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An investigation of the potential of polypropylene and its blends for use in recyclable high voltage cable insulation systems

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Abstract Most modern extruded high voltage cables employ cross-linked polyethylene (XLPE) as the insulation material. XLPE has excellent thermo-mechanical properties, is relatively cheap and has a low dielectric loss, which make it an ideal material for this application. Unfortunately, XLPE is not easily recycled at the end of its lifetime leading to questions concerning its long-term sustainability. A previous investigation in this series considered the potential of a range of ethylene-based systems to provide suitable recyclable alternatives to XLPE. Whilst blending could allow systems having similar thermo-mechanical and electrical properties to XLPE to be designed, it was not possible to obtain better performance than XLPE using these systems. Polypropylene offers, potentially, a route to improved insulation systems by virtue of its higher melting point and excellent dielectric properties. However, traditional isotactic polypropylenes have always had the problem of being too brittle for inclusion into practical cable designs. Recently a broad range of propylene co-polymers having improved ductility have become available, which may prove more suitable. The current study compares traditional isotactic and syndiotactic polypropylenes to a range of commercially available propylene co-polymers and focuses on their morphology, thermal, thermo-mechanical and electrical properties. These parameters were then taken together to identify the most suitable candidate materials for future cable applications. The use of blending as a means to further optimise the various material properties was also explored.

Introduction

Extruded cables based on polymeric materials have now largely superseded older paper/oil designs for medium and high voltage applications [1]. Materials such as low density polyethylene (LDPE), poly-vinyl chloride (PVC), ethylene propylene rubber (EPR) and ethylene–vinyl acetate (EVA) are easy to process and are excellent electrical insulators making them suitable for electrical cable designs. For example, PVC is widely used for light duty equipment and power cables as it has adequate mechanical and electrical properties around room temperature [2]. However, for high power transmission cables, additional factors, such as the need to retain adequate mechanical integrity and good insulation properties at high temperatures, flexibility at low temperatures and the need to reduce transmission losses as much as possible, have to be considered. For these reasons, cross-linked polyethylene (XLPE) remains the material of choice for the current generation of extruded high voltage transmission cables. Compared to LDPE, XLPE has dramatically improved thermo-mechanical stability at high temperatures, wrought by virtue of a cross-linked network, combined with excellent dielectric properties [3]. Unfortunately, the same cross-linked network results in a system that cannot be easily recycled at the end of its service life, although various schemes for re-use have been proposed [4–6].

Minimising the environmental impact of human activity through recycling and re-use is becoming more important

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both politically and technologically. Consequentially the recyclability of cable materials is becoming a serious concern, especially in the context of increasing landfill costs. This indicates that there is now a critical need to move away from XLPE towards recyclable alternatives for the next generation of extruded high voltage cables. With this in mind, a number of notable studies into the electrical and thermal properties of LDPE and its blends [7–9], HDPE and its blends [10] and finally LDPE/HDPE blends [9, 11, 12] have been undertaken. Whilst many of these materials have excellent dielectric properties and are easily recyclable at the end of life using existing waste channels, it was found that HDPE is too brittle and LDPE softens at too low a temperature for incorporation into a cable [9]. Improved thermo-mechanical performance can, however, be achieved by blending LDPE with small amounts of HDPE [9] offering a recyclable composite insulation system with comparable electrical and thermo-mechanical properties to XLPE.

Whilst the above ethylene-based systems could be used to provide recyclable replacements for XLPE for the next generation of high voltage cables, if enhanced dielectric properties and increased operating temperatures are required, then propylene-based materials would be more suitable. Indeed, isotactic polypropylene (iPP) was considered during the early stages of cable development [13, 14], but was not widely accepted due to its inherent rigidity and the reduced electrical strength that results from the formation of large spherulites [15, 16]. Nevertheless, the use of syndiotactic rather than isotactic polypropylene (sPP) may overcome many of these difficulties by virtue of its improved ductility and increased spherulitic nucleation density [13, 14]. In addition, recently a wide range of propylene co-polymers have become commercially available which also offer improved ductility and therefore, with suitable thermal processing, may offer additional candidate materials for future enhanced propylene-based cable systems [17].

Here we report on a study of a range of propylene-based co-polymers as well as traditional isotactic (iPP) and syndiotactic (sPP) polypropylene. These are prepared through a traditional Ziegler–Natta (ZN) catalyst process and were obtained commercially and therefore represent a typical cross-section of currently available systems. We have considered their thermal, thermo-mechanical and electrical properties as well as their morphology to assess which of these materials provide the best balance of properties for use in the next generation of high performance extruded high voltage power cables. Finally, we explore the usefulness of blending as a means of further optimising properties.

Experimental

Materials

Six different polyethylenes supplied by Sigma-Aldrich Chem. Co. were studied in this investigation (Table 1). Two of these represent typical isotactic (iPP) and syndiotactic (sPP) polypropylenes, respectively. Three materials are ethylene co-polymers with co-monomer contents ranging from 2 to 40% and are designated PE*x* where *x* indicates the ethylene content. Finally PB12 is a propylene–butene co-polymer containing 12% butene.

Blending

Four binary blends were prepared by the process of solution blending according to published techniques [11], as detailed in Table 2. The required pellets of each material were carefully weighed using a digital balance (Ohaus) and placed into xylene (1% w/v concentration); the xylene was then boiled with vigorous stirring for a period of 20 min, a reflux condenser being used to recirculate any solvent vapours. Meanwhile the same volume of methanol was cooled to ~0 °C in a freezer. After blending was complete, the xylene solution was poured into the methanol with vigorous stirring. The resulting precipitate was allowed to cool, filtered to remove the solvent and then dried at room temperature to constant mass in a drying cabinet vented externally. Final degassing was carried out in aluminium trays for 1 h at 200 °C under dynamic vacuum.

Sample preparation

Samples of the required polymer or blend were melted at 200 °C for at least 2 min and then pressed into the required form. After pressing, the samples were held at this temperature for ~5 min to relax and were then either quenched directly into water at 25 °C or crystallised isothermally in oil baths (Grant, accuracy ± 1 °C). Plaques nominally

Table 1 Polymers used in this investigation

Material	Co-unit content	Co-unit type	M_w (g/mol)	M_n (g/mol)
iPP	–	–	163,000	47,700
sPP	–	–	157,000	43,200
PE02	2	Ethylene	283,000	36,000
PE12	12	Ethylene	135,000	47,700
PE40	~40	Ethylene	49,000	10,400
PB12	12	Butene	254,000	74,000

Table 2 Blends investigated in this study

Designation	Composition
Blend 1	20% iPP in sPP
Blend 2	50% iPP in sPP
Blend 3	20% iPP in PE40
Blend 4	50% iPP in PE40

1.5 mm in thickness were prepared using a hydraulic workshop press and aluminium moulds; strips 50 mm in length by 5 mm width were then cut for mechanical testing. Film samples of 70 µm nominal thickness for electrical breakdown testing were prepared using a Grasby-Specac 25.011 hydraulic press equipped with constant thickness film maker.

Isothermal crystallisation times were inferred by melting ~0.1 g of sample between a clean microscope and cover slip (sample thickness ~1 mm) and viewing visually the crystallisation process using a polarising optical microscope equipped with a Mettler FP82 temperature controlled hotstage. The hotstage was calibrated using a temperature probe, itself calibrated in ice/water mixture and boiling distilled water, respectively. The time for crystallisation was inferred by viewing three separate samples of each material and waiting for complete impingement of spherulitic forms, once this had occurred the time was noted. The specimen was then checked for any further changes over a similar timescale, if no such changes were observed then the original time was taken as the crystallisation time (or time to impingement) otherwise the time was revised accordingly and re-checked using a fresh sample. Samples which did not show evidence of observable nucleation within an hour were rejected and fresh samples were prepared, crystallisation being attempted at a lower temperature.

