918

Table 2 Blends used in these investigations

Designation	Composition
Blend A	20% HDPE in LDPE
Blend B	20% HDPE in EVA09
Blend C	20% HDPE in EVA20
Blend D	20% HDPE in EVA33
Blend E	20% HDPE in EVA40

medium grade filter paper and then dried for ~ 48 h to constant mass in a drying cabinet vented externally. The material was finally degassed under dynamic vacuum for 1 h at 150°C in aluminium trays.

Films of 40 mm diameter and nominal thickness $60\ \mu\text{m}$ were prepared between aluminium foil disks using a Grasby Specac 25.011 press with constant thickness film maker accessory maintained at 150°C . Plaques of nominal thickness 1.7 mm and 10 cm square were prepared using a three part aluminium mould and a hydraulic workshop press (model PRM 12) with heated platens maintained at 150°C , the mould being similarly lined with aluminium foil to prevent the polymer from sticking.

The thermal treatment was identical for both sets of samples; after loading the samples into the appropriate mould and allowing ~ 2 min for the polymer to melt, the pressure was increased to ~ 3 Ton and the polymer was then allowed to relax for 5 min. A subset of samples was then quenched directly into cold water at $\sim 20^\circ\text{C}$ and the rest were immediately transferred to a temperature-controlled oil bath for isothermal crystallization. For the latter sample set, a crystallisation temperature of 117°C was chosen to represent the midrange of the available isothermal conditions for the HDPE component and to maximise its enhancing effect on the AC breakdown strength [44]. Whilst parallel direct measurements of crystallisation using a hotstage and microscope showed that 10 min is enough to ensure complete crystallisation of the HDPE component [43] an hour was allowed before subsequent quenching into cold water. Following quenching or isothermal crystallisation, the foils were removed and the samples washed in distilled water and then dried under dynamic vacuum for 25 h to remove any absorbed water [11].

Plaque samples were compared to those produced for electrical testing by differential scanning calorimetry (discussed below) and any samples showing a discrepancy were rejected and fresh samples were prepared. A particular problem with polymers high in VA content was their tendency to stick to the aluminium foils used in the sample preparation. In order to avoid damaging the surfaces, the foils were removed overnight in a 10% solution of hydrochloric acid dissolved in distilled water.

Sample characterisation

Differential scanning calorimetry was performed on 2–5 mg samples contained in standard aluminium DSC cans using a Perkin Elmer DSC-7 instrument. All scans were obtained at a heating rate of 10 K/min and the instrument was calibrated periodically using high purity indium.

Samples for scanning electron microscopy (SEM) were microtomed at -20°C to reveal an internal surface (RMC MT7 Cryo-ultramicrotome) then etched for 30 min in a

standard permanganic reagent composed of 1% potassium permanganate dissolved in an acid mixture composed of five parts sulphuric acid, two parts phosphoric acid and one part water [45]. After etching the reagent was quenched using one part hydrogen peroxide in four parts dilute sulphuric acid. Samples were then washed in distilled water followed by methanol. Samples were mounted onto standard aluminium SEM stubs, gold coated and then examined in a Cambridge instruments Stereoscan 360 at 20 kV.

Pieces 45 mm length and 4 mm width were cut from pre-crystallised plaques for dynamic mechanical thermal analysis (DMTA), a hand cutting tool was used to ensure consistency from sample to sample. DMTA experiments were performed using a Rheometrics RSA II materials tester and a dual cantilever fixture. Rhios v 4.4.4 data acquisition software was used to collect data every 10°C in the range -20 – 150°C using a fixed strain of 0.2% and fixed frequency of $100\ \text{rad s}^{-1}$. Similarly shaped dumbbell samples were used for tensile testing, which was performed at room temperature using an Instron 4301 tensile testing machine at a fixed speed of 5 mm/min. Three repeat runs of the mechanical tests were performed on independent samples to generate the average values reported here.

The electrical breakdown rig is discussed in detail elsewhere [41–44, 46] and testing was performed according to ASTM D149-87. Samples were placed between opposing 6.25 mm polished steel ball bearings in a tank containing silicone fluid (Dow Corning 200/20 CS). An increasing voltage (AC 50 Hz) ramp at 50 V/s was applied to this arrangement until the sample failed. In total, 20 tests on four thin film samples were performed and data analysis was performed using Weibull statistics on commercial software (Reliasoft Weibull 7++).

Results

Differential scanning calorimetry

Starting materials

Differential scanning calorimetry melting traces of the LDPE and the four EVA co-polymers following quenching are shown in Fig. 1a. As the VA content is increased from 0 to 40 mol.%, the peak melting temperature decreases from 108 to $\sim 40^\circ\text{C}$ and the enthalpy associated with the transition is reduced from 110 to $\sim 14\ \text{J/g}$. Using the value of $293\ \text{J/g}$ for a perfect crystal [12], the latter values correspond to a fall in crystallinity with increasing VA content from 38 to 5%. Both the melting points and crystallinity values are remarkably similar to those reported elsewhere for comparable EVA co-polymers [13], which indicates

