THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Thermoplastic Insulation for High Voltage Cables

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Göteborg, Sweden, 2020

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Cover:
"A Pikachu figurine 3D-printed from a thermoplastic blend"

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ABSTRACT

High voltage direct current (HVDC) cables that seamlessly integrate renewables have an important contribution to the modern world's efforts towards a more sustainable future. Extruded HVDC cables that efficiently and reliably transport electricity require robust insulation materials with good thermomechanical and dielectric properties. Peroxide-crosslinked polyethylene (XLPE) has been the conventional insulation material for extruded HVDC cables. However, peroxide crosslinking releases by-products that need to be removed, necessitating an expensive and time-consuming degassing procedure. Furthermore, XLPE is a thermoset material, which cannot be recycled by re-extrusion. Thermoplastic materials are therefore sought after as more sustainable material alternatives for HVDC cable insulation. Blends that contain isotactic polypropylene (iPP) are of great interest due to the thermomechanical reinforcement that its high melting crystals can offer. However, iPP alone is too brittle. Blends comprising iPP and softer components like polyethylene could give properties desired in cable insulation, but the incompatibility between iPP and LDPE must be considered. This thesis presents reactive compounding as a strategy to form PP–PE-type copolymers in-situ in a recyclable ternary blend comprising an ethylene-glycidyl methacrylate copolymer, a maleic anhydride-grafted polypropylene and low density polyethylene (LDPE). The material demonstrated excellent thermomechanical and DC dielectric properties, reflecting this novel strategy as a promising one for the design of recyclable insulation materials for future HVDC cables.

NOMENCLATURE

DC   Direct-current

DMA   Dynamic mechanical analysis

HDPE   High density polyethylene

HVAC   High voltage alternating current

HVDC   High voltage direct current

iPP   Isotactic polypropylene

LDPE   Low-density polyethylene

PE   Polyethylene

PP   Polypropylene

SEM   Scanning electron microscopy

PUBLICATIONS

This thesis consists of an extended summary of the following appended papers:

Paper I   **Recyclable Polyethylene Insulation via Reactive Compounding with a Maleic Anhydride-grafted Polypropylene,** Yingwei Ouyang, Massimiliano Mauri, Amir Masoud Pourrahimi, Ida Östergren, Anja Lund, Thomas Gkourmpis, Oscar Prieto, Xiangdong Xu, Per-Ola Hagstrand, Christian Müller. *ACS Applied Polymer Materials*, 2020. (DOI: 10.1021/acsapm.0c00320)

The author has published the following papers which are not included in the thesis:

Paper II   **Click chemistry-type crosslinking of a low-conductivity polyethylene copolymer ternary blend for power cable insulation,** Massimiliano Mauri, Anna I Hofmann, Diana Gómez-Heincke, Sarath Kumara, Amir Masoud Pourrahimi, Yingwei Ouyang, Per-Ola Hagstrand, Thomas Gkourmpis, Xiangdong Xu, Oscar Prieto, Christian Müller, *Polymer International*, 2019, **69**, 404-412.

Paper III   **Electrical Characterization of a New Crosslinked Copolymer Blend for DC Cable Insulation,** Sarath Kumara, Xiangdong Xu, Thomas Hammarström, Yingwei Ouyang, Amir Masoud Pourrahimi, Christian Müller and Yuriy V. Serdyuk, *Energies*, 2020, **13**, 1434.

CONTRIBUTION REPORT

Paper I   Main author, All sample preparations, DSC, shear rheometry, thermomechanical measurements and SEM imaging, and data analysis.

Paper II   Co-author. Sample preparation.

Paper III   Co-author. Sample preparation.

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Chapter 1

INTRODUCTION

1.1 The energy problem

The industrial revolution was a major turning point in the history of human civilisation. Ever since the seminal invention of the Watt steam engine by Scottish mechanical engineer, inventor and chemist James Watt, humans have become increasingly reliant on mechanisation and automation which has increased our demand for energy. The global demand for energy is predicted by the World Energy Council to increase by at least 35% (compared to 2010) by 2030.[1] Meanwhile, the world faces two major problems – global warming and the depletion of finite resources. Fossil fuels for instance is a non-renewable source of energy that has been and still is being burnt for energy, generating greenhouse gases that undoubtedly contribute to global warming. The modern world requires sustainable solutions to cope with our ever-increasing energy demand in order to protect our planet and our future generations.

Various technologies have been developed with a vision to eliminate our reliance on non-renewable resources like fossil fuels. These include the harnessing of renewable energy, but also technologies for energy storage and transmission. Renewable energy infrastructures such as solar and wind farms are often located far away from populated areas, and therefore need to be coupled with efficient systems for energy storage and transmission. Furthermore, the amount of energy available from such renewable energy infrastructures varies depending on the weather, which would result in the intermittence of energy supplies. The use of non-

renewables to feed the global demand for energy can only be fully phased out if the energy supply from renewables is reliable enough. By connecting various renewable energy infrastructures and populated areas with a power grid, those who usually rely on solar energy can still get energy from wind turbines elsewhere along the power grid on a cloudy day. That of course, is only true if the power grid is connected by power cables that transport electricity efficiently.

1.2 High voltage direct current (HVDC) cables for a sustainable future

Currently, energy transport systems are largely dominated by high-voltage alternating current (HVAC) technology, but high voltage direct current (HVDC) lines are increasing in popularity.[2, 3] This is due to the much lower electrical losses that occur in HVDC cables compared to HVAC cables when transporting electricity over several hundred kilometres,[2, 4, 5] as in the case of the earlier-mentioned power grids that integrate renewables. To boost the performance of these cables, electrical power has to be increased.[5, 6] This can be achieved by increasing either current and voltage since both are proportional to electrical power.[6] However, high currents are associated with energy loss via Joule heating.[5, 6] As a result, great efforts in the field have been invested in the development of cables of increasing voltages. The implications of the higher voltages however are higher temperatures and electric fields, which have to be considered in cable design.