Characterisation

Differential scanning calorimetry (DSC) of ~5 mg samples was undertaken using a Perkin Elmer DSC-7; melting traces were obtained at 10 K/min and the instrument was calibrated using high purity indium. Samples for morphological examination were microtomed and then chemically etched for a period of 6 h in a 1% solution of potassium permanganate in an acid mixture composed of 2 parts water, 2 parts phosphoric acid and 5 parts sulphuric acid, according to published techniques [18]. They were then mounted onto standard aluminium SEM stubs, gold coated and examined at 20 kV in a Cambridge Instruments Stereoscan 360 scanning electron microscope (SEM).

Tensile testing was undertaken at room temperature using an Instron 4301 tensile tester at a fixed speed of 5 mm/min (gauge length 25 mm). Dynamic mechanical thermal analysis (DMTA) was undertaken at temperatures between −20 and 140 °C using a Rheometrics RSA II at a fixed frequency of 100 rad/s and an applied strain of 0.02%. A dual cantilever geometry (40 × 5 mm) was used for most of the tests. For some of the low modulus materials this was impractical and therefore a parallel plate compression fixture (diameter 12 mm) was used in its place and to ensure linearity, a fixed 1% compressive strain was applied.

Electrical breakdown tests were performed according to ASTM D149-87 using a standard testing protocol [3, 9, 11, 12, 17]. Testing was undertaken on film samples placed between opposing 6.25 mm steel ball bearings immersed in a tank of silicone fluid (Dow 200/20 CS). An increasing AC (50 Hz) voltage was then applied at a rate of 50 V/s until failure. The results from 20 such tests per material were analysed using Weibull statistics (Reliasoft Weibull 7++).

Results: single component systems

Crystallisation behaviour

Figure 1 shows a plot of the time to impingement for all six co-polymers, averaged over three separate samples and as expected, the crystallisation time increases exponentially with the crystallisation temperature [19]. At any given crystallisation temperature, iPP crystallises much more rapidly than sPP as expected [20]. Unexpectedly, PE12 displays almost identical crystallisation behaviour to iPP while, in PB12 and PE40 the co-unit acts in the expected manner to hinder crystallisation [21]. PE02 crystallises significantly more quickly than iPP despite its increased

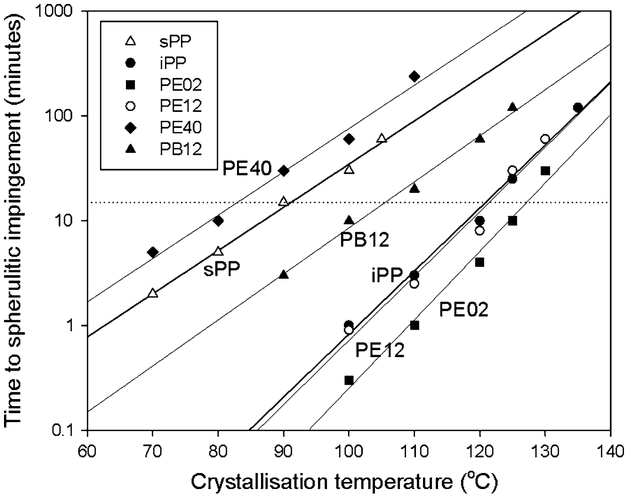

Fig. 1 Measured time to impingement of all five materials from optical measurements of three separate samples

ethylene co-monomer content, increased molecular weight and higher polydispersity (Table 1). Out of all the materials, PE40 displays the slowest crystallisation rates, probably by virtue of its much higher co-monomer content [21].

For convenience, a single isothermal crystallisation temperature was selected to prepare further samples for analysis; this was chosen to give an impingement time of 15 min (as indicated by the dotted line in Fig. 1). To ensure that complete isothermal crystallisation occurs under these conditions, a 1 h crystallisation time was allowed. Figure 1 shows that under these conditions a crystallisation temperature of 120 °C is appropriate for iPP, PE02 and PE12, 90 °C is appropriate for sPP, 100 °C for PB12 and 80 °C for PE40.

Differential scanning calorimetry

Figure 2a shows typical DSC melting traces for samples quenched directly from the melt arranged in order of decreasing enthalpy from top to bottom. Isotactic polypropylene has a singular melting transition located at ~160 °C and the highest enthalpy of all the materials considered of ~80 J/g, indicating a crystallinity of 38% [22]; these values are broadly consistent with other investigations [17, 21]. sPP also displays a singular melting transition which is located at ~125 °C and a corresponding enthalpy of ~30 J/g (crystallinity of 14%); these values are again broadly consistent with other investigations of this type of material [20].

PE12, by contrast, shows two distinct melting transitions. The upper at ~163 °C is close to that of the iPP and the lower at ~125 °C is close to that typically expected from high density polyethylene [9, 11]. This, along with its almost identical crystallisation behaviour to iPP (see Fig. 1), suggests that phase separation of ethylene and propylene rich sequences is occurring in this propylene/ethylene co-polymer (i.e. the two components crystallise essentially independently). For PE02, PB12 and PE40, increasing co-unit concentration lowers the melting point and enthalpy as reported elsewhere in analogous sets of random propylene–ethylene co-polymers [17, 21]. By contrast, PE40 has a broad melting transition extending from 80 to 150 °C and an enthalpy of only ~6 J/g indicating a crystallinity of <5%. Comparing the observed melting temperatures above with the selected crystallisation temperatures indicates that there is a consistent undercooling of ~35 K across all materials.

Figure 2b shows analogous melting traces following isothermal crystallisation for 1 h as described above. In some cases, the resulting melting transitions and enthalpies are very similar to those seen after quenching. Unlike the sets of random propylene–ethylene co-polymers considered in our previous studies, which exhibited significant γ populations after isothermal crystallisation [17, 21], complimentary wide angle X-ray scattering on the current