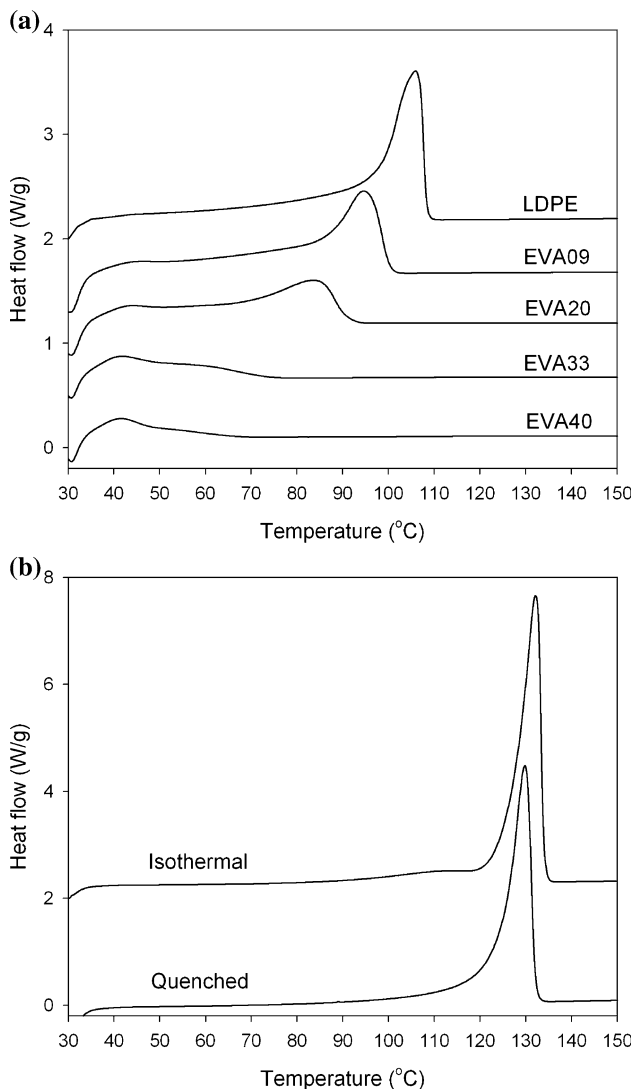


Fig. 1 DSC melting traces of **a** LDPE and the four EVA copolymers following quenching, **b** HDPE following quenching and isothermal treatment

that the current materials do not display any anomalous behaviour. However, it is clear from these data that co-polymers high in VA content may be unsuitable for cables due to their low melting temperatures; XLPE by contrast, shows a softening transition near 105 °C [46, 47].

The analogous melting behaviour of the HDPE is shown in Fig. 1b, it is possible to crystallise this material either by quenching or isothermally over a broad range of temperatures. On quenching, this sample forms a single melting peak centred at 130 °C and after isothermal crystallisation at 117 °C, the peak is centred at 132 °C, consequentially the melting behaviour of this material shows very little dependence on the thermal history. The enthalpy varies between 170 and 185 J/g with slightly higher values obtained after isothermal crystallisation. The single peak

obtained following isothermal crystallisation confirms that the given crystallisation time (1 h) is sufficient to crystallise this material completely in isolation.

Blends

The melting behaviour of the five blends following quenching is shown in Fig. 2a, blends B through E in order contain EVA co-polymers of increasing VA content (Table 2). Two major DSC peaks are obtained from each binary blend with some intermediate features as reported elsewhere [18, 20–22, 43, 44, 48] and in this case, the higher melting peak is associated with the HDPE component and the lower melting peak with the LDPE or EVA component. In the case of Blend A, the two major melting peaks are merged with an intermediate feature at ~115 °C

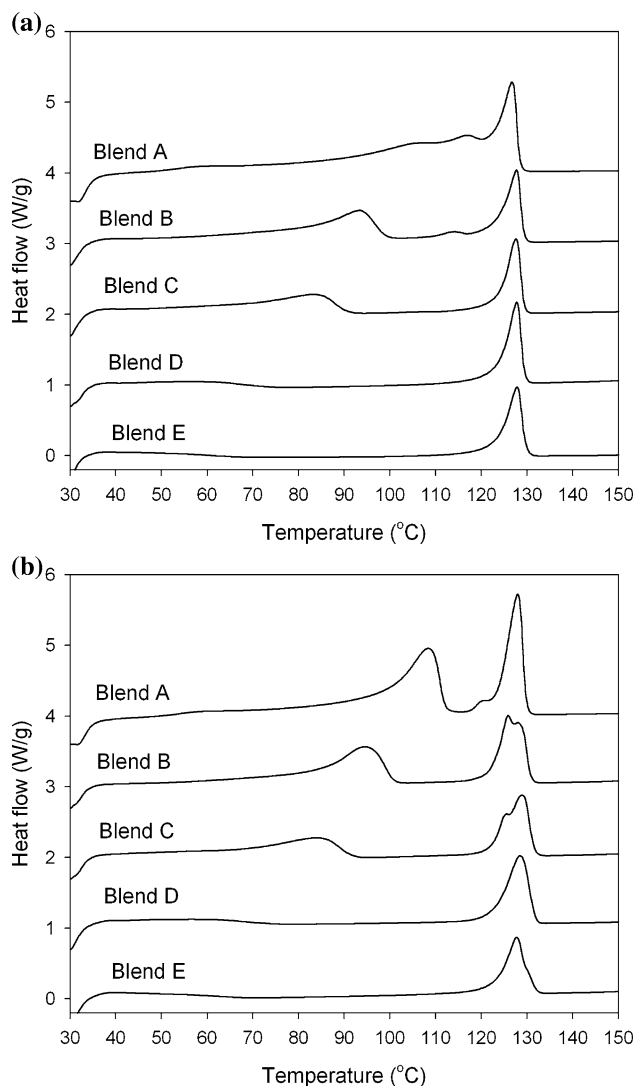


Fig. 2 DSC melting traces of the five blends following **a** quenching, **b** isothermal crystallisation

indicative of extensive co-crystallisation [43, 44], whilst Blend B shows some evidence of a similar intermediate peak at ~ 114 °C. The remaining blends appear to be completely phase separated as evidenced by two distinct melting peaks and no intermediate features. The enthalpies of the peaks are as expected based on the concentrations of the components; for example, in all blends, the enthalpy associated with the melting of the HDPE rich phase is ~ 32 – 40 J/g. This indicates that the blends have the correct proportion of HDPE as in some blends (i.e., blend E) it is difficult to deconvolute the low crystallinity peak associated with the EVA component and to measure its enthalpy directly.