These harsher conditions do not pose huge problems in overhead transmission lines since they are readily insulated by the surrounding air. However, overhead lines are unpopular due to their visual impact on the environment.[2] Furthermore, they are not suitable for the electrical transmission across seas[2, 7] which are required for the extensive integration of renewables. There is therefore growing demand for undersea and underground HVDC cables,

but these cables require robust insulation materials that can withstand the higher temperatures and electrical fields that arise from the high voltages. Paper-oil-type systems and extruded systems are some types of insulation that have been developed for HVDC cables.[2, 3, 8] The latter has gained increasing popularity due to the significant advantages it offers over the former.[3] These include the capability to withstand higher operation temperatures (at least 90 °C) that allows for higher transmission capacity,[2, 3, 9] lighter weight, simpler jointing procedures, and the elimination of environmental concerns over oil leakages.[3, 9]

In extruded cables, a polymeric insulation layer is wrapped around the conducting core. (Figure 1) This insulation layer not only needs to have good electrical insulation properties but must also support the weight of the conducting core throughout the lifetime of the cable (~50 years). During its lifetime, a cable is heated to around 70-90 °C[2, 4, 10] (or higher depending on the voltage) during operation. However, it also experiences tougher conditions during overload situations such as during a lightning strike, when temperatures can go up to 140 °C.[2] Under these conditions, the insulation layer is subjected to a compressive stress by the conducting core which can go up to around 4 kPa for a 3000 mm^2 copper core. This is substantial given the cable lifetime and the high temperatures that the insulation layer will experience. If the mechanical integrity of the insulation material is insufficient at high temperatures, the insulation layer will soften and cause gradual sinking of the conducting core. This will eventually lead to electrical breakdown and therefore must be avoided.

In addition to good thermomechanical properties, it is also crucial that the cable insulation material possesses low electrical DC conductivity. If the material's DC conductivity is not kept to low levels, there will be substantial residual electrical current that will generate heat to create a temperature gradient in the insulation layer. This temperature gradient is

proportional to the electrical field squared.[2] This means that a large temperature gradient will lead to a higher electrical field, but also that the enhanced electrical field will increase the temperature gradient further, leading to thermal runaway.[11] Clearly, it is important that the insulation materials in HVDC cables are well-engineered to cope with the conditions that they will undergo during their lifetime.
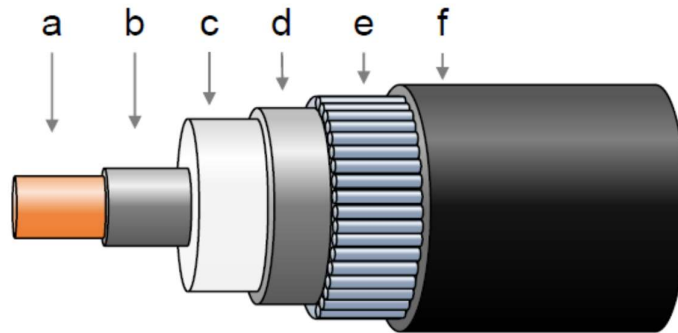

Figure 1. Schematic of a typical extruded underground high voltage cable: (**a**) conducting core, (**b**) inner semiconducting layer, (**c**) insulation layer, (**d**) outer semiconducting layer, (**e**) metallic screen, and (**f**) outer sheath.[12]

1.3 Project aim

As the world continues to face major challenges such as global warming and the depletion of non-renewable resources, development of extruded HVDC cable technologies are crucial in the world's efforts towards a more sustainable future. The objective of my project is to develop new material solutions for HVDC cables, with a focus not only on material properties but also sustainability – through the design of thermoplastic blends that offer recycling possibilities via re-extrusion.

Chapter 2

INSULATION MATERIALS FOR EXTRUDED HIGH VOLTAGE CABLES

2.1 Low density polyethylene and the need for crosslinking

Low density polyethylene (LDPE) is a non-polar polymer consisting of long and short chain branches. (Figure 2) The long chain branches impart flow properties ideal for cable extrusion. More importantly, LDPE can be produced with very high cleanliness. Unlike the linear polyethylenes, LDPE is made in high pressure reactors without catalysts.[13] The absence of catalyst residues in LDPE makes the material very clean, offering a huge advantage in terms of dielectric properties. However, LDPE has a severe limitation. It has a wide and low melting peak (T_m) at around 110 °C, and already starts to soften at ~90 °C. As the LDPE crystals melt, the LDPE polymer chains slide past each other when subjected to even low stresses, causing loss of mechanical integrity.
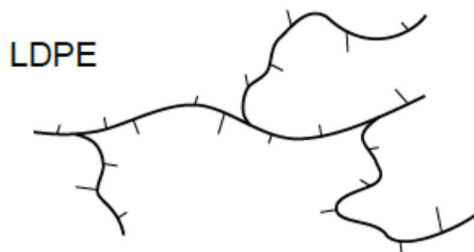

Figure 2. Schematic of the structure of low density of low density polyethylene (LDPE).[12]

For HVDC cable applications, the mechanical performance of LDPE at elevated temperatures must be improved by introducing a network that holds above the melting point of LDPE. The mechanical properties of LDPE above its melting peak (T_m) can be enhanced by forming crosslinks in the material. A crosslink is defined by IUPAC as 'a small region in a macromolecule from which at least four chains emanate'.[14] With sufficient crosslinks, a network of LDPE chains is formed, resulting in a crosslinked material that does not flow even above the LDPE T_m. Such behaviour is due to the connection of LDPE chains in the network that prevent the chains from sliding past each other, resulting in excellent mechanical properties at high temperatures.

2.2 Chemically crosslinked polyethylene

Crosslinking of LDPE with dicumyl peroxide to form crosslinked polyethylene (XLPE) (Figure 3) is the conventional solution used in HVDC cables.[2] Although XLPE has enhanced thermomechanical properties, the crosslinking reaction with peroxides generates byproducts like water, methane, water, α-methylstyrene, acetophenone, cumyl alcohol.[15, 16] These species compromise the cleanliness of XLPE and can result in the deterioration of the material's properties. As a result, XLPE has to be subjected to a degassing procedure after crosslinking in order to remove these unwanted byproducts.[17] Degassing involves the heating of the cable to 50-80 °C for long times prior to jacketing, which is unfortunately a costly and time-consuming process.[18] Alternatives that eliminate the need for degassing would be more sustainable and are therefore sought after.
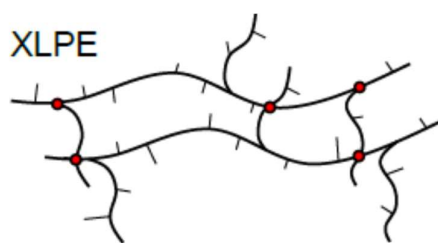
Figure 3. Schematic of the structure of crosslinked polyethylene (XLPE), where the red circles indicate chemical crosslinks.[12]