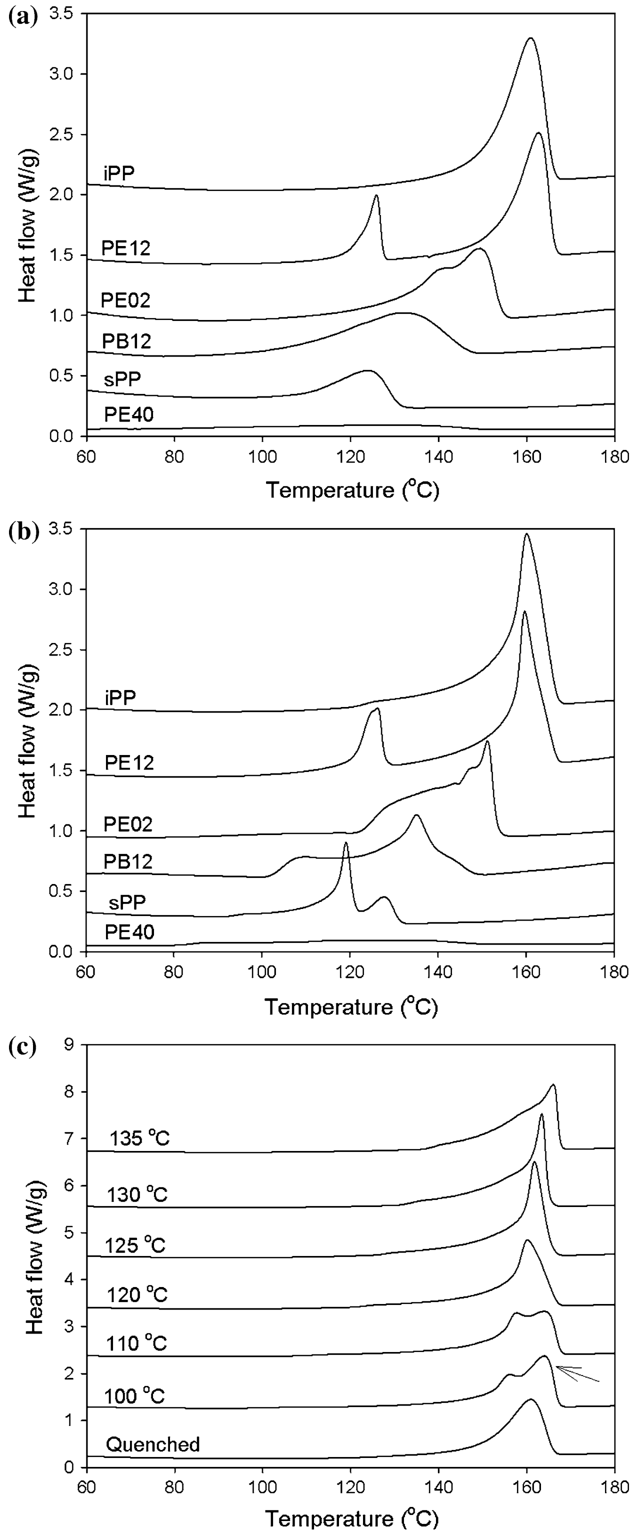

Fig. 2 DSC melting endotherms from **a** quenched samples, **b** isothermally crystallised samples, **c** iPP crystallised at various temperatures to illustrate reorganisation effects. *Curves* displaced for clarity

series did not reveal any evidence of γ crystals [23]. This behaviour indicates that not only do the current ZN catalysed materials lack the random distribution of defects required for the formation of the γ phase [21] but also that the double melting peaks occur as a result of reorganisation during the DSC scan. Figure 2c illustrates this behaviour in iPP crystallised isothermally at different temperatures. After quenching or crystallisation at low temperatures, extensive reorganisation occurs during the DSC scan to give the upper melting peak (arrowed)—this is the peak that is detected in quenched samples. As the crystallisation temperature is increased, the upper melting peak is diminished and is replaced by the lower melting peak with a bi-modal behaviour evident at intermediate crystallisation temperatures (i.e. 110 °C). Such reorganisation effects account for the lowering of the apparent melting points of iPP and PE02 after isothermal crystallisation, as well as the observed multi-modal melting behaviour of sPP and PB12, shown in Fig. 2b. Increasing the DSC scan rate is one way to overcome such problems and allow the true melting point to be determined. However, at the high scan rates required, instrumental thermal lag becomes a serious issue leading to much greater inaccuracies.

With the possible exception of PE40, whose melting behaviour occurs over a very broad temperature range (so is difficult to quantify), and taking into account variations in observed melting point due to the above reorganisation effects, all the materials appear to melt at a higher temperature than the 105 °C typically associated with the softening transition in XLPE [3, 24]. Therefore, despite the increased variability inherently associated with the current ZN catalysed materials, compared to the previously studied random propylene co-polymers [17, 21], at least five out of the six investigated materials appear to be suitable as high performance cable materials, at least from the point of view of their melting behaviour.

Morphology

Figure 3 shows the morphology of selected quenched samples. iPP shows some evidence of spherical domains (Fig. 3a) whereas sPP, PE02 and PB12 all show a uniform lamellar texture devoid of spherulites, an example of which is shown in Fig. 3b. All of these materials possess a relatively high crystallinity and appreciable melting enthalpies in the DSC so the presence of distinct crystal forms in these materials is not surprising [15, 17, 25]. By contrast, PE12 (Fig. 3c) exhibits a two-phase texture which is consistent with its bi-modal DSC melting behaviour. It is well known that in ZN catalysed polymers such as these, that the defects are strongly concentrated in the molecules with the lowest molecular weight [26]. In this case the shortest most "defective" or "ethylene rich" molecules undergo a physical phase separation to form broadly circular domains within the majority propylene rich phase. Not surprisingly, the domains, being composed primarily of more defective, lower molecular weight material, have etched more strongly than the surrounding matrix [18]. Finally, PE40 exhibits a "featureless matrix" (at SEM resolution) which is consistent with its very low crystallinity as measured by DSC.

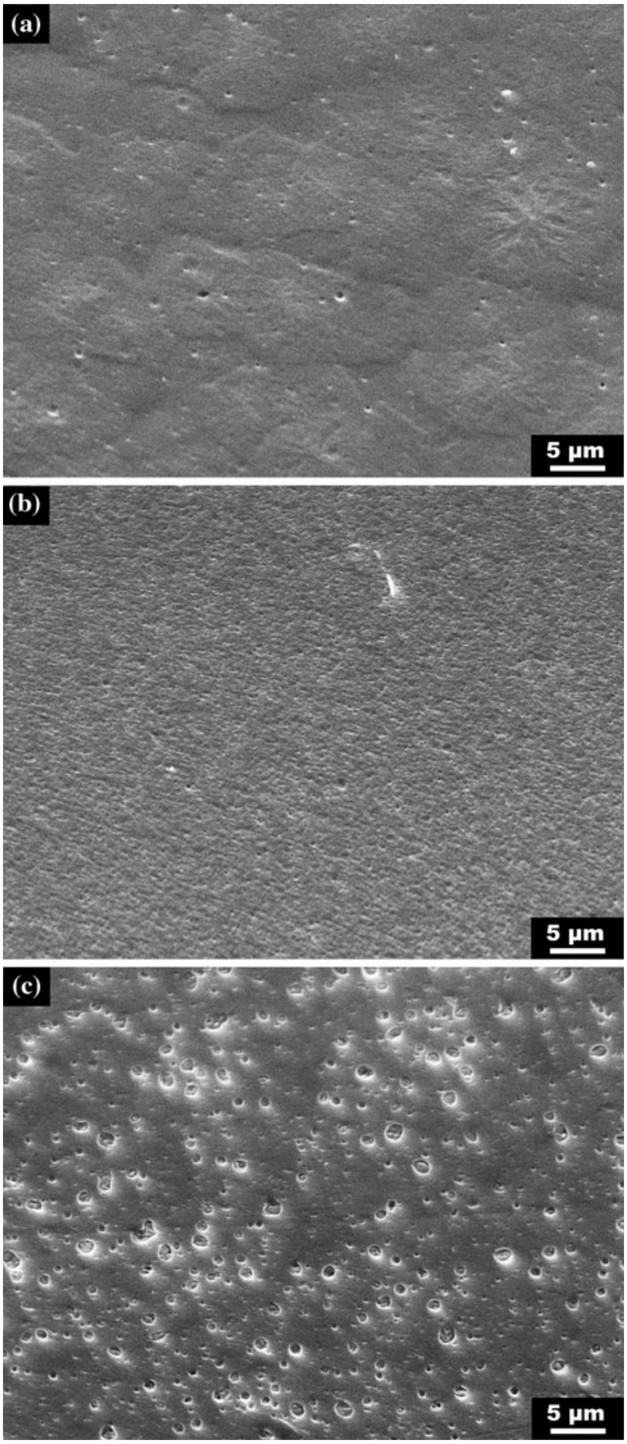

Fig. 3 SEM micrographs of quenched samples **a** iPP, **b** PE02, **c** PE12

Isothermal crystallisation results in much more organised textures as shown in Fig. 4. iPP (Fig. 4a) displays small, well-defined spherulites ~30 μm in diameter with prominent boundaries, whereas sPP (Fig. 4b) shows similar forms (~20 μm in diameter) but with rather more diffuse boundaries. By contrast, PE02 (Fig. 4c) displays a uniform lamellar texture, rather similar to that observed on quenching the same material (see Fig. 3b) and an absence of spherulitic forms, again PE12 (Fig. 4d) displays a two-phase texture again, rather similar to that exhibited after quenching. Given its similar crystallinity to sPP, PB12 (Fig. 4e) displays a texture of spherulites (diameter ~50 μm) with diffuse boundaries. Finally the rather low crystallinity PE40 displays no evidence of crystal forms at SEM resolution so is not shown here. A similar progression, from well-defined spherulitic morphologies to non-crystalline disorganised textures with increasing co-unit content, has been reported elsewhere [17, 25] and the current series, with few exceptions, appears to follow this morphological trend.