The analogous melting behaviour after isothermal crystallisation is shown in Fig. 2b. In this case, Blend A shows two well-separated peaks along with an intermediate minor feature at ~ 119 °C associated with co-crystallisation [43]. In the case of blends B and C, the melting trace from the HDPE component appears to be ‘doubled’ although the precise ratio of the two peaks depends on which sample is chosen for the analysis. This also appears to be scan rate dependent, at faster scan rates (40 K/min) the lower temperature peak is dominant, whereas at slower scan rates (1.25 K/min) the higher temperature melting peak is dominant. Therefore, the ‘doubled’ peaks are probably a combination of DSC scan rate effects and possibly incomplete crystallisation of the HDPE. In Blends D and E, a single peak is always obtained but at a melting point comparable to that obtained from the quenched HDPE (see Fig. 1b) indicating that in these blends an hour is insufficient to completely crystallise the HDPE component. A similar effect of insufficient crystallisation of the HDPE in EVA blends containing high VA co-polymers was reported previously in tertiary blend systems [42]. Nevertheless, in each blend system, isothermal crystallisation has allowed the HDPE component to crystallise to some degree within a molten matrix of LDPE or EVA as required [43, 44].

Although the sample preparation route and the HDPE component has been changed, Blend A shows a remarkably similar melting behaviour to PE1 crystallised under the same conditions [42]. This was also shown to be the case in a series of LDPE/HDPE blends where the HDPE and LDPE components were systematically changed [44]; the blends showed remarkably similar melting behaviour with very few exceptions.

Morphology

Starting materials

Figure 3 shows the morphology of rapidly quenched samples. With increasing VA content, the morphology

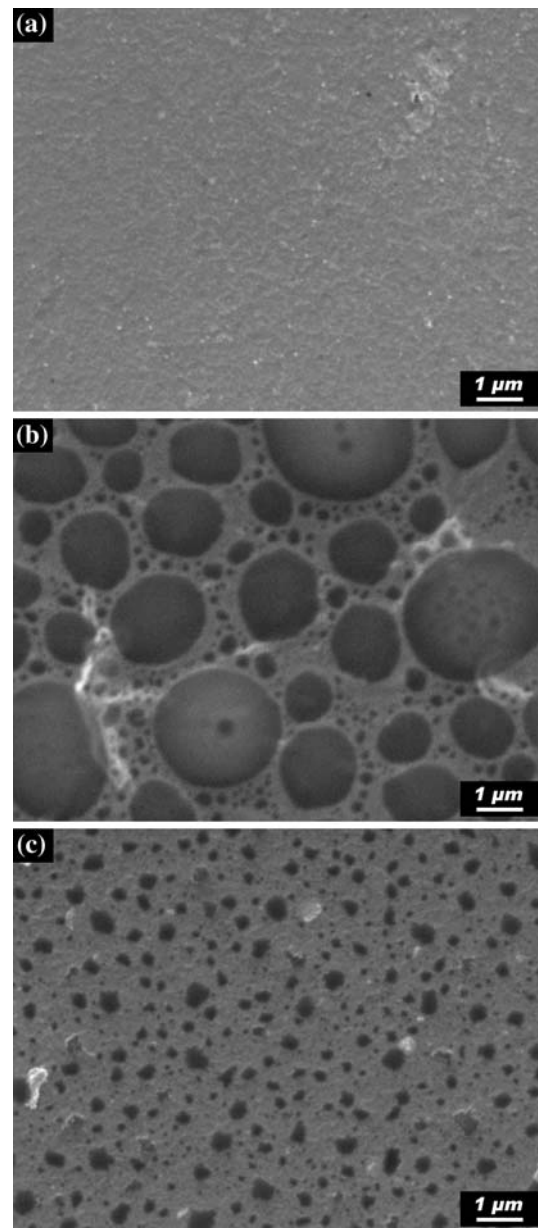


Fig. 3 SEM micrographs of EVA co-polymers after quenching: **a** EVA09, **b** EVA33, **c** EVA20

shows less evidence of a ‘lamellar texture’, such textures are often shown at SEM resolution as a ‘featureless matrix’ [42, 43]. Quenched LDPE shows a uniform texture and EVA09 retains this texture (Fig. 3a), increased VA content then results in a ‘spongy’, voided texture after etching, the most extreme example of this occurs in either EVA40 or EVA33 (Fig. 3b). This unexpected effect could be due to local spatial variations in VA content causing increased etching rates in more polar regions of the sample or some other etching artefact [45]. The same effect has been reported on etching PE/polyaniline blends where the polar

polyaniline component is preferentially attacked by the etchant leaving the PE phase relatively intact [49]. In EVA20 (Fig. 3c), an intermediate texture is obtained with much voiding but clear evidence of a lamellar texture in the intervening regions. In these five materials, the lamellar texture is fine and indistinct by SEM and diminishes with increasing VA content as the crystallinity is reduced. Under the current conditions of a fast quench, spherulitic forms are clearly not present, however, under slower cooling spherulites have been reported in EVA co-polymers with a low VA content [12]. However, in an analogous manner to the loss of lamellar texture reported above, these are disrupted by increasing amounts of VA.

By contrast, HDPE (Fig. 4) shows a much better developed crystal texture with large, broad lamellae in agreement with its higher melting enthalpy obtained by DSC. The crystal texture, although quite clear after quenching (Fig. 4a), appears to be somewhat coarser and much better developed after isothermal crystallisation (Fig. 4b). However, there was no evidence of classical spherulitic forms in any of the samples examined, rather a random array of interpenetrating lamellar crystals forms.