The crosslinking of polyethylene via click chemistry, which is by-product free, has been explored as an alternative to conventional XLPE.[19-22] These novel materials have been reported to have thermomechanical and electrical properties comparable to those of peroxide crosslinking.[19-22] Despite these promising results, these materials, like conventional XLPE, are thermoset. The chemical crosslinks that provide impart high temperature stability also disallow reprocessing the material at the end of its life by extrusion due to its inability to melt.[9]Although one could argue that XLPE can be ground and recycled in the form of fillers,[23] materials that can be recycled by re-extrusion are even more attractive. Re-extrusion is a form of primary mechanical recycling. Materials that can be recycled this way preserve their value to a greater extent after reprocessing compared to XLPE that is ground into fillers. In other words, polymeric materials that can be reprocessed in the melt are more sustainable alternatives to XLPE. Additionally, these materials, also known as thermoplastics, undergo neither the crosslinking nor the degassing procedures which make their production more energy efficient. (Figure 4) Thermoplastic blends have clear advantages from a sustainability viewpoint and have therefore gained significant attention in the field in recent years.
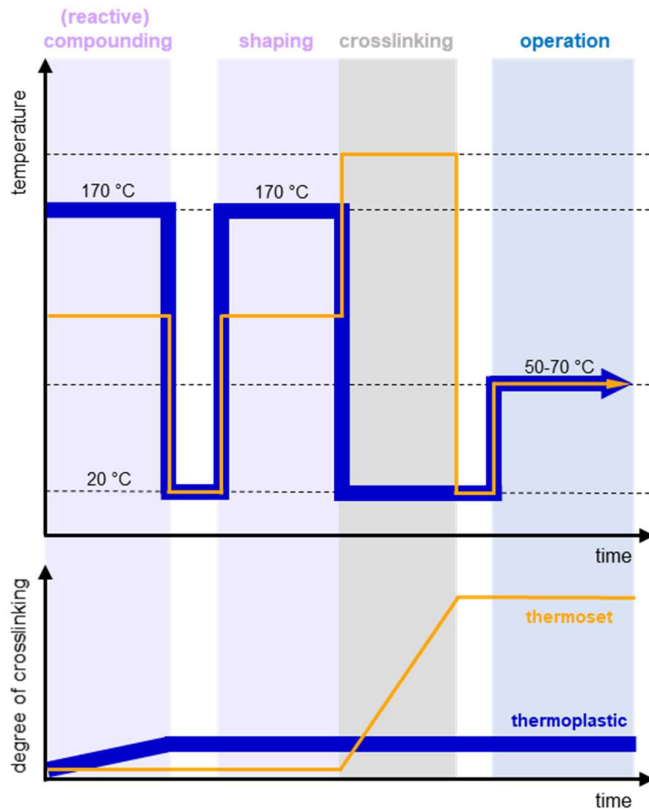
Figure 4. Schematic of the experienced temperature and degree of crosslinking of a traditional *thermoset* cable insulation material (orange line) and a *thermoplastic* insulation material (blue line) during compounding and shaping (purple), the heat activated crosslinking step (grey), which is absent for the thermoplastic material, and operation (blue).

2.3 Physical crosslinking for thermoplasticity

In order to achieve both thermoplasticity and improved thermomechanical properties in LDPE-based blends, a network that holds at the desired temperatures but dissociates upon further heating are required. With the right choice of polymers, physical crosslinks such as polymer crystals, glassy polymer domains and hydrogen bonding moieties[24, 25] can fulfil these requirements. Studies on thermoplastic materials for high voltage cable insulation have been focused on polymer blends that are held together at elevated temperatures

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by polymer crystals that melt at higher temperatures than those of LDPE. In such systems, these higher melting polymer crystals act as network points where polymer chains are 'locked' together below the melting temperature of the crystals. A load-bearing network is attained when these crystals extend throughout a material and are connected via tie-chains and trapped entanglements.[26]

2.3.1   Polyethylene blends

This concept can be applied in polyethylene blends. While the extensive branching in LDPE limits the lamellae thickness of LDPE crystals resulting in the low melting point and poor thermomechanical performance of LDPE, thicker crystalline lamellae can be obtained in the more linear polyethylenes. High density polyethylene (HDPE), for instance, has a melting peak at around 130 ˚C. However, HDPE is polymerised with transition metal catalysts such as Ziegler-Natta and Philips catalysts in low pressure reactors[13] which compromises the material's cleanliness. By adding small amounts of HDPE to LDPE, an improvement in thermomechanical performance relative to LDPE can be achieved while benefitting from the toughness and ultra-high cleanliness of LDPE. However, this is only so if HDPE is well-dispersed throughout the material to form a network.

Fortunately, the dispersion of HDPE in LDPE can be controlled by various parameters. The dispersion of HDPE is governed by the blend microstructures obtained at the end of processing, which is dependent on processing conditions and the nature of the polymers. In blends of LDPE and HDPE, the degree of phase separation of the two polymers in the solid state depends on their melt miscibility. High miscibility in the melt and fast cooling rates will give rise to fine-grained microstructures whereas slow cooling rates and/or poor melt miscibility

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lead to higher degree of phase separation in the solid state.[26] Factors that influence the melt

miscibility of the two polymers include blend stoichiometry, molecular weights of either

polymer, and the degrees of short and long chain branching in LDPE.[27-31] By tuning these

parameters, LDPE/HDPE binary blends can be formulated to resist deformation when subjected

to stress above the melting temperature of LDPE. Andersson et al. demonstrated that such

blends with HDPE content as low as 1-2 wt% were able to arrest creep at 115 ˚C, which is

above the LDPE T_m.[26]

Electrical properties of LDPE/HDPE blends have also been investigated. Like

mechanical properties, the electrical properties of these materials are also influenced by blend

microstructure, which can be optimised with appropriate processing parameters and

formulation composition.[32-34] Dodd et al. formulated a blend comprising 20% HDPE, which,

when extruded into cable geometries, outperformed both LDPE and XLPE in terms of electrical

breakdown strength. While electrical breakdown occurred in LDPE and XLPE at ~350 and 200

kV respectively, the LDPE/HDPE binary blend did not experience breakdown even at the

maximum experimental limit of 400 kV.[35] These promising results were attributed to the higher

density and degree of crystallinity of HDPE.

The thicker lamellae of HDPE also appear to be beneficial to the blends in terms

of DC dielectric properties. An HDPE/LDPE blend with an even lower HDPE content of 1 wt%

has been reported by Andersson et al. to exhibit a DC-conductivity value of 10^{-15} S m^{-1} at an

elevated temperature of 70 °C and high electrical fields of 30 and 40 kV mm^{-1}. This DC

conductivity value is approximately one order of magnitude lower than both XLPE and neat

LDPE.[10] The thick HDPE lamellae appear to be very efficient at suppressing the mobility of

charge carriers in the material to produce such impressive results.[10] Evidently, HDPE/LDPE blends show good potential as thermoplastic insulation materials for high voltage cables.