Finally, the two-phase texture exhibited by PE12 over all crystallisation conditions, together with its bi-modal DSC melting behaviour and its rather similar isothermal crystallisation behaviour to iPP (see Fig. 1) suggests that ethylene sequences are being excluded during isothermal crystallisation (i.e. PE12 crystallises rather similarly to iPP). Furthermore, the distinctive lack of spherulites, even under isothermal conditions, and the unexpectedly rapid crystallisation associated with PE02 suggests that this material may contain a nucleating agent. Rather similar morphologies to that shown in Fig. 4c are reported elsewhere in polypropylene systems which have been deliberately nucleated with dibenzylidene-sorbitol [27].

Tensile testing

Typical stress–strain curves obtained from the Instron tensile tester are shown in Fig. 5 for all six materials considered. The stress was proportional to the strain up to ~2% which allowed the modulus to be calculated. All of the materials, with the exception of PE40, showed a similarly high modulus of ~10^9 Pa, which is in line with earlier studies [17]. Following quenching (Fig. 5a), iPP exhibits a brittle failure at ~10% strain, whereas PE12 exhibits a similar failure at ~15% strain. The remaining materials, with the exception of PE40, show a characteristic necking behaviour above ~20% strain and thereafter do not recover their original shape on removal from the tester. By contrast, PE40 shows a much lower modulus (~10^6 Pa) and recovers its original dimensions immediately after removal from the tester (i.e. it has a rubbery nature). Under isothermal conditions (Fig. 5b) the characteristics are very similar, the exception being that PE12 now exhibits a brittle failure at a much lower strain.

By contrast, similar tests on XLPE [3] and analogous ethylene-based systems [9] reveal a modulus at room temperature of ~10^8 Pa, therefore the majority of the current propylene-based systems, with the exception of PE40, are much stiffer than XLPE at room temperature, which may make them unsuitable for cable applications. Whilst the brittle nature of iPP is widely appreciated [13], the fact that PE12 shows a very similar behaviour was

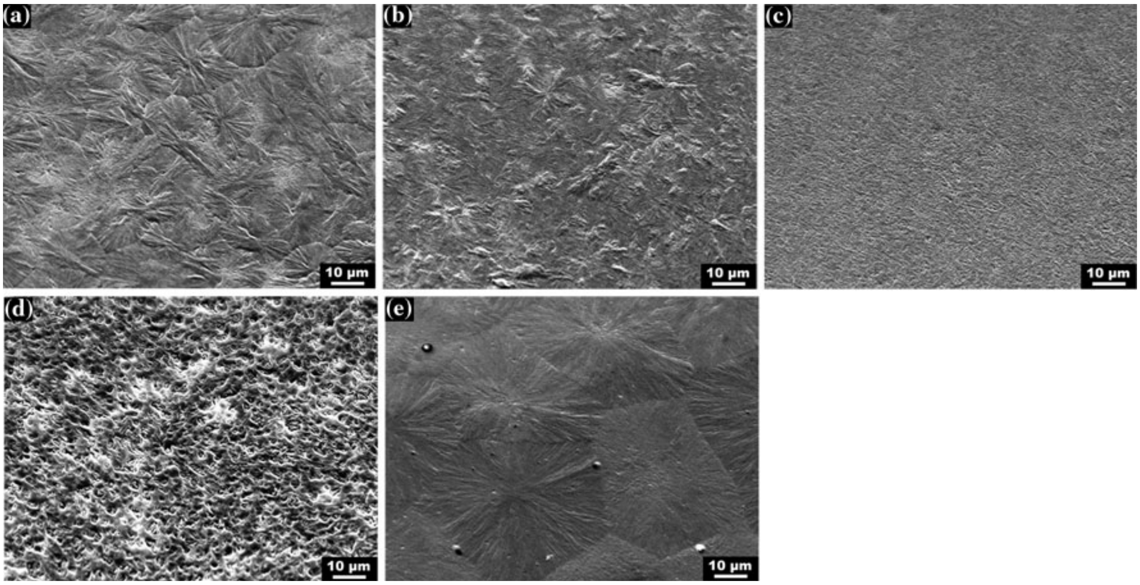

Fig. 4 SEM micrographs of **a** iPP crystallised at 120 °C, **b** sPP crystallised at 90 °C, **c** PE02 crystallised at 120 °C, **d** PE12 crystallised at 120 °C, **e** PB12 crystallised at 100 °C

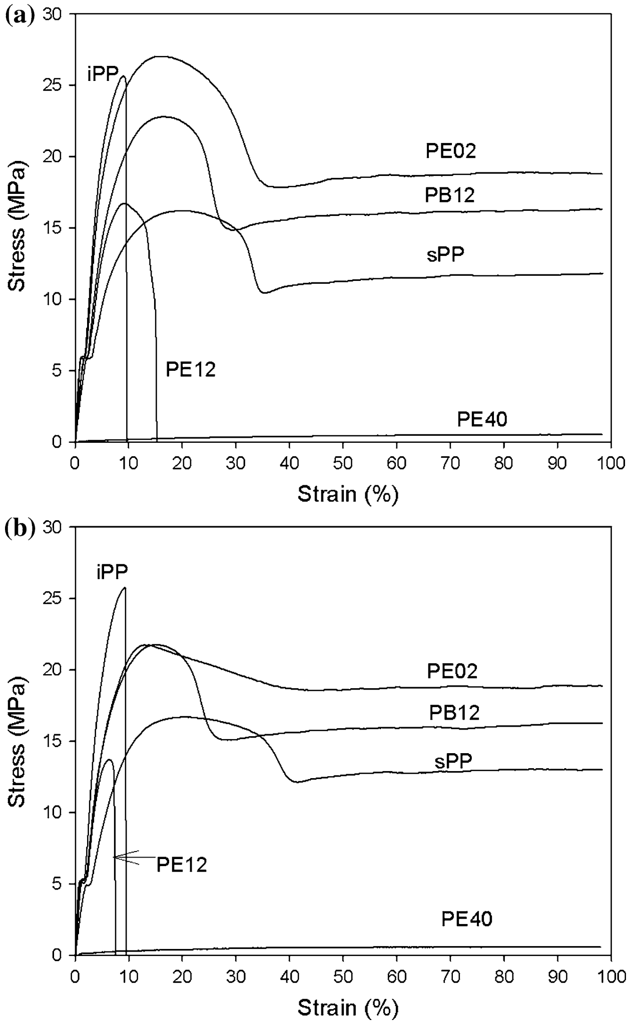

Fig. 5 Tensile test results from **a** quenched samples, **b** isothermally crystallised samples