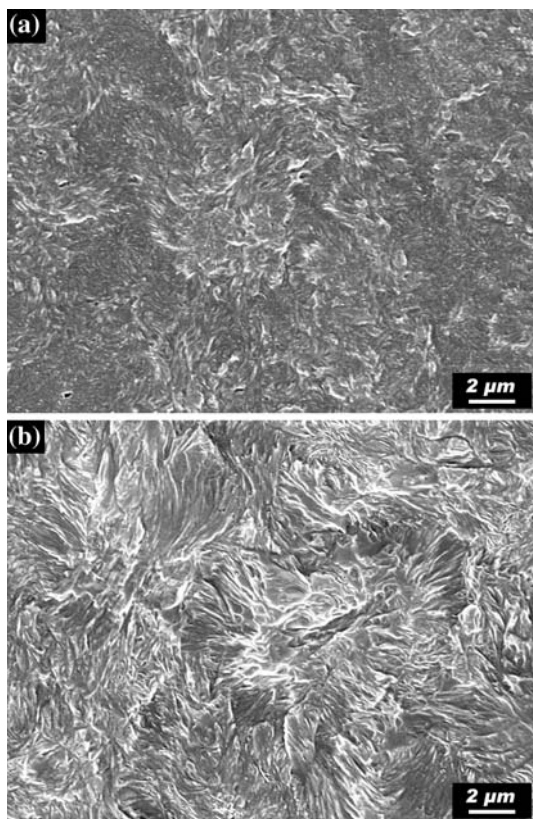


Fig. 4 SEM micrographs of HDPE following **a** quenching, **b** isothermal crystallisation

Blends

Figure 5 shows a selection of micrographs obtained from the quenched blend systems. Blend A (Fig. 5a) shows a uniform texture of fine lamellae, very similar to quenched LDPE or quenched PE1 [42]. At SEM resolution, the texture appears to be single phase, which agrees with its largely singular DSC melting trace. By contrast, blends with EVA co-polymers of increasing VA content show increasing levels of phase separation as the VA content is increased [16] and a characteristic ‘domain structure’ [15–28]. Blend B (Fig. 5b) shows a two phase texture of HDPE rich inclusions within an EVA rich matrix. In this case, the borders between the two phases are ‘fuzzy’ and somewhat indistinct, indicating that some co-crystallisation still occurs as indicated by the corresponding DSC melting trace. In addition, many of the domains are elongated suggesting that a degree of mixing between the two phases still occurs in the melt. In Blend C, these domains are circular and much more distinct (Fig. 5c) indicating increasing phase separation between the components. Finally, in Blends D and E (Fig. 5d), the HDPE rich domains are very distinct and sit proud of the surface of the sample, indicating an increased etching rate of the more polar EVA phase [49]. In all of these systems, there is no evidence of any clear crystal texture within the HDPE rich inclusions, which is unexpected considering that HDPE in isolation develops a clear crystalline texture after quenching (see Fig. 4a). This may suggest that the crystals formed in this phase on quenching are either too small to resolve by SEM or alternatively, the observed effect may be due to an artefact of the etching process associated with the presence of the polar EVA phase [47].

Figure 6 shows analogous micrographs of isothermally crystallised samples. Blend A displays a uniform texture of open-banded spherulites (Fig. 6a) in agreement with the textures obtained from blend PE1 [42] and similar isothermally crystallised HDPE/LDPE binary blends [43, 44]. In Blend B an open, but nevertheless two-phase texture of coarse HDPE crystals within an EVA rich matrix occurs (Fig. 6b) with some evidence of circular domains. Similar, but less space filling textures were also obtained in the corresponding EVA09/PE1 blend [42], consequentially, the increased HDPE content in the current blends is having the required effect of increasing the density of the HDPE rich phase in the EVA matrix, as required for good electrical performance [43]. In Blend C (Fig. 6c), largely circular domains are obtained indicative of a greater degree of phase separation between the HDPE and EVA rich phases. In this case, many of the HDPE rich domains are characterised by a cluster of isothermally crystallised coarse crystals and there is some evidence of crystals of HDPE

Fig. 5 SEM micrographs of quenched blends: **a** Blend A, **b** Blend B, **c** Blend C, **d** Blend E