2.3.2 Polypropylene blends

Apart from polyethylene blends, polypropylene (PP) blends have also gained significant attention as thermoplastic alternatives in high voltage cable insulation and such materials have even been developed into commercial products.[36] This is due to the good dielectric properties of isotactic polypropylene (iPP) and most importantly its high melting point of at least 160 °C (cf. HDPE with T_m ~130 °C), which would allow the voltage and cable operation temperature to be increased if the material is well engineered.[37] However, iPP is too stiff and is brittle at low temperatures which makes neat iPP unsuitable for cable insulation.[37]

To obtain a softer polypropylene-based material, one possibility is to use syndiotactic polypropylene (sPP). sPP has higher flexibility than iPP,[38] and demonstrate excellent thermal stability and dielectric properties.[2, 39] However, its cost limits its commercial applicability.[2, 39] Therefore, extensive research have been conducted on polypropylene blends that incorporate softer components to reduce material brittleness. Unfortunately, incompatibility is a major challenge especially when polyethylene is the softer component – unlike HDPE and LDPE, PP and PE are not melt-miscible. This means that PE and PP phase separate strongly. This is often detrimental to the mechanical properties of PE/PP blends. Several strategies have been used to cope with these challenges in the design of polypropylene-based blends for HVDC cable insulation.[40-46]

One way to incorporate soft components to polypropylene is by covalently linking polypropylene with comonomers (eg. ethylene, butylene) in copolymers. Several studies have shown the potential of single copolymer materials in high voltage insulation.[40, 44-46] Reduction in the degree of phase separation and spherulite sizes have been shown to improve low temperature flexibility and electrical strength. This can be achieved with the right comonomer, appropriate comonomer distribution, copolymer molecular weights and cooling rates.[44-46]

Another strategy is to have a two-component system comprising of PP and a soft PP-copolymer.[40-43] A blend comprising 50% iPP and 50% ethylene/propylene copolymer (9 mol% ethylene) studied by Green et al. exhibited excellent mechanical and electrical properties. At low temperatures, the stiffness of the blend was comparable to XLPE but higher than XLPE at higher temperatures of 120-130 °C. The blend also demonstrated superior performance in electrical breakdown tests, surviving voltages of up to 400 kV (while XLPE did not).[37, 43] This strategy is definitely one of great potential.

This concept of blending PP with a softer component has also been explored with more advanced processing technologies. Multistage copolymerisation technologies have been used to produce heterophasic PP copolymers (HECO) where the PP matrix is first produced followed by the soft components which end up embedded in the PP matrix. The advantage of this processing method is the higher efficiency of mixing. This is reflected in the improved mechanical properties of HECO materials, which have been used as PP impact copolymers.[47-49] These materials could be of interest in high voltage insulation applications, however to our knowledge, electrical characterisation of such materials has not been reported.

Several ways that thermoplastic polypropylene-based blends can be engineered for use in high voltage cables have now been presented, with some materials showing good potential for future application. The materials discussed so far have polypropylene as the base resin. LDPE-based blends reinforced at high temperatures by the incorporation of small amounts of PP could have an added advantage of ultra-low DC conductivity due to the high cleanliness of LDPE. Such blends are analogous to the LDPE/HDPE blends described earlier in the chapter but are more complex due to the incompatibility of the LDPE/PP polymer pair. This can be overcome either by adding a PP-rich copolymer that has good compatibility with LDPE,[50-52] or by having a ternary system containing PP in an LDPE matrix compatibilised by a third component. Although a variety of copolymers have shown compatibilisation effects in PP-PE blends,[53-56] the latter strategy is novel in the field of high voltage insulation. In the next chapter, our work (**Paper I**) on a thermoplastic LDPE-based ternary blend prepared via reactive compounding based on this strategy will be presented.

Chapter 3

POLYETHYLENE MELT REINFORCEMENT WITH CHEMICAL AND PHYSICAL CROSSLINKS VIA REACTIVE COMPOUNDING

In this chapter, we explore the concept of an LDPE-based blend held together by a combination of chemical and physical crosslinks in order to achieve improved thermomechanical properties and thermoplasticity while achieving low electrical DC conductivity. (**Paper I**) To achieve this, we incorporated a small amount of polypropylene to the LDPE-based blend. The idea was to achieve thermomechanical boost from the high melting polypropylene crystals via physical crosslinks that can also dissociate above the PP T_m to allow for recycling via re-extrusion. Since the incompatibility of polypropylene and polyethylene necessitates material design that encourages increased interaction between the two polymers, our choice of polypropylene was a maleic anhydride-grafted (isotactic) polypropylene (PP-*graft*-MA) that has been shown to react with the branched statistical ethylene-glycidyl methacrylate copolymer p(E-*stat*-GMA). The by-product free reaction between these two polymers during compounding forms the basis of the compatibilisation effects and chemical crosslinks in our material, leading to improved mechanical stiffness above the LDPE T_m.

