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Reactive Antioxidants for Peroxide Crosslinked Polyethylene

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ABSTRACT

Three synthesised reactive (graftable) antioxidants, r-AO, with hindered phenol and hindered amine antioxidant functions, were examined for their grafting efficiency in polyethylene and their retention and stabilising performance in peroxide-crosslinked polyethylene pipe material. Their level of grafting in un-crosslinked high density polyethylene, HDPE, and the extent of their retention in highly peroxide-crosslinked HDPE (PEX_a) material (both laboratory prepared samples and PEX_a pipes produced by commercial processes) were determined after stringent solvent extraction methodologies. The uniformity of distribution of the r-AOs in the PEX_a pipes (across the length and thickness of the pipes) were examined using infrared-microscopy and compared with similarly produced PEX_a pipes containing commercial antioxidants having the same antioxidant functions. The extent of interference of the graftable hindered phenol and hindered amine antioxidants with the peroxide crosslinking process in the PEX_a materials was assessed by comparing the level of crosslinking achieved against analogously prepared samples containing a conventional hindered phenol antioxidant (Irganox 1076).

The results obtained showed that the presence of the graftable (r-AOs) antioxidants did not affect the level of crosslinking of the PEX_a pipes which remained high (>85%) and that they were retained to a very high extent in the PEX_a material after solvent extraction, and are very uniformly distributed across the length and thickness of PEX_a pipes. The long-term stabilising performance of the graftable r-AOs in the PEX_a material (in both laboratory prepared samples and in peroxide crosslinked pipes produced by commercial processes) was also examined using complimentary methods: oxidative induction time (OIT) before and after solvent extraction, physical embrittlement following oven ageing at 125°C, as well as by a hydrostatic pressure tests conducted (with water inside and air outside) at 115°C and 2.5 MPa pressure. The stabilising efficacy of the r-AOs was compared with that of conventionally stabilised PEX_a material containing analogous antioxidant functions produced in the same way. The level of retention (in the pipes) of the graftable antioxidants and their long-term stabilising performance was shown to be significantly higher than that of the conventional AOs under all the test conditions used here.

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Keywords: Crosslinked polyethylene; reactive antioxidants, PEX pipes, antioxidant performance

1. INTRODUCTION

Polyethylene, PE, is typically modified by crosslinking so as to enhance its performance properties and market appeal. Crosslinking is generally achieved chemically through the use of peroxides, silanes or high energy radiation (the crosslinked polyethylene is referred to as 'PEX' material). Gamma or electron beam irradiation of PE in the solid state, for example, result in major improvements in its wear resistance and tensile properties at elevated temperatures. This observation was one of the drivers for using, for example, ultra-high molecular weight polyethylene, UHMWPE, in orthopaedic implants [1, 2]. For electrical cables, a two-step process is typically used to crosslink the polymer, in which a silane molecule is grafted first onto the polymer followed by crosslinking through hydrolysis in the presence of a catalyst (PEX_b material) [3]. Crosslinking PE with organic peroxides, which takes place normally at elevated temperatures and pressures, e.g. in an 'Engel Process' [4], gives rise to stronger polymers with better resistance to stress cracking [5]. One of the main applications of peroxide-crosslinked polyethylene, PEX_a, (mainly high density polyethylene, HDPE) is in water pipe systems, especially for district heating and potable water distribution networks.

There are many advantages from using plastic pipes, compared to metal pipes: lower weight and installation costs, greater resistance to corrosion, safety and long service life [6]. The lifetime of PEX_a pipes is traditionally predicted using data from pressure tests conducted on pipes which were subjected to different internal stresses at high temperature and measuring the time to rupture [7]. The current service life requirement for hot-water polyolefin PEX_a pipes is around 50 years [8]. Effective thermal stabilisation during manufacturing and service life of PEX pipes is, therefore, critical for their success. A combination of conventional hindered phenol and hindered amine antioxidants is generally used in pipe formulations [8-10].