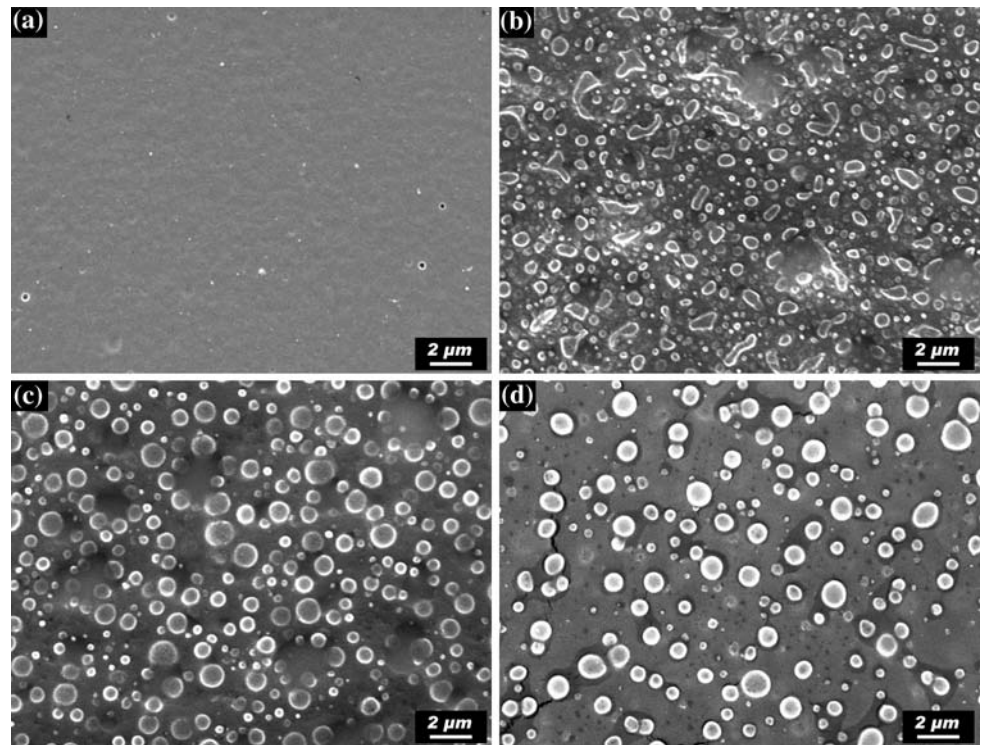
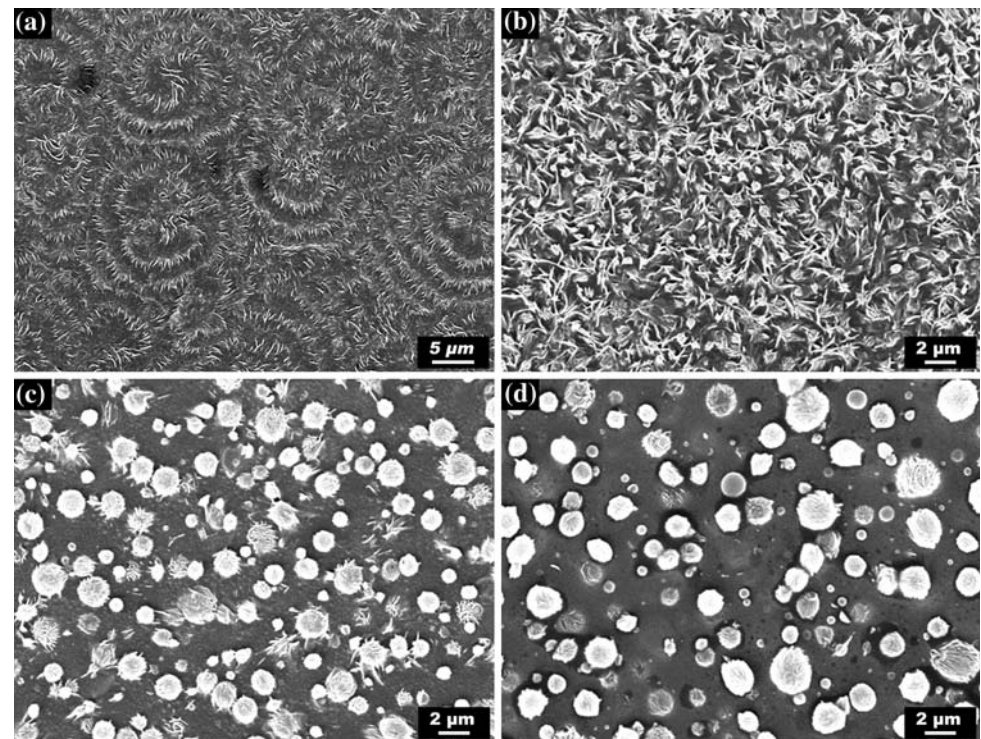


Fig. 6 SEM micrographs of isothermally crystallised blends: **a** Blend A, **b** Blend B, **c** Blend C, **d** Blend D



within the surrounding matrix. However, some of the smaller domains appear to be featureless and rather like those exhibited after quenching which may explain the ‘doubled’ HDPE peak in the DSC (i.e., that an hour is

insufficient time to crystallise completely the HDPE phase in this blend). At the highest VA contents (Fig. 6d), most of the HDPE rich domains appear to be quenched with only a few showing evidence of isothermal crystallisation in

agreement with their DSC behaviour. There is also little evidence of HDPE crystals within the EVA rich matrix suggesting an increased level of phase separation in the melt.

Overall, the microstructures follow the general patterns established for the previous EVA/PE1 blends [42] with increased space filling and density of HDPE rich domains in the current blends as anticipated. Furthermore, in blends of LDPE and HDPE [43], it has been shown that small domains of HDPE in an LDPE can have deleterious effects on dielectric performance, this suggests that choosing EVA co-polymers with too high a VA content might detrimentally influence the dielectric properties. Since these materials have already been excluded as potential candidates for extruded cable systems due to their low melting points, this is not a serious issue.

Tensile testing

Starting materials

The mechanical properties of HDPE or indeed all of the blends did not vary much with crystallisation route, consequentially, Fig. 7a includes data only for quenched HDPE. Out of all of the materials, HDPE shows the highest overall modulus and evidence of necking at $\sim 40\%$ strain, although none of the samples failed up to the strains used here. Starting with LDPE, which is significantly softer than HDPE, with increasing VA content the co-polymers show steadily reduced levels of mechanical modulus and a more rubbery behaviour [9, 15]. EVA40, in particular, recovers almost immediately to its original shape on removal from the tester. Consequentially, the addition of VA into a co-polymer allows the control of mechanical modulus, providing, potentially a useful range of mechanical properties from very stiff materials like HDPE to very rubbery materials such as EVA40 [9]. Whilst rubbery rather than stiff materials might be advantageous in a cable, the low melting point of these particular polymers may make them unsuitable for use as replacements for XLPE in traditional extruded high voltage cables.

Blends

As mentioned above, the mechanical properties do not vary greatly with crystallisation route, however, for completeness, the mechanical properties for quenched and isothermal crystallisation routes are shown as Fig. 7b and c, respectively. The blends all show a higher modulus compared to their respective LDPE or EVA co-polymers (shown in Fig. 7a) due to the presence of the stiffer