3.1 Chemical crosslinking reaction between polypropylene and polyethylene

The epoxy group in p(E-*stat*-GMA) and the succinic anhydride group on PP-*graft*-MA are responsible for the linkages between the two polymers (reaction scheme in figure 5). However, the succinic anhydride group itself cannot be involved in a nucleophilic attack on the electrophilic epoxy in p(E-*stat*-GMA). The cyclic succinic anhydride in PP-*graft*-MA has to be opened by a nucleophile like water to form two carboxylic acid groups. These carboxylic acid group can then react with the epoxy group in p(E-*stat*-GMA) to covalently link the two polymer chains via an ester bond (with the generation of a hydroxyl group), without the release of any byproducts.
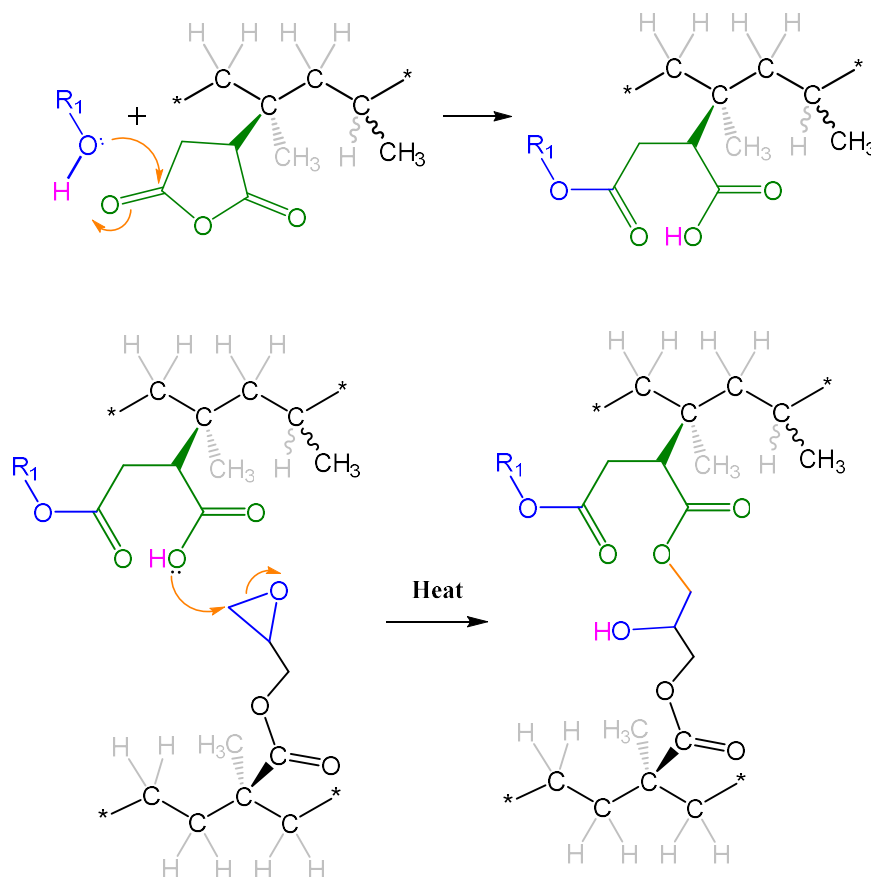

Figure 5. (**a**) Activation of PP-*graft*-MA by ring opening through reaction with water leading to two carboxyl groups, and (**b**) activated succinic anhydride reacts with an epoxy group, part of the GMA comonomer of p(E-*stat*-GMA); the second carboxyl group carries a generic R_1

group because ring opening can occur by reaction with water ($R_1 = H$) but also another carboxyl group or a hydroxyl group that was formed through an epoxy opening reaction.

The first step readily occurs under atmospheric conditions, as evidenced by our variable temperature FTIR measurements on PP-*graft*-MA. (Figure 6a) At 40 °C, the FTIR spectrum of PP-*graft*-MA features two carbonyl absorbance peaks 1718 cm^{-1} and 1781 cm^{-1} corresponding to the stretches of the carboxylic acid groups of the ring-opened anhydride and the closed anhydride respectively. The conversion between these two forms is reversible, and comparison of the spectra of PP-*graft*-MA at increasing temperatures show that higher temperatures favour the closed anhydride form. This is due to the increased evaporation of water at elevated temperatures. At 170 °C, despite a significantly diminished 1718 cm^{-1} acid, the proportion of acid available sufficed for the acid-epoxy reaction to occur to an appreciable extent in a binary blend containing 4:1 ratio of p(E-*stat*-GMA) and PP-*graft*-MA, which contains epoxy and acid groups at a 1:1 molar ratio. This was evidenced by further FTIR analysis of the binary blend, which was compounded at this temperature.

An increase and decrease in intensity of the 1718 cm^{-1} acid and 1781 cm^{-1} anhydride peaks respectively were observed in the binary blend after annealing at 170 °C for 20 minutes. (Figure 6c) As the epoxy-acid reaction proceeds, the number of anhydride groups present decreases because the acid groups cannot undergo intramolecular ring closure to reform the anhydride once an ester bond is formed between p(E-*stat*-GMA) and PP-*graft*-MA.
The reaction between the two polymers is also apparent when comparing the absorbance intensity at 911 cm^{-1}, (Figure 7) that corresponds to the epoxy group, in neat p(E-*stat*-GMA) and the binary blend. This absorption peak was three times more intense in the former than in

the latter, which suggests one-third of the epoxy groups in the binary blend are consumed during compounding.

