Propylene based systems for high voltage cable insulation applications

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Abstract. Crosslinked polyethylene (XLPE) remains the material of choice for extruded high voltage cables, possessing excellent thermo-mechanical and electrical properties. However, it is not easily recyclable posing questions as to its long term sustainability. Whilst both polyethylene and polypropylene are widely recycled and provide excellent dielectric properties, polypropylene has significantly better mechanical integrity at high temperatures than polyethylene. However, while isotactic polypropylene is too stiff at room temperature for incorporation into a cable system, previous studies by the authors have indicated that this limitation can be overcome by using a propylene-ethylene copolymer. Whilst these previous studies considered unrelated systems, the current study aims to quantify the usefulness of a series of related random propylene-ethylene co-polymers and assesses their potential for replacing XLPE.

1. Introduction
Whilst paper/oil cable systems are still commonplace, their use is being gradually phased out in favour of extruded cables employing a solid dielectric medium. The dielectric material of choice is polyethylene, which is cheap, has a very low electrical loss and can be easily processed. However, it must be able to withstand in-service conductor temperatures up to ~90 °C and for this reason, crosslinked polyethylene (XLPE) is widely used due to its enhanced thermo-mechanical stability [1]. However, this material is not easily recycled, posing questions as to its long term sustainability.

Traditional thermoplastics such as polyethylene and polypropylene are currently widely recycled so provide, potentially, a suitable replacement for XLPE in cables over the medium to long term. However, previous studies of ethylene based systems indicate that they lack the required thermo-mechanical stability at high temperatures [2]. In recent years a number of novel new propylene based co-polymers have become available through the use of novel catalyst systems [3] which provide a much more viable option. Propylene based systems have the advantage of offering a much higher melting point than ethylene based systems, making them capable of withstanding high operating temperatures without the need to crosslink. In this regard, previously [4], we have considered a range of unrelated propylene-based co-polymers. We report here on a complementary investigation of a range of related random propylene-ethylene co-polymers and assess their suitability for future recyclable extruded cable systems.
2. Experimental

2.1. Materials and preparation
Five different propylene based systems supplied by Borealis were studied, as detailed in Table 1. HD244 is a standard isotactic polypropylene, SA233 is a random heterophase propylene-ethylene copolymer whereas the remaining materials are random propylene-ethylene copolymers. Preparation of ~1.7 mm thickness plaques was undertaken using a hydraulic press and aluminium moulds. Preparation of 70 µm films for electrical testing was undertaken using a Grasby Specac 25.011 hydraulic press with constant thickness film maker. All samples were pre-melted at 200 °C for 2 min, pressed, and then allowed to relax for a further 5 min. Samples were then either quenched directly into water at 25 °C or crystallised isothermally between 100 and 125 °C in an oil bath. Crystallisation times ranged between 15 min and 24 h so as to ensure the maximum extent of crystallisation.

Table 1: Polymers used in this investigation

| Designation | Ethylene content (%) |
|-------------|----------------------|
| HD244       | 0                    |
| RD204       | 2.2                  |
| RD226       | 3.4                  |
| RD208       | 4.9                  |
| SA233       | ~10                  |

2.2. Sample characterisation
Thermal analysis of ~5 mg samples was undertaken using a Perkin Elmer DSC-7 at a scan rate of 10 K/min. Samples for morphological investigation were micromoulded and then etched for a period of 6 hours in a 1% solution of potassium permanganate dissolved in an acid mixture composed of 2 parts water, 5 parts phosphoric acid and 5 parts sulphuric acid according to published techniques [5]. Samples were then mounted onto standard aluminium SEM stubs, gold coated and examined at 20 kV in a Cambridge Instruments Stereoscan 360 scanning electron microscope. Tensile testing was undertaken at 5 mm/min using an Instron 4301 tensile tester. Dynamic mechanical thermal analysis was performed using a Rheometrics RSA II at a fixed frequency of 100 s⁻¹ and a strain of 0.02 % using a dual cantilever geometry. Dielectric breakdown tests were performed according to ASTM D149-87 using opposing 6.25 mm steel ball bearings immersed in a tank of silicone fluid. An increasing 50 Hz AC voltage was applied at a rate of 50 V/s until failure. The results from 20 such tests were then analysed using Weibull statistics.

3. Results

3.1. Thermal analysis
The assignment of the various melting peaks was made with reference to complimentary wide angle X-ray scattering performed on the same samples according to published procedures [6]. A common behaviour with increasing crystallisation temperature was observed. After quenching, a singular melting peak associated with α crystals was always obtained, whilst at intermediate crystallization temperatures, reorganization occurs during the DSC scan, resulting in a “doubling” of this peak. Finally, at the highest crystallization temperatures, an additional lower melting peak, associated with γ crystals, appears which then increases in intensity with further increases in crystallization temperature.

With increasing ethylene content, the latter peak associated with γ crystals becomes more intense and also first appears after crystallization at lower temperatures. In HD244 it first appears after crystallization at 125 °C (arrowed, figure 1a) whereas in RD204 it appears at 120 °C or above (arrowed, figure 1b). In RD226 the same peak (arrowed, figure 1c) first becomes significant after crystallization at 110 °C and finally, in RD208 and SA233 it is apparent after crystallization at 100 °C.
In all these materials, the maximum $\gamma$ content, obtained after crystallization at 125 °C, ranged from ~5 % in HD244 to ~70 % in SA233. Finally, by considering any fixed crystallization temperature, both the melting peak and enthalpy decrease with increasing ethylene content.