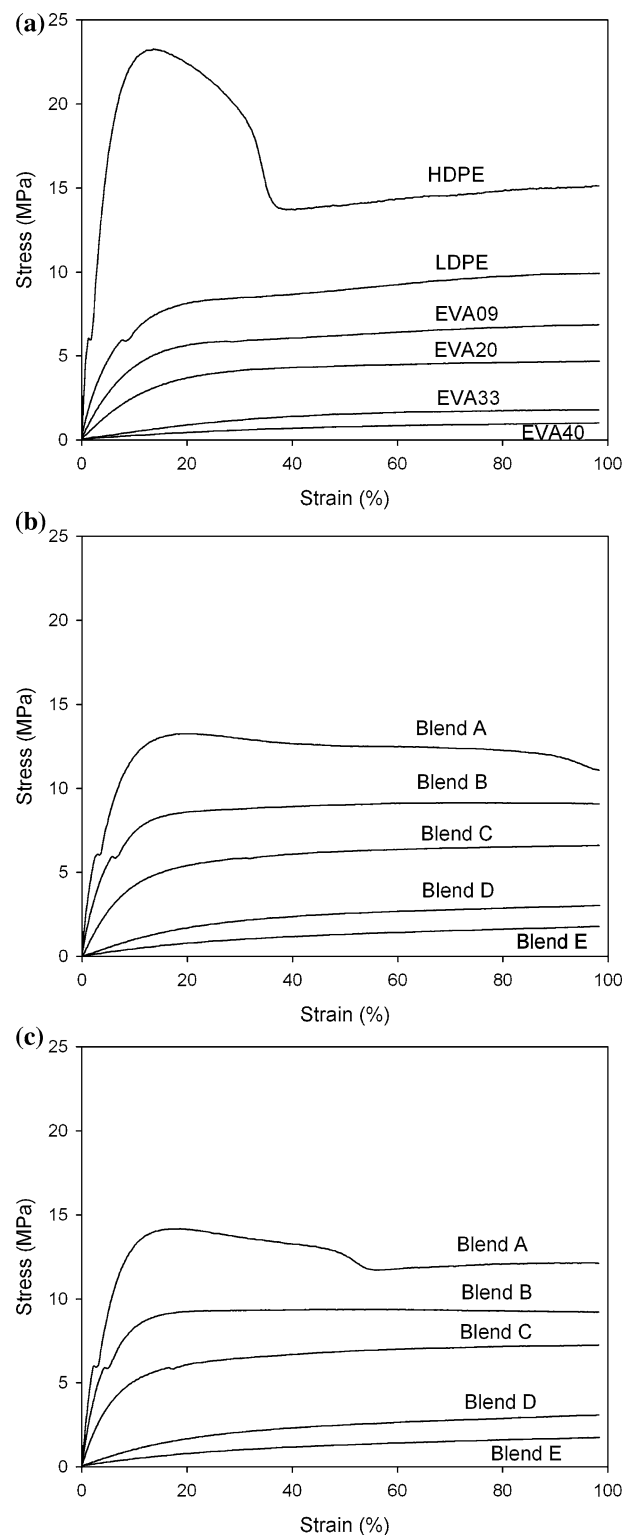


Fig. 7 Stress–strain plots of **a** the starting materials, **b** quenched blends, **c** isothermally crystallised blends

component [17, 19, 20, 28, 48], which in this case is HDPE. Blend A, in addition, shows evidence of necking at $\sim 50\%$ strain particularly in the isothermally crystallised

sample (Fig. 7c). In common with the starting materials, the mechanical modulus decreases with increasing VA content.

Dynamic mechanical thermal analysis (DMTA)

Starting materials

Figure 8a shows the modulus as a function of temperature for the materials before blending. As noted above, the modulus of the materials does not depend greatly on the crystallisation conditions, consequentially, for clarity only results for quenched HDPE are shown here. In an analogous fashion to the tensile testing results presented above, the inclusion of VA provides materials with a lower mechanical modulus compared to LDPE. Whilst this might be an advantage at low temperatures in terms of ease of installation, increasing the VA content also reduces the ‘working range’ of the materials (i.e., the maximum temperature where the sample can retain good mechanical rigidity). Previous work [46] shows that for XLPE the modulus typically varies from 10^8 Pa at room temperature decreasing rapidly from 10^7 to 10^6 Pa at ~ 100 °C. In this case, a modulus of $\sim 5 \times 10^{-6}$ Pa might be considered unacceptable, which limits the working range of XLPE to typically 95 °C.

In the case of HDPE, the modulus at room temperature is much higher than XLPE (10^9 Pa) and does not decrease to $<10^7$ Pa until 120 °C, such a material would, therefore, be good for an extruded cable if it were not for its high rigidity at room temperature. LDPE shows much more favourable characteristics at room temperature compared to XLPE, however, its modulus falls rapidly above ~ 70 °C limiting its usefulness at high temperatures. Increasing amounts of VA result in materials, which are even softer at room temperature but with the disadvantage of a much reduced working range. Unfortunately, none of the materials studied here provide the ideal balance of low-temperature flexibility and high-temperature rigidity required in a practical extruded high voltage cable.

Blends

Data for quenched and isothermally crystallised blends are shown in Fig. 8b and c, respectively. These exhibit similar trends and values of modulus to those reported in the literature [21, 24, 25]. There are only subtle differences exhibited due to the different crystallisation routes, most significantly, the useful working range and modulus are increased somewhat compared to the respective LDPE or EVA components with the most improvement being obtained after isothermal crystallisation. In both cases, Blend A offers significantly improved thermo-