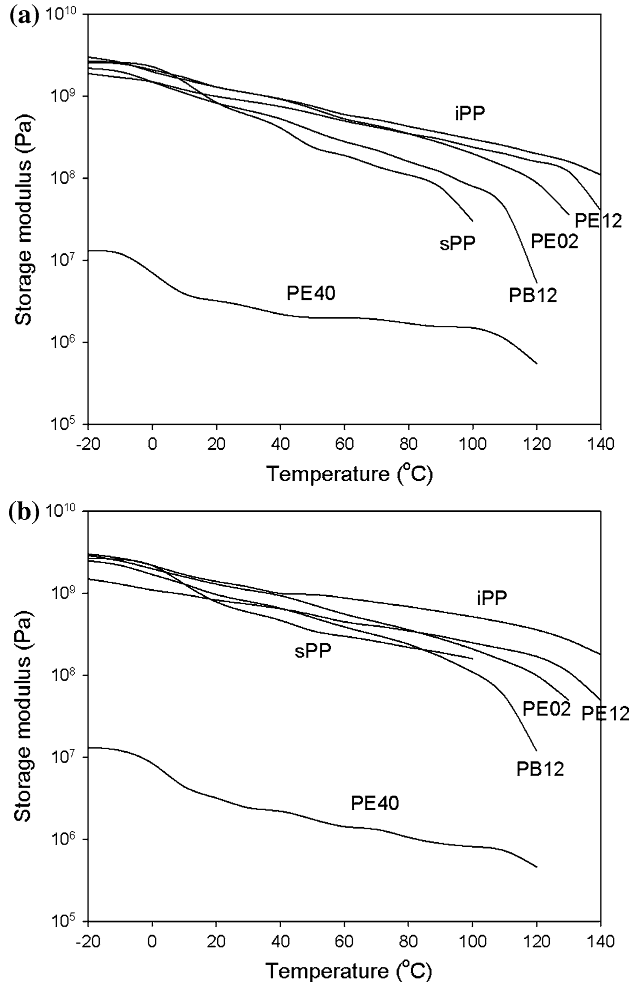

Fig. 6 DMTA test results from **a** quenched samples, **b** isothermally crystallised samples

initially somewhat surprising. However, it is thought that this is due to the two-phase morphology of this material; the interfaces between the ethylene rich domains and the surrounding propylene rich matrix could act as sites for crack propagation. Clearly, for a cable application, a more flexible, less brittle system is preferred, which clearly rules out both iPP and PE12.

Dynamic mechanical thermal testing

Values of the mechanical modulus measured as a function of temperature are shown in Fig. 6 and, as in the tensile testing results shown above, the crystallisation route has only a minor effect on mechanical modulus. The results at room temperature confirm those obtained from tensile testing; five materials show a rather similar behaviour, whereas PE40 displays a significantly lower modulus. Despite the rubbery behaviour of PE40, its modulus is constant at $\sim 10^6$ Pa and only decreases significantly from its room temperature value above 100 °C. Out of the remaining materials, iPP shows the highest modulus and sPP the lowest, whereas PE02, PE12 and PB12 display intermediate values with PB12 having the lowest modulus. Clearly the inclusion of a co-monomer serves to lower the modulus and improves the mechanical flexibility [17], with 1-butene having a greater effect for the same co-monomer content. Compared with XLPE, which has a modulus which falls from 10^8 Pa at room temperature to $\sim 10^7$ pa at 90 °C and $<10^6$ Pa at 110 °C [3], and LDPE which exhibits very poor mechanical properties above 60 °C [9], all of the current polypropylenes exhibit a significantly improved modulus at higher temperatures. Whilst a high modulus at low temperatures may cause problems for cable installation, the good high temperature performance could be a significant advantage at cable operating temperatures, conferring sufficient mechanical integrity to the cable without the need for cross-linking.

Electrical breakdown testing

Weibull plots of the electrical breakdown test results are shown in Fig. 7. Unlike the mechanical properties or melting behaviour, which show very little dependence on the crystallisation route, the electrical breakdown strength is significantly influenced by this variable. Under conditions of quenching (Fig. 7a), all six materials with the exception of PE40 exhibit a characteristic Weibull breakdown strength of 160–170 kV/mm and a shape parameter ranging between 12 and 20. By contrast, PE40 has a breakdown strength of only 49 kV/mm with a shape parameter of only 5. By contrast, identical tests on XLPE tapes (not shown here for clarity) reveal breakdown strengths of between 130 and 150 kV/mm, so under conditions of a rapid quench, five of the six materials outperform XLPE.

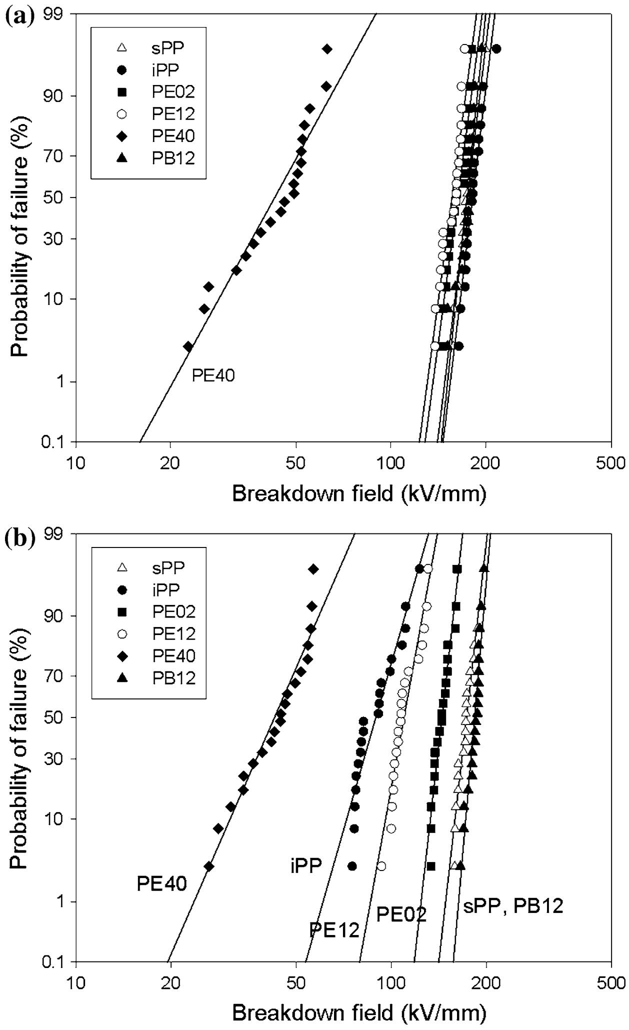

Fig. 7 Electrical breakdown results from **a** quenched samples, **b** isothermally crystallised samples

However, under conditions of isothermal crystallisation (Fig. 7b), the breakdown performance of iPP and PE12 are significantly reduced [17] whereas the other materials offer comparable (within the experimental uncertainties of ±10 kV/mm) breakdown strengths to their quenched counterparts. Under isothermal crystallisation conditions, either spherulites with prominent boundaries or two-phase structures are formed in iPP and PE12, respectively. It therefore appears that the same boundary regions that serve to increase mechanical brittleness also serve to reduce electrical breakdown strength [15–17]; both the mechanical brittleness and poor breakdown strength provide us with very good reasons for rejecting both iPP and PE12 as potential candidate cable materials.

Discussion

Whilst all of the materials so far examined exhibit one or more desirable properties, none possess all of the requirements of low temperature flexibility, high temperature integrity and high breakdown strength required of an ideal thermoplastic insulation system. Further optimisation of the properties is therefore required before any of the current materials would be suitable for future recyclable cables. Out of the six materials considered, sPP and PE40 provide the most desirable combination of good breakdown strength and thermo-mechanical performance. Blends based on these materials and iPP will be examined to determine if their thermo-mechanical and electrical breakdown properties can be further optimised. In a manner akin to previous HDPE/LDPE blends [9, 11, 12], crystallisation was performed at 120 °C for 1 h to ensure complete crystallisation of the iPP within a molten matrix of either sPP or PE40.