Although considerable amount of work has been published on the stabilisation and assessment of the lifetime performance of PEX pipes in the presence of thermal antioxidants, one of the main issues remains to be associated with the physical and chemical loss of conventional thermal antioxidants (AOs) which ultimately leads to brittle fracture and failure of the pipes [8-15]. The high free radical scavenging ability of hindered phenolic and aminic AOs, which are critical to their antioxidant action, would also inadvertently lead to their 'sacrificial' chemical loss due to their interference with the free radical crosslinking process [16-18]. In addition, antioxidant losses have been shown [9, 10] to occur through physical migration and leaching into the contact environment. This would not only compromise the long-term stabilising performance of the antioxidants but could give also health and safety concerns for potable water pipe applications.

It is clear, therefore, that there is a need for developing new stabilisation technologies for polyolefin PEX_a pipes that are highly durable but without the associated health and safety issues relating to loss and migration of stabilisers and transformation products to the contact environment. The work described here focuses on the application of procedures using reactive (graftable) antioxidants (**r-AOs**) in peroxide-crosslinked HDPE material (PEX_a pipes) in an attempt to address the concerns raised by these issues. Three polymer-reactive antioxidants, one containing hindered phenol and two with a hindered amine functions, were synthesised and characterised. The grafting efficiency and the extent of retention of these antioxidants were examined in laboratory-produced non-crosslinked and highly peroxide-crosslinked PE samples as well as in PEX_a pipes produced by commercial processes. The level of interference of these r-AOs with the crosslinking process was investigated and compared with that of conventional stabilising systems containing the same antioxidant functions, in addition to assessing the extent of their retention in the PEX_a material following stringent solvent extraction protocols. The long-term stabilising (LTTS) performance of the r-AOs-PEX_a pipes was compared to that of the conventionally stabilised PEX_a material produced using analogous antioxidant functions and production method.

2. EXPERIMENTAL

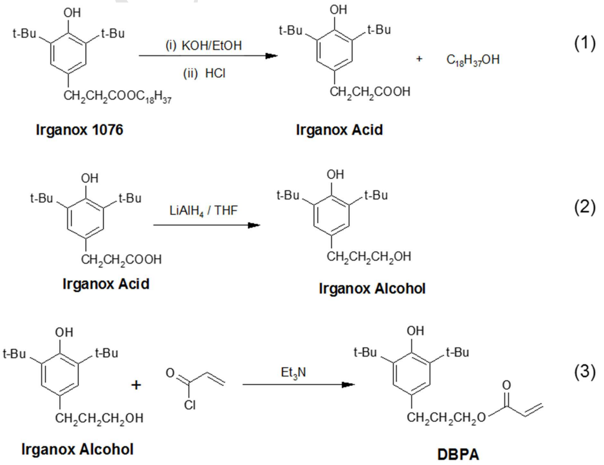
2.1. Materials

The polyethylene pipe grade polymer used was a high density polyethylene, HDPE, powder supplied by Lyondell Basell with the trade name Lupolen 5261Z Q456 having MFR (190^{o}C/21.6 kg) of 2 g/10 min and density of 0.954 g/cm^3, unless otherwise specified. The HDPE used for producing laboratory peroxide-crosslinked samples (**PEX$_{aL}$**) was stabilised with either the synthesised reactive antioxidants (r-AOs) containing hindered phenol and hindered amine antioxidant functions (see structures later) or with the conventional commercial hindered phenol, Irganox 1076. The polymer used for the PEX$_a$ pipes produced by commercial manufacturing processes was similarly stabilised with the r-AOs but with an additional pipe produced containing a combination of Irganox 1076 and a conventional (undisclosed) hindered amine, c-HAS; both Irganox 1076 and the c-HAS were ex. BASF. For grafting reactions, the peroxide (2, 5-dimethyl-2,5-bis(t-butyl peroxy)hexane (Trigonox 101, coded **T101**), ex. AzkzoNobel, was used. Additionally, two other peroxides were used for polymer crosslinking reactions in PEX$_{aL}$ and PEX$_a$ pipes, a di-tertiary-butyl peroxide (**TB**) and 2, 5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (Trigonox 145, **T145**), both ex. AkzoNobel. HPLC grade dichloromethane (DCM) and xylene (Fisher Scientific) were used without further treatment for the extraction of the stabilised and crosslinked polymer samples. All NMR solvents (Goss Scientific) were used as received.