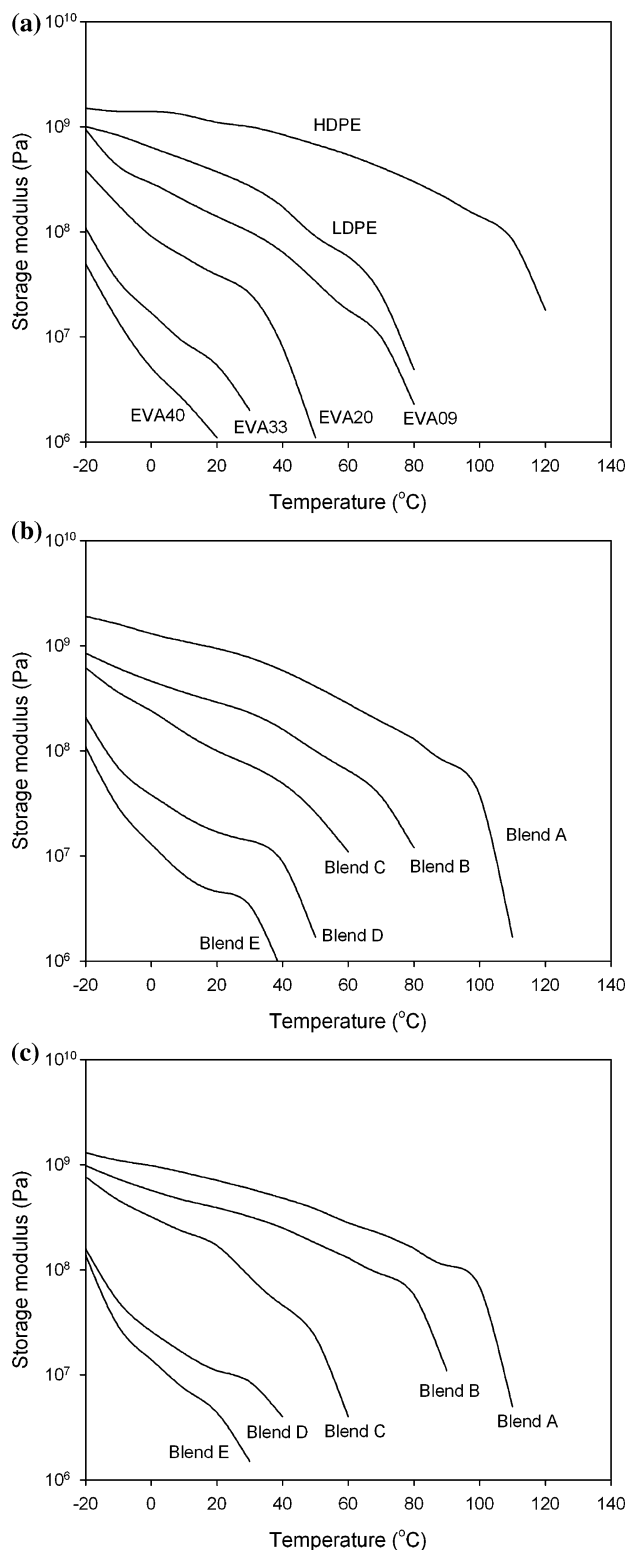


Fig. 8 DMTA curves from **a** the starting materials, **b** quenched blends, **c** isothermally crystallised blends

mechanical performance compared to LDPE in isolation, extending its useful working range to ~ 110 °C whilst retaining good flexibility at room temperature. These are

properties, which are required in any potential replacement for XLPE.

Unfortunately, whilst the presence of HDPE does improve the thermo-mechanical performance of all of the blend systems, increasing the working range without increasing the modulus too much at room temperature, the effect of increasing VA content in reducing the modulus and working range remains. Consequentially, for a practical cable system, blends with HDPE appear to be a useful way of enhancing the thermal and thermo-mechanical properties of LDPE and as such a blend of 20% HDPE in LDPE potentially offers a suitable recyclable alternative to XLPE for extruded cables. Whilst it is doubtful that the working range of Blends C through E are sufficient for a practical cable [46] and their melting points are probably too low, Blend B offers a reasonable thermo-mechanical performance up to ~80 °C and sufficient flexibility at room temperature. In reality, there exists a trade off at low VA contents between sufficient working range and enhanced treeing resistance afforded by the presence of the EVA component. Blends of HDPE with EVA09 could, therefore, provide a useful framework for designing novel semi-conductive EVA-based cable systems.

Electrical breakdown testing

Starting materials

Figure 9a shows Weibull plots of the breakdown data obtained from the various materials before blending and Table 3 contains associated numerical values of Weibull mean and shape parameter. HDPE displays the highest breakdown strength (~168 kV/mm), which is maximised by isothermal crystallisation (~186 kV/mm). In agreement with the earlier work [42] and other reports [7, 8], the quenched low crystallinity materials starting with LDPE (~148 kV/mm) display reducing dielectric breakdown values as the VA content is increased down to ~77 kV/mm for EVA40. It is clear from the point of view of the electrical properties that isothermally crystallised HDPE is the best material to replace XLPE, however, it suffers from the disadvantage of having a high mechanical modulus at room temperature. LDPE provides a comparable breakdown performance to tested XLPE tapes (not shown here for clarity), however, as outlined above, LDPE in isolation shows a poor mechanical integrity at high temperatures.

Blends

The blends offer significantly higher dielectric breakdown strength compared to their respective LDPE or EVA components. Quenched samples (Fig. 9b) display reduced