Results: blend systems

Differential scanning calorimetry

Figure 8a contains typical DSC melting traces from the four quenched blends. In all of the blend systems, the melting peak at ~160 °C can be associated with the iPP component and this is larger in Blends 2 and 4 as anticipated (see Table 2). In Blends 1 and 2, a second melting peak associated with the sPP component is easy to locate at ~125 °C whereas the low crystallinity PE40 component is much more difficult to detect in Blend 4, manifesting itself as a broad "hump" in Blend 3 (arrowed). The compositions of all the blends were checked by determining the enthalpy of the peak associated with the iPP and comparing it to the results obtained by crystallising this material in isolation over at least three separate samples from the degassed blends. In all blends the composition was accurate to ±5%

across the samples; that is in the blends, the iPP peak showed an enthalpy of ~16 and ~40 J/g for blends containing 20% and 50% iPP, respectively.

Figure 8b shows analogous data for the isothermally crystallised blends. Blends 1 and 2 show an almost identical melting behaviour to their quenched counterparts with the exception of a small peak at ~135 °C, which may indicate that a small fraction of the sPP has undergone isothermal crystallisation. However, the behaviour of the iPP component is quite different in Blends 3 and 4. The double melting behaviour again indicates that significant reorganisation of the iPP is occurring during the DSC scan itself, as wide angle X-ray analysis did not reveal any corresponding γ population. The reorganisation which serves effectively to "anneal" crystals from the lower melting to the upper melting peak is clearly more pronounced in Blend 3 which has the lowest in iPP content. This would indicate a progressive reduction of the thermodynamic stability of the iPP crystals that are formed isothermally within a molten matrix composed of an increasing concentration of PE40 (which is effectively an amorphous material).

The similarity of the melting behaviour of the PE40 and sPP components to those manifested after quenching

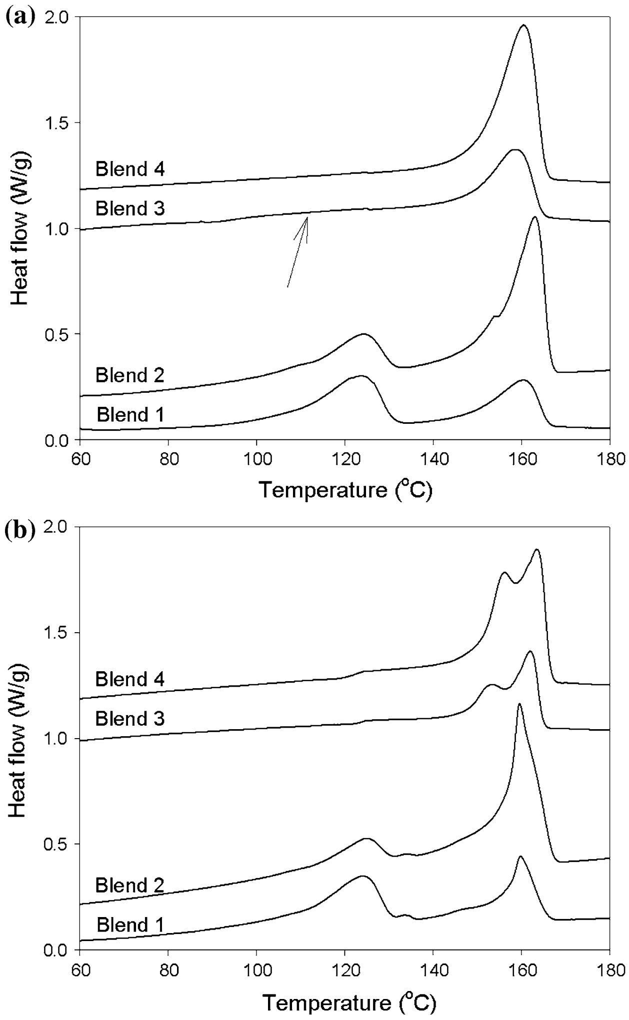

Fig. 8 DSC results for the blends **a** quenched, **b** isothermally crystallised

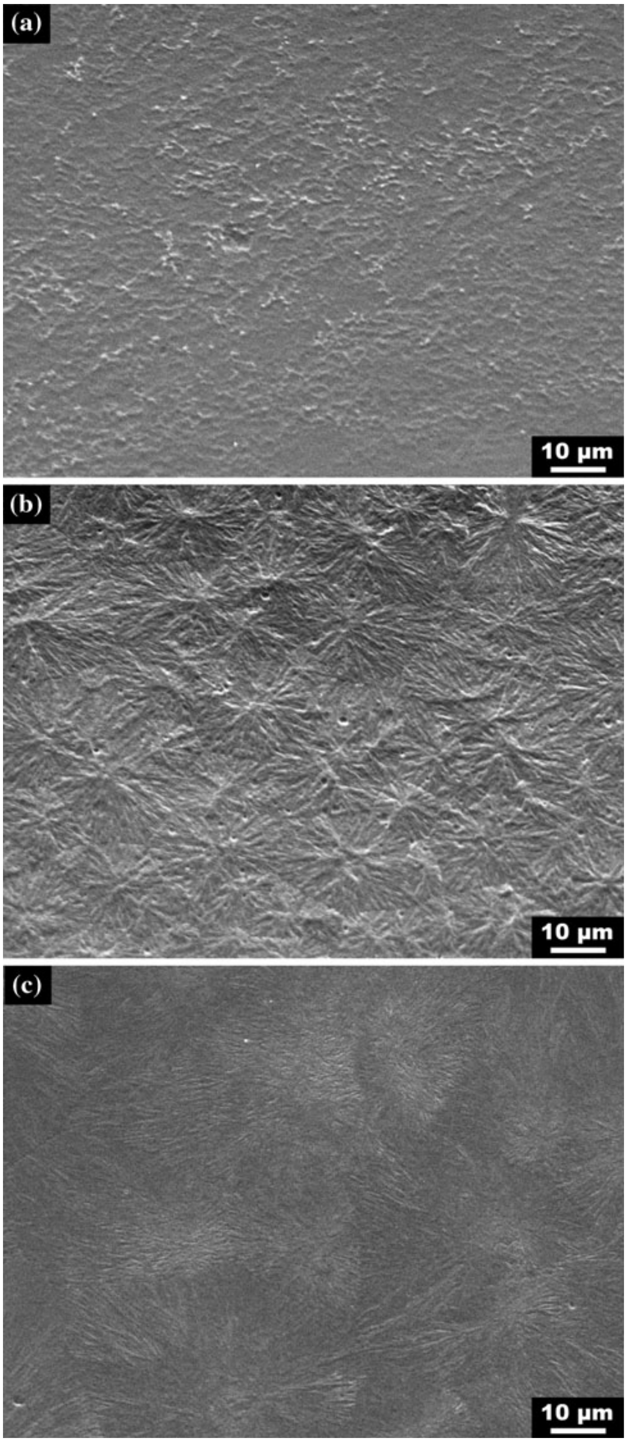

Fig. 9 SEM micrographs of quenched blends **a** Blend 1, **b** Blend 2, **c** Blend 4

indicates that these components undergo very little crystallisation at 120 °C, as required.

Morphology

Figure 9 contains SEM micrographs of the quenched blend systems. Blends 1 and 2 exhibit crystals of iPP in a matrix of sPP; in Blend 1 (Fig. 9a) these crystals are isolated and do not possess any long range order whereas, in Blend 2 (Fig. 9b), a texture of open spherulites is formed. In Blend 3 very little lamellar detail can be resolved whereas, in Blend 4 open, tenuous spherulitic structures are observed (Fig. 9c).