Based on our FTIR measurements, reactive compounding of p(E-*stat*-GMA) and PP-*graft*-MA at 170 °C has been shown to be a viable method of linking PE and PP chains in-situ, which was one of our goals. However, a gel content of 66% was measured in the studied binary blend (cf. XLPE which has a gel content of 72%). This material has a high density of chemical crosslinks that make it thermoset and cannot be recycled by re-extrusion. Therefore, the binary blend was diluted with LDPE to form a ternary blend of 24:6:70 p(E-*stat*-GMA):PP-*graft*-MA:LDPE, with an aim to achieve reinforcement above the LDPE T_m while behaving as a thermoplastic material.
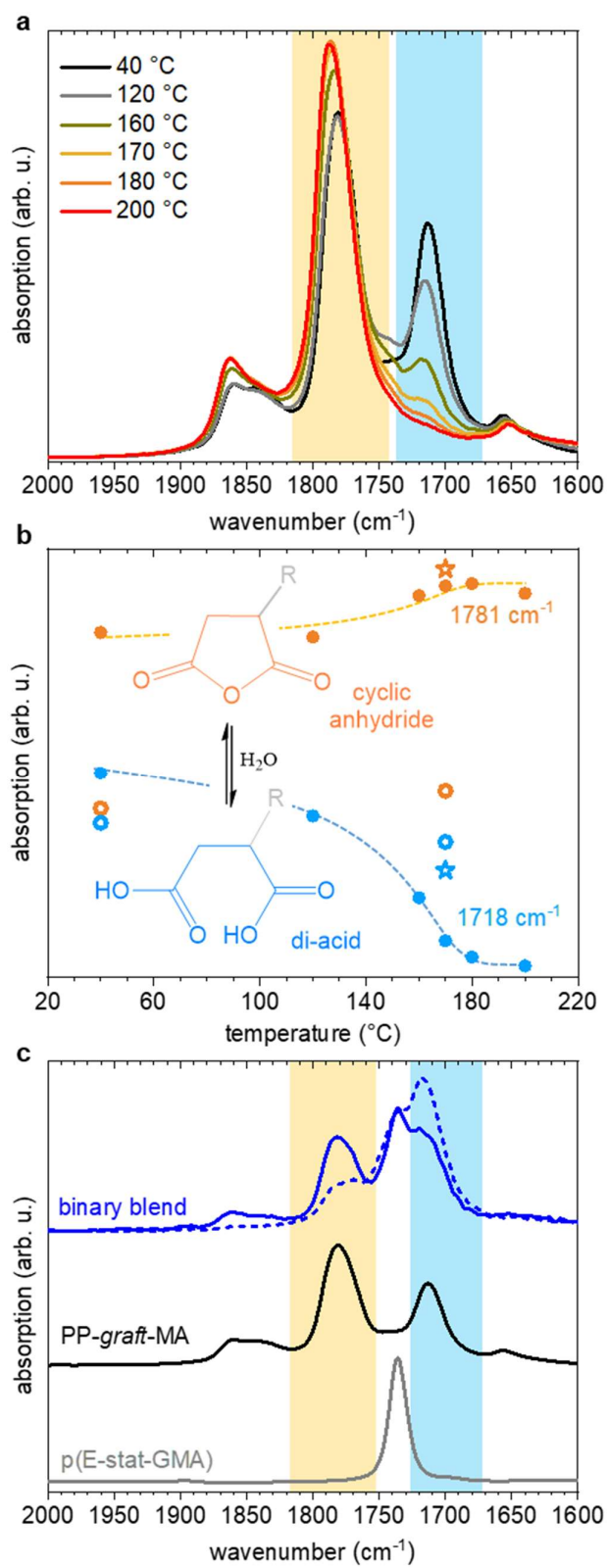
Figure 6. (a) FT-IR spectra of PP-*graft*-MA at increasing temperatures from 40 °C to 220 °C, **(b)** absorbance intensity at 1718 cm^{-1} for the acid (blue) and 1781 cm^{-1} for the anhydride (orange) plotted against temperature for PP-*graft*-MA (filled circles), the binary blend (hollow circles), and the binary blend after 20 min at 170 °C (hollow star); inset: reaction scheme of the reversible conversion between the cyclic anhydride and opened di-acid forms of the succinic anhydride grafted onto polypropylene, where R = polypropylene chain, and **(c)** FT-IR spectra measured near room temperature of p(E-*stat*-GMA) (grey, solid), PP-*graft*-MA (black, solid), the binary blend compounded for 5 min at 170 °C (blue, solid) and the same binary material after annealing at 170 °C for 20 min (blue, dashed).
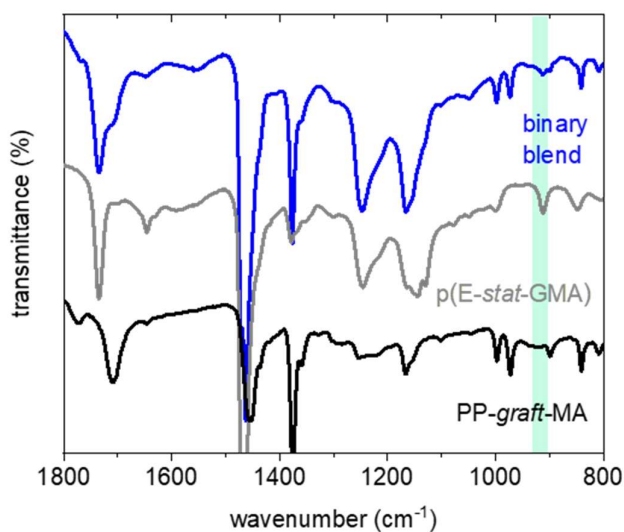

Figure 7. ATR FT-IR spectra of the 4:1 p(E-*stat*-GMA):PP-*graft*-MA binary blend (blue), p(E-*stat*-GMA) (grey) and PP-*graft*-MA (black), measured at room temperature.

3.2 Thermomechanical performance

Dynamic mechanical analysis (DMA) experiments reflected a lower rubber plateau of the diluted ternary blend compared to the binary blend above the melting temperature of LDPE. (Figure 8) This confirms our success in reducing the density of chemical crosslinks between p(E-*stat*-GMA) and PP-*graft*-MA with LDPE dilution. Fortunately, the ternary blend shows a higher modulus than LDPE above the LDPE T_m, reflecting that melt-reinforcement is still achieved in this diluted blend.
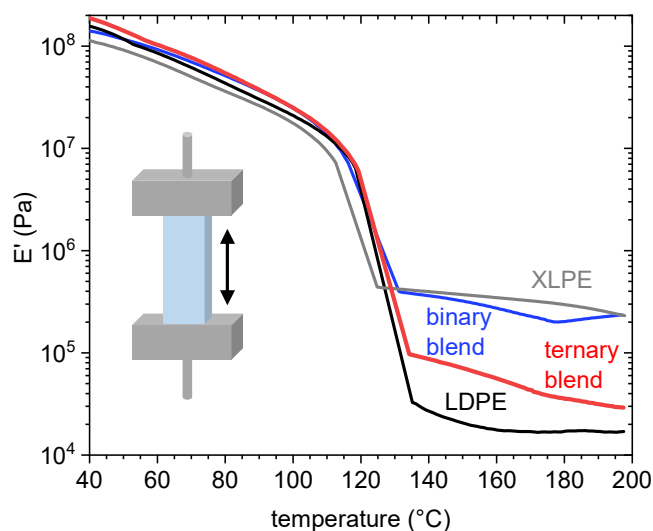

Figure 8. Storage modulus measured with DMA as a function of temperature of the 4:1 p(E-*stat*-GMA):PP-*graft*-MA binary blend compounded at 170 °C for 5 minutes (blue) and the 24:6:70 p(E-*stat*-GMA):PP-*graft*-MA:LDPE ternary blend compounded at 170 °C for 10 minutes (red), as well as references LDPE (black) and XLPE, i.e. LDPE crosslinked with 1 wt% DCP at 200 °C (grey); inset: schematic of the oscillatory DMA measurement indicating the direction of the applied stress.