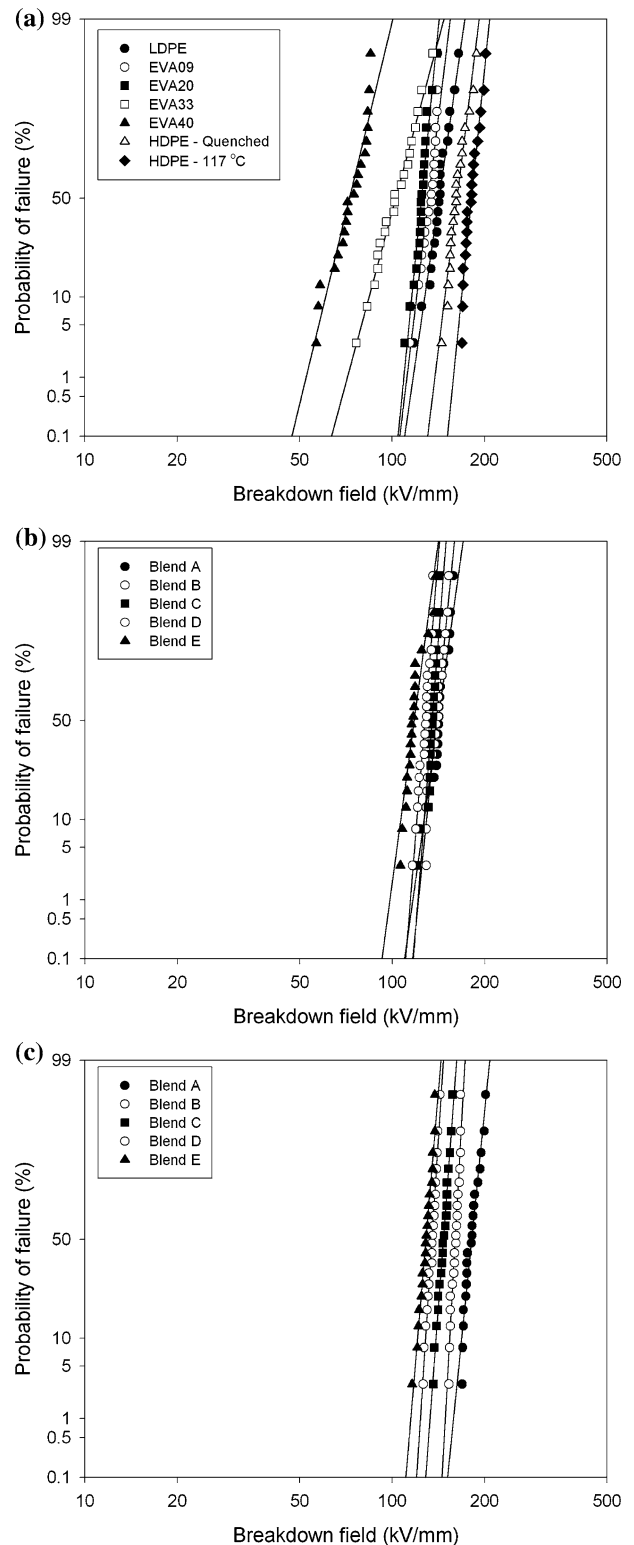


Fig. 9 Dielectric breakdown (Weibull plots) for **a** the starting materials, **b** quenched blends, **c** isothermally crystallised blends

performance compared to isothermally crystallised samples (Fig. 9c), which generally display the highest values of dielectric breakdown strength (Table 3). Therefore, the

Table 3 Numerical values of breakdown, typical uncertainty 10 kV/mm

Sample	Crystallisation route	Breakdown field (kV/mm)	Shape parameter
LDPE	Quench	148	14
EVA09	Quench	135	22
EVA20	Quench	128	20
EVA33	Quench	110	7
EVA40	Quench	77	10
HDPE	Quench	168	14
HDPE	Isothermal	186	18
Blend A	Quench	145	17
Blend B	Quench	143	20
Blend C	Quench	137	33
Blend D	Quench	130	28
Blend E	Quench	122	13
Blend A	Isothermal	168	26
Blend B	Isothermal	163	40
Blend C	Isothermal	150	28
Blend D	Isothermal	137	33
Blend E	Isothermal	132	26

presence of HDPE in sufficient quantity is having a beneficial effect on the breakdown strength of the blends, whilst this advantage was seen before in a series of LDPE/HDPE blends [43, 44], the concept has now been extended to a series of EVA/HDPE blends. In this case, whilst crystallising HDPE in a matrix of an EVA co-polymer with a high VA content shows a reduced breakdown strength compared to the equivalent HDPE/LDPE blend, adding HDPE in sufficient quantity clearly provides a way of mitigating the reduction in dielectric properties wrought by the presence of the VA. The improvement in the dielectric properties following isothermal crystallisation is probably a result of the improved space filling nature of the HDPE component [43]; on quenching such a component normally forms spherical domains in the EVA matrix (see Fig. 5), whereas on isothermal crystallisation, provided the VA content is not too high, space filling HDPE crystals within an EVA matrix can be formed (see Fig. 6).

Discussion

All of the current blends offer better dielectric performance than their respective LDPE or EVA co-polymers. However, we must also consider thermal and mechanical constraints in selecting materials suitable to replace XLPE in cables. Clearly blends of 20% HDPE in LDPE provide the best all round performance, combining good thermo-mechanical performance, sufficiently low modulus at room temperature,

reasonably high melting point and high dielectric strength. However, the inclusion of an EVA co-polymer may be beneficial in some cable applications, particularly where some degree of tree retardancy is important [3] and high temperature operation is not critical. However, too much VA can lead to reduced melting point, reduced working range and a significantly reduced electrical breakdown strength. Nevertheless, a blend of 20% HDPE in EVA09 appears to offer an acceptable breakdown performance, a working range up to ~ 80 °C and a melting point >90 °C and might, therefore, provide a reasonable starting point for the design of future EVA-based cable systems.

Conclusions

1. The effect of increasing VA content was studied in a series of EVA co-polymers, in these systems the melting temperature, crystallinity, mechanical modulus and breakdown strength all reduced as a function of increasing VA content as reported elsewhere. The morphologies of such samples showed initially a crystalline texture giving way to a less distinct, more amorphous like texture. The particular permanganic etchant used is clearly not optimised for highly polar polymers as artefacts were present in the EVA co-polymers high in VA content. Clearly, the etching procedure would need to be refined in order to study the supermolecular structure of these materials in more detail.
2. Too much VA does not lead to properties, which would be considered beneficial for an extruded high voltage cable. However, a small amount of VA does not appear to cause too many detrimental effects and may be beneficial in terms of improving tree retardancy.
3. The addition of HDPE to an EVA co-polymer or to LDPE generally results in improved thermo-mechanical, mechanical and dielectric properties. The DSC and morphological investigations showed that an increasing amount of phase separation occurs between the HDPE and the EVA phase with increasing VA content as reported elsewhere.
4. Isothermally crystallised blends of 20% HDPE in either LDPE or EVA09 result in composite systems with improved properties compared to EVA or LDPE in isolation and are comparable to XLPE but without the need to crosslink. Such systems would, therefore, be useful as candidate materials for future extruded recyclable cable systems.
5. However, in order to provide thermo-mechanical properties better than XLPE, a different polymeric system is required. An investigation of different types of polypropylene would seem to be a suitable way

forward, owing to its high melting point and good breakdown performance, however, its high rigidity compared to XLPE needs to be overcome. This will form the topic of further investigations under the current programme.

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