Similar morphologies are exhibited after crystallisation at 120 °C (Fig. 10), Blend 1 contains individual crystals of iPP in an sPP matrix (Fig. 10a) and in Blend 2 (Fig. 10b) these crystals are organised into spherulitic forms containing short "blocky" crystals. In Blend 3 (Fig. 10c) the organisation is such that tenuous spherulitic forms can be resolved in the SEM and finally, in Blend 4 the spherulites become more space filling and are better resolved at SEM resolution (Fig. 10d).

With both sPP and PE40 as matrix, blends with iPP contents of only 20% tend to form individual crystals within that matrix, whereas increasing the iPP content to 50% leads to open spherulitic forms. Whilst the structures are clearly more apparent and better organised following isothermal crystallisation, the crystallisation of iPP is clearly impeded in Blends 3 and 4 as suggested by the DSC data.

Tensile testing

Figure 11a shows tensile testing data for the quenched blends. Blends 1 and 2 exhibit the characteristic "necking" behaviour that was previously associated with several of the co-polymers but, crucially, the two blends do not show the brittle behaviour associated with iPP. The modulus of both systems at small strains is $\sim 10^9$ Pa and is therefore similar to sPP. By contrast, Blends 3 and 4 exhibit a rubbery behaviour, with no signs of necking, but with a higher modulus than PE40, $\sim 10^7$ and 10^8 Pa, respectively; clearly the iPP has a stiffening effect.

After isothermal crystallisation (Fig. 11b), all four blends show the brittle fracture behaviour associated with iPP. Blends 1 and 3, having the least iPP content, show the highest strain at failure, ~20 and 40%, respectively, whilst the corresponding blends with 50% iPP show less favourable properties. Again more iPP leads to a more brittle material. This indicates that isothermal crystallisation of the iPP under conditions where large spherulites are formed (see Fig. 10) has detrimental effects on the mechanical properties, even within a blend system.

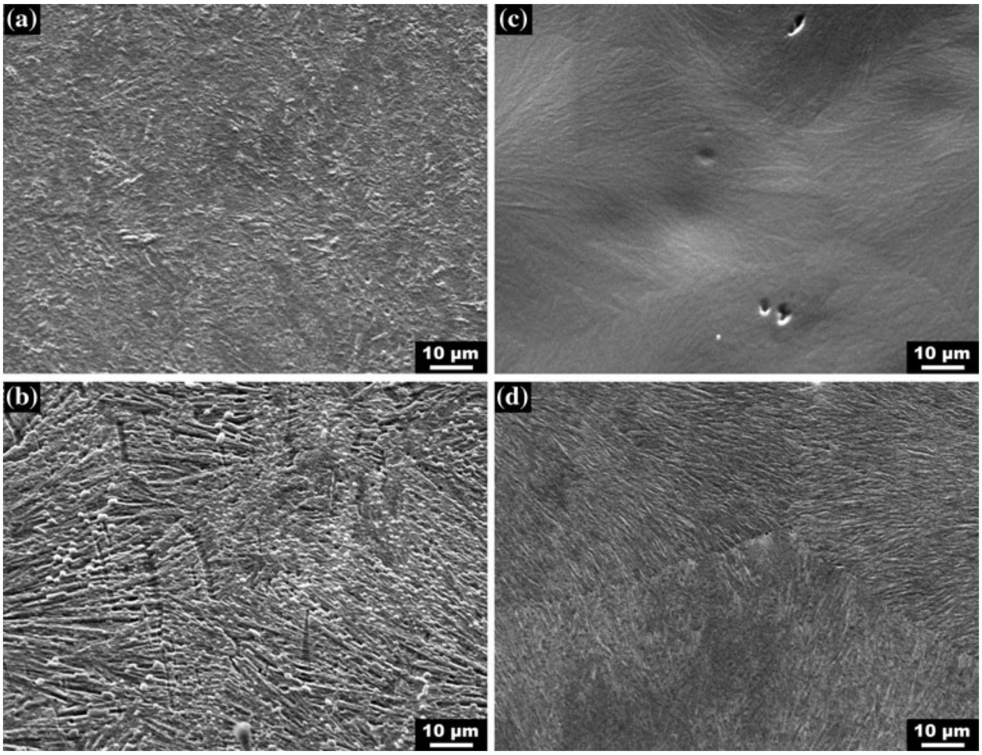

Fig. 10 SEM micrographs of isothermally crystallised blends **a** Blend 1, **b** Blend 2, **c** Blend 3, **d** Blend 4

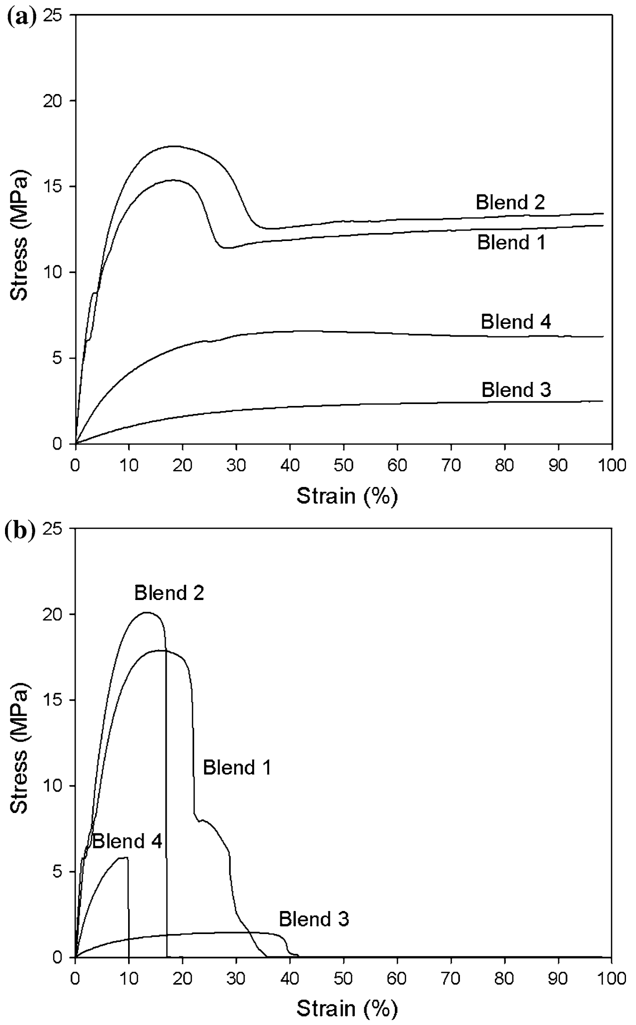

Fig. 11 Tensile test results from **a** quenched blends, **b** isothermally crystallised blends

Dynamic mechanical thermal testing

Figure 12 shows DMTA data from quenched and isothermally crystallised samples. As discussed above, Blends 1 and 2 possess a modulus at room temperature of $\sim 10^9$ Pa so are probably too stiff for use in cables. However, Blends 3 and 4 offer a useful compromise in properties with Blend 4 (50% iPP in PE40) approaching the “ideal” thermo-mechanical characteristic associated with XLPE [3]. Despite these issues, all the blends appear to give sufficient mechanical rigidity at temperatures exceeding 110 °C, with the high temperature stability being improved after isothermal crystallisation (Fig. 12b). Unfortunately, such blends can show brittle behaviour (Fig. 11b), particularly in those systems that exhibit distinct inter-spherulitic boundaries, for example, Blend 4. In this regard rapid crystallisation is preferable to isothermal crystallisation.