To find out if the extent of melt-reinforcement in the ternary blend was sufficient to resist tensile deformation over long times at elevated temperatures, we ran some creep tests. In these tests, the ternary blend was subjected a stress of 1 kPa (which corresponds to ~1x sample weight) at temperatures above the LDPE T_m. After two hours, the ternary blend maintains low and stable creep strain of less than 30% at 120 °C and 130 °C, where the LDPE matrix would have been molten. (Figure 9) These exciting results led us to further experiments to understand how this material is reinforced at these elevated temperatures.
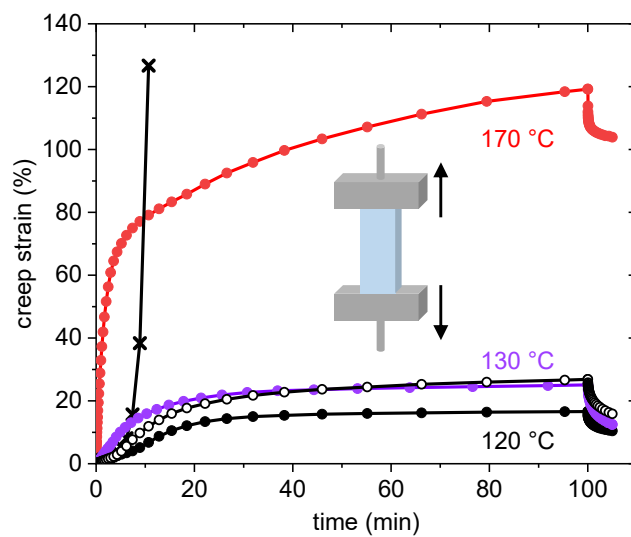

Figure 9. Creep strain at a constant stress of 1 kPa (equivalent to the sample weight) at 120 °C, 130 °C and 170 °C, of the 24:6:70 p(E-*stat*-GMA):PP-*graft*-MA:LDPE ternary blend compounded at 170°C for 10 minutes (filled circles), and at 120 °C for the ternary blend after a second extrusion at 170°C for 5 minutes (hollow circles) and also the 24:6:70 p(E-*stat*-GMA):PE-*graft*-MA:LDPE blend (crosses); inset: schematic of the creep measurement indicating the direction of the applied stress.

3.3 Understanding the melt-reinforcement effect

The main motivation behind the incorporation of PP-*graft*-MA is that its PP crystals have a melting peak of 155 °C which can act as physical crosslinks in the material to achieve good thermomechanical properties and thermoplasticity.

One method of evaluating the involvement of the PP crystals in PP-*graft*-MA in the melt-reinforcement of the ternary blend is by analysing the DMA curve of the ternary blend. (Figure 8) The curve shows a decrease in modulus of the rubber plateau below and above the T_m of PP-*graft*-MA. This is due to the loss of physical crosslinks when the PP crystals melt. Contributions to the melt-reinforcement effect in the ternary blend by chemical and physical crosslinks can be separated by estimating the number of crosslinks in the blend below and above the T_m of PP-*graft*-MA within the rubber plateau region, for instance at 140 °C and 170 °C. The number of crosslinks in a material relates to its network density, which can be calculated from the molecular weight between crosslinks M_c using the equation:

$$M_c = \frac{\rho R T}{E'}$$

where ρ is the density, R the universal gas constant, T the temperature, and E' is the storage modulus ($\rho = 0.789$ g cm^{-3} at 140 °C; $\rho = 0.770$ g cm^{-3} at 170 °C). An estimation of the number of network points per 10^3 carbons (-CH$_2$-) can then be attained by dividing $14 \cdot 10^3$ g mol^{-1} with M_c. At 140 °C and 170 °C, the ternary blend exhibited storage moduli of ~87 kPa and ~43 kPa respectively. Calculations based on these values show that, per 10^4 carbons, the ternary blend has 4 network points at 140 °C but this is reduced to 2 network points at 170 °C. These numbers suggest that the physical network points provided by the PP crystals contribute to approximately half the crosslinks in the network that reinforces the material between the melting temperatures of polyethylene and polypropylene.

The contribution of the PP crystals in PP-*graft*-MA is also evidenced in further creep experiments, where the sample was subjected to 1 kPa (Figure 9) While the ternary blend arrests creep at 120 °C and 130 °C, the material showed a much higher creep strain of more than 100% after 2h at 170 °C, which is above the T_m of PP-*graft*-MA. Furthermore, a ternary blend where PP-*graft*-MA was replaced with its polyethylene analogue underwent rapid extension even at 120 °C, yielding in just 10 minutes. These experiments confirm that both the PP crystals in PP-*graft*-MA and the chemical crosslinks between PP-*graft*-MA and p(E-*stat*-GMA) are significant in their contributions to the ternary blend's promising thermomechanical properties. (Figure 10)
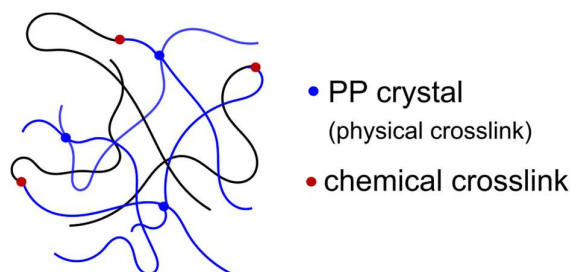

Figure 10. Schematic of a network held together by both chemical crosslinks between PP-*graft*-MA and p(E-*stat*-GMA) and the physical crosslinks provided by the PP crystals in PP-*graft*-MA.

When considering the factors that result in the melt-reinforcement of LDPE in the ternary blend, it is not just the network formation by chemical and physical crosslinks that we should consider. Without good dispersion of the crystals in PP-*graft*-MA, physical crosslinking in the system via the PP crystals would not be effective. The degree of phase separation between PP and PE in our ternary blend should not be large. Indeed, the cryofractured surfaces of our binary and ternary blends imaged by scanning electron microscopy (SEM) showed fine-grained microstructures. (Figure 11) In contrast, distinct phase separation is observed in a reference

blend of 4:1 isotactic PP: LDPE (same weight ratio as our binary blend), which featured polypropylene domains on the micrometer length scale. This proves that the PP– PE-type copolymers formed from the reaction between PP-*graft*-MA and p(E-*stat*-GMA) had a compatibilisation effect that allowed for the blend's improved thermomechanical properties.