Whilst the details of the crystallization of these materials are clearly complex, the increasing prevalence of the $\gamma$ phase and the reduction in melting point and enthalpy with increased co-polymer content are in line with similar studies on well characterised propylene-ethylene co-polymers [6]. Most importantly, from the perspective of future cable designs, all the materials considered here display a melting peak in excess of 120 °C, which is significantly higher that the ~105 °C which is normally associated with XLPE [7].

![Figure 1: DSC traces from (a) HD244, (b) RD204, (c) RD226](image)

3.2. Morphology

After quenching, small spherulites were observed in HD244 and RD204 as shown in figure 2a, but in co-polymers with > 3 % ethylene content these were replaced with a uniform lamellar texture (figure 2b).

![Figure 2: SEM micrographs of quenched samples (a) RD204, (b) RD226](image)

Crystallisation at higher temperatures reduces the nucleation density and so larger spherulites form. In HD244 and RD204 crystallised at the highest temperatures, these possess distinct boundaries (figure 3a). At higher ethylene contents, or at lower crystallisation temperatures, their boundaries become less distinct as shown in figure 3b. Under isothermal crystallisation, spherulitic forms generally persist up to ~5 % ethylene content; in SA233 the morphology is always a uniform texture of fine lamellae. The above effects of crystallisation temperature and ethylene content on morphology are in line with complementary studies on a range of well characterised random metallocene propylene-ethylene co-polymers [8].
3.3. Tensile testing
After quenching (figure 4a), all five materials display a characteristic necking behaviour [4] after ~20 % imposed strain and do not fail under the loadings imposed here. With increasing isothermal crystallisation temperature, samples low in ethylene content display a much more brittle behaviour. The end result of this is that, at the highest crystallisation temperatures (figure 4b), both HD244 and RD204 catastrophically fail at strains of 15 % and 28 % respectively. These materials both exhibited characteristic brittle fracture surfaces when subsequently examined under an optical microscope. By contrast, the remaining materials, which are higher in ethylene content, retain the necking type behaviour. Whilst none of these materials display the ideal rubbery behaviour associated with XLPE [9], clearly, materials having an ethylene content in excess of ~2 % are required to avoid an unwanted brittle-fracture type of behaviour after crystallising at higher temperatures.

3.4. Dynamic mechanical thermal analysis
The modulus measured at small strains did not show a significant dependence on crystallisation conditions, therefore only data pertaining to quenched samples are shown in figure 4c. The behaviour is in line with the previous propylene co-polymers [4] and HD244 shows, at room temperature, a typical modulus of ~10^9 Pa. This is far greater than the ~10^8 Pa which is typical of XLPE [9]. Nevertheless, with increasing ethylene content, significant reductions in the modulus are achievable, with SA233 showing the most favourable properties. It is clear from the figure that good thermo-mechanical stability is maintained up to ~110 °C without the need for cross-linking.

3.5. Dielectric breakdown
Figure 5 shows breakdown data for various materials. After quenching, the Weibull scale parameter is typically ~180 kV/mm, which is considerably higher than the ~150 kV/mm associated with polyethylene systems [2]. The measured value is independent of ethylene content within the uncertainty associated with these measurements (± 10 kV/mm). However, differences occur between the materials following crystallisation at higher temperatures; in particular HD244 exhibits a significantly poorer breakdown performance when crystallised at 115 or 125 °C (figure 5a) as does...
RD204 after crystallisation at 125 °C (figure 5b). The prominent spherulitic boundaries which occur under these crystallisation conditions could explain these results and also the rather poor (brittle) mechanical behaviour of these systems. The remaining materials all exhibit a breakdown strength which is largely independent of crystallisation route, within experimental uncertainties (figure 5c).

**Figure 5**: Weibull plots for (a) HD244, (b) RD204, (c) RD226

4. Conclusions
A range of propylene-ethylene co-polymers were examined and the changes in melting behaviour and morphology were in line with previous investigations. Samples low in ethylene content crystallised at higher temperatures were mechanically brittle and had poor electrical strength which could be associated with the rather prominent spherulitic boundaries observed in these cases. A certain amount of ethylene is required to reduce the mechanical modulus, improve the elasticity and ensure that the breakdown strength remains high over all crystallisation conditions. Out of the materials considered here, SA233, a co-polymer containing ~10 % ethylene, offers the most optimal properties for use in a future recyclable extruded high voltage cable.

5. References
[1] Vahedy V 2006 IEEE Electr. Insul. Mag. 22 13-18
[2] Hosier I L, Vaughan A S and Tseng W 2007 Proc. 9th Intern. Conf. on Solid Diel. 184 – 7
[3] Langhauser F, Kerth J, Kersting M, Kolle P, Lilge D and Muller P 1994 Angew. Makromol. Chem. 223 151-64
[4] Hosier I L, Reaud S, Vaughan A S and Swingler S G, 2008 Conf. Rec. of the 2008 Intern. Symp. on Electr. Insul. 502-5
[5] Olley R H, Bassett D C 1982, Polymer 23 1707-10
[6] Hosier I L, Alamo R G and Lin J S, 2003 Macromolecules 36 5623-36
[7] Hosier I L, Vaughan A S, Campus A and Nilsson U 2007 Proc. 9th Intern. Conf. on Solid Diel. 227-30
[8] Hosier I L, Alamo R G, Lin J S 2004 Polymer 45 3441-55
[9] Martin C P 2004 The impact of mechanical stress on the mechanical integrity of XLPE cables, PhD Thesis, University of Southampton.

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