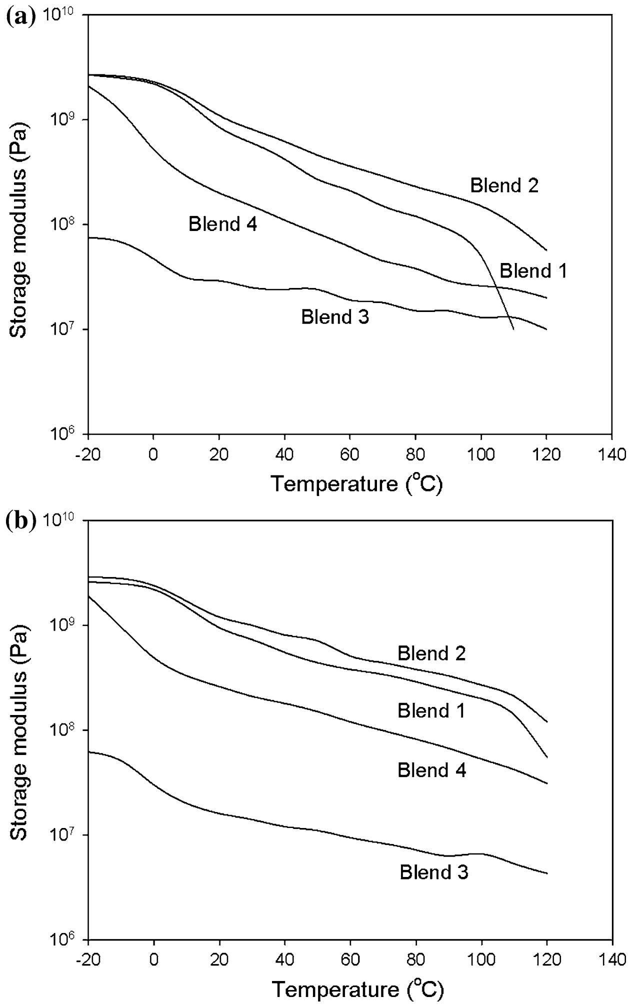

Fig. 12 DMTA results from **a** quenched blends, **b** isothermally crystallised blends

Electrical breakdown testing

Figure 13a shows the electrical breakdown data for the quenched blends. Blends 1 and 2 offer comparable breakdown performance to sPP ($\sim$180 kV/mm); the addition of iPP to sPP clearly has a negligible effect on the electrical properties. Blend 3 shows the lowest breakdown strength of the four blends ($\sim$130 kV/mm) but is significantly improved compared to PE40 ($\sim$50 kV/mm, see Fig. 7a); the addition of iPP therefore overcomes the low breakdown strength associated with PE40 in isolation. The addition of further iPP (Blend 4) increases the breakdown strength, but only to $\sim$140 kV/mm.

Figure 13b shows analogous data for isothermally crystallised samples, the relative order of the blends is preserved and Blends 1 and 2 exhibit no significant change in their electrical breakdown strengths compared to quenching. By contrast, Blends 3 and 4 show markedly lower breakdown strengths than their quenched counterparts ($\sim$120 and

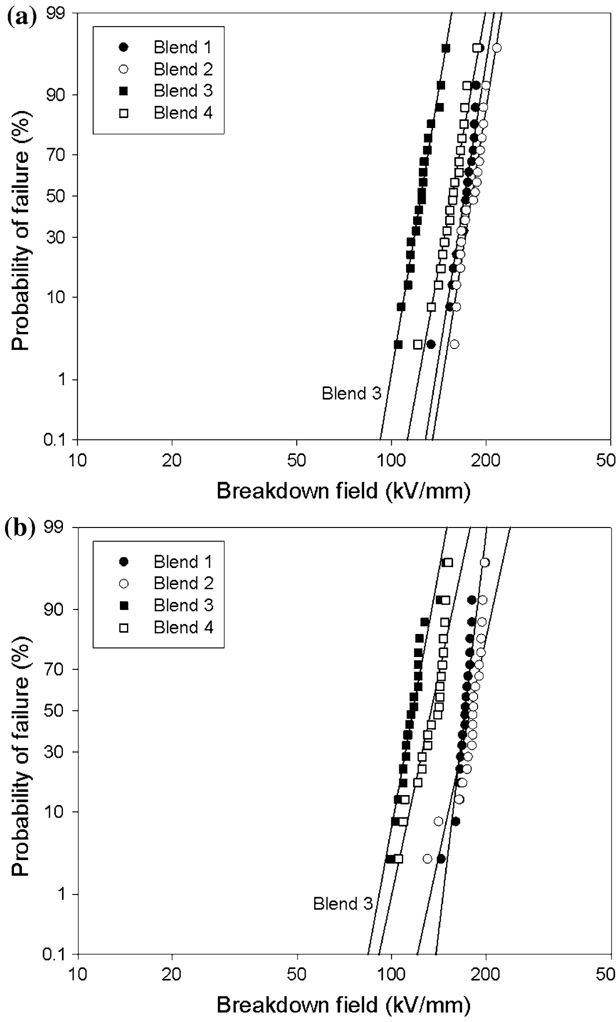

Fig. 13 Electrical breakdown results from **a** quenched blends, **b** isothermally crystallised blends

~140 kV/mm, respectively). Despite these problems, unlike iPP crystallised isothermally (see Fig. 7b) none of the blends exhibit a dramatic decrease in breakdown strength following isothermal crystallisation suggesting that the inter-spherulitic regions have been reinforced electrically by the addition of the low melting component.

Discussion

Blends 1 and 2 clearly offer the best breakdown performance out of the four blend systems, but are too stiff at room temperature for use in a practical cable. In particular, after isothermal crystallisation these blends take on the brittle nature of iPP.

PE40 clearly has very desirable mechanical properties but has very poor breakdown performance. By adding iPP, its breakdown performance can be dramatically improved without sacrificing mechanical properties. Out of the two PE40-based blends considered, Blend 4 offers very similar thermo-mechanical properties to XLPE, combined with a breakdown strength which is much better than that measured from comparable XLPE samples. Rapid crystallisation of this material ensures the highest breakdown strength combined with good mechanical flexibility at low temperatures and adequate mechanical integrity up to 120 °C. By contrast, isothermal crystallisation has deleterious effects on mechanical properties and can reduce the electrical breakdown strength to a degree.

Conclusions

1. Six propylene-based systems have been studied by differential scanning calorimetry, scanning electron microscopy, tensile testing, dynamic mechanical thermal analysis and by electrical breakdown testing to determine which could be suitable for inclusion into future recyclable high voltage cables.
2. Whilst all six materials had sufficiently high melting temperatures for cable applications, five of the materials had a mechanical modulus that was too high and the remaining material had a mechanical modulus that was too low for cable applications. However, these materials do have the advantage that their mechanical properties are retained up to sufficiently high temperatures for cable applications without the need for cross-linking.
3. Two of the materials, iPP and PE12 showed rather brittle behaviour and poor electrical breakdown performance when crystallised at high temperatures and were rejected early on as candidate cable materials. Whilst all of the materials studied exhibit one or more desirable characteristics, none possesses all of the requirements of low temperature flexibility, high temperature integrity and high breakdown strength required by an ideal thermoplastic insulation system.
4. The technique of blending was used to determine if such an optimal balance of mechanical, thermal and electrical properties could be achieved using the current materials. Two pairs of blends based on sPP and PE40 were investigated and iPP was incorporated at concentrations of 20 and 50%.
5. A blend containing 50% iPP in PE40 (Blend 4) appears to provide the best balance of properties for use in a future cable system; rapidly crystallising these systems gives sufficient mechanical flexibility combined with adequate electrical breakdown strength whilst slow crystallisation can be deleterious for mechanical properties and makes the materials more brittle.

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