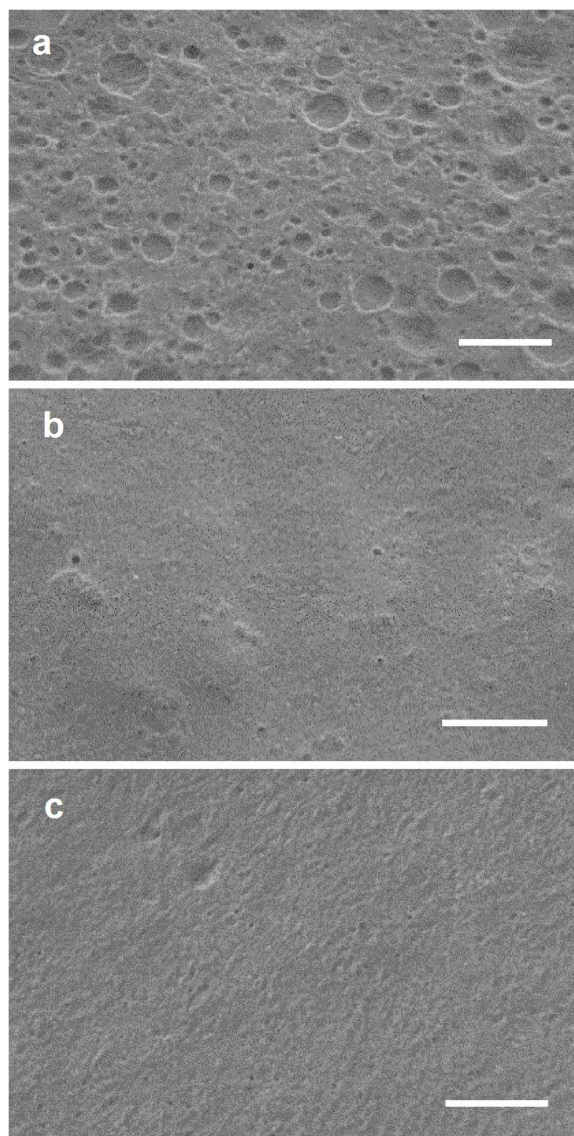**Figure 11.** SEM images of cryofractured samples of (**a**) 4:1 LDPE:PP blend, (**b**) 4:1 p(E-*stat*-GMA):PP-*graft*-MA binary blend, and (**c**) the 24:6:70 p(E-*stat*-GMA):PP-*graft*-MA:LDPE ternary blend, where the scale bar corresponds to 5 μm.

3.4 Electrical characterisation

In addition to mechanical integrity at elevated temperatures, excellent DC dielectric properties are crucial in insulation materials for HVDC cables. After 18 h at 70 °C (typical cable operating temperature) and 30 kV mm^{-1}, the ternary blend exhibited electrical DC conductivity σ_{DC} of ~$(4.4 \pm 0.4) \cdot 10^{-14}$ S m^{-1}. (Figure 12) Compared to LDPE, which shows σ_{DC} ~ $(2.5 \pm 0.3) \cdot 10^{-14}$ S m^{-1} under the same conditions, the electrical performance of the ternary blend may seem less ideal but values of both materials are at least within the same magnitude. Due to the presence of polar groups and the lower degree of cleanliness in the copolymers, it is unsurprising to obtain slightly higher σ_{DC} values. Furthermore, the σ_{DC} of the ternary blend was comparable to degassed XLPE, which, under the same conditions, showed a σ_{DC} value of ~ $(4.0 \pm 0.4) \cdot 10^{-14}$ S m^{-1},. These electrical results reflect that the ternary blend possesses good potential for high voltage insulation.
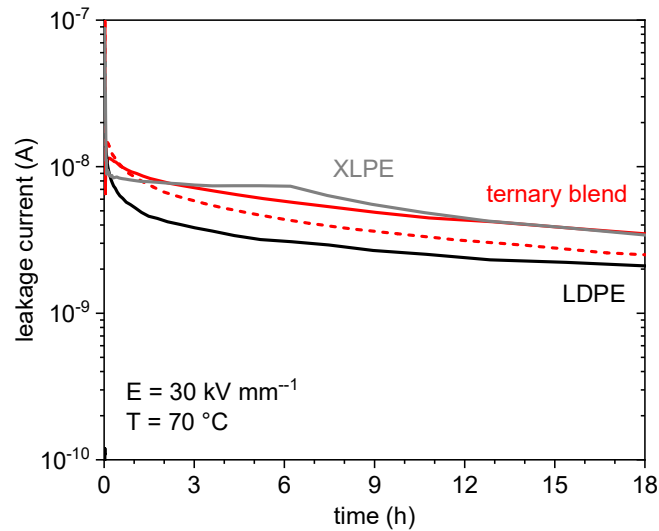

Figure 12. Volume leakage current as a function of time for the 24:6:70 p(E-*stat*-GMA):PP-*graft*-MA:LDPE ternary blend after first extrusion at 170 °C for 10 min (solid red line) and

after the second extrusion at 170 °C for 5 min (dashed red line), neat LDPE (solid black line) and XLPE (grey).

3.5 Demonstration of thermoplasticity and recyclability

In addition to electrical and thermomechanical properties, the concept behind this material was also largely driven by our aim towards more sustainable insulation materials. We recycled our ternary blend by first cutting it up into small fragments followed by re-extrusion and melt-pressing at 170 °C. The feasibility of these procedures confirms the thermoplasticity of our material. To investigate the recyclability of the material, we measured the creep properties and DC conductivity of the re-extruded ternary blend. Fortunately, the recycled blend still showed low creep strain of less than 30% at 120 °C (Figure 9) and low DC conductivity $\sigma_{DC} \sim (3.0 \pm 0.3) \cdot 10^{-14}$ S m^{-1}, similar to the value achieved prior to re-extrusion. (Figure 12) The maintenance of good thermomechanical and electrical performance in the re-extruded ternary blend confirms its recyclability.

Chapter 4

CONCLUSION AND OUTLOOK

With the increasing emphasis on environmental-awareness and sustainability today, robust thermoplastic insulation materials will be in high demand for future HVDC technologies. A variety of promising material concepts towards thermoplastic insulation have been, and we add to this with a novel strategy that reinforces LDPE in the melt with small amounts of PP via reactive compounding. Despite having only 6 wt% of polypropylene-*graft*-maleic anhydride, this LDPE-based material was held together by a combination of chemical and physical crosslinks, resulting in wonderful thermomechanical properties as demonstrated in creep tests. The blend also had good electrical insulation properties, displaying very low DC conductivity values similar to those of XLPE. Additionally, recyclability of the material was shown, with no significant losses in properties even after re-extrusion at 170 °C.

In addition to this reactive compounding route, it would also be interesting to explore LDPE-based blends that incorporate small amounts of PP prepared by non-reactive compounding. A wide range of copolymers have been designed for the compatibilisation of PP-PE blends, yet studies on such ternary blends have not been reported in the high voltage insulation field. Such blends could benefit from lower sensitivity to processing conditions since chemical crosslinking is omitted. Furthermore, the non-reactive route eliminates the need for reactive polar groups. This could lead to blends with very low DC-conductivity. Such blends could also be easier to recycle since the stability of the chemical crosslinks after repeated

recycling cycles do not have to be considered. If successful, this strategy would open yet more

possibilities for recyclable high voltage insulation materials.

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