2.2. Synthesis of Reactive Antioxidants

2.2.1. Synthesis of the reactive hindered phenol 3-(3’,5’-di-tert.-butyl-4’-hydroxy phenyl) propyl-1-acrylate, DBPA

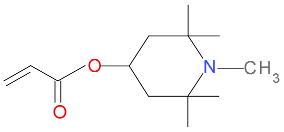
The synthesis of DBPA was performed according to **Scheme 1.** The first step involved the conversion of Irganox1076 into the corresponding Irganox acid, reaction 1, as described earlier [19]. The Irganox acid was then reduced to the corresponding alcohol. 50 g Irganox acid (0.18mol) in 200ml THF was added drop-wise to a THF solution containing LiALH$_4$ (10.2 g in 200 ml) followed by 2h reflux. 20 ml ethyl acetate and 150 ml NH$_4$Cl solution (aqueous, saturated) were added and shaken vigorously. The organic layer formed was decanted and was made slightly acidic. The residue formed was extracted with diethyl ether (3 x 200ml) and dried over anhydrous magnesium sulfate, filtered and the solvent evaporated. The oily residue was dissolved and crystallized from petroleum ether (450ml). The resulting Irganox alcohol (rn. 2), was a white solid powder (crude weight 32g, yield 67%), M.p. 64-66°C). 25g of Irganox alcohol was mixed in 250 ml toluene solution containing 13.2 ml of triethylamine, and 7.8ml (0.95M) acryloyl chloride in 200 ml toluene was added dropwise followed by vigorous stirring (magnetic) for 3 hours at room temperature under an inert atmosphere. The toluene solution was washed several times with sodium hydrogen carbonate solution, followed by water and then dried over anhydrous magnesium sulphate. The solvent was allowed to evaporate in a fume cupboard at room temperature leaving a thick oily yellow product which was filtered through a glass-sintered Buchner funnel. The DBPA product, reaction 3, was characterised by FTIR and NMR, see Section 2.3.



Reaction Scheme 1: Synthetic reaction for the preparation of DBPA

2.2.2. Synthesis of the reactive hindered amine 4-acryloyloxyl 1,2,2,6,6-pentamethyl piperdine, AOPP

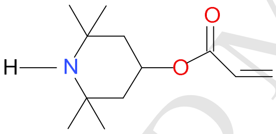
1,2,2,4,4-pentamethyl-4-piperidinol (0.3M) and methyl acrylate (0.27M) were mixed in 250 ml HPLC grade toluene. 9 ml (0.03M) of titanium isopropoxide (Tipox) was added and the solution which was refluxed for 48h under an inert atmosphere. After cooling, 100ml of 5% sodium bicarbonate was added, filtered and two layers were separated. The unreacted 1,2,2,4,4,-pentamethyl-4 piperidinol (insoluble in hexane) was removed; the organic layer was evaporated and the resulting solid was recrystallized from hexane. The hexane solution was dried over magnesium sulphate and the solvent was evaporated to give yellowish oily liquid with a yield of around 80% characterised by FTIR and NMR as **AOPP, I.**



AOPP, I

2.2.3. Synthesis of the reactive hindered amine 4-acryloyloxyl 1,2,2,6,6-tetramethyl piperdine, AOTP

2,2,4,4-tetramethyl-4-pipereidinol (15.7g, 0.1M) and methyl acrylate (8.5 ml, 0.093 M) were mixed in 250 ml HPLC grade toluene. 3 ml of titanium isopropoxide (Tipox) was added, refluxed for 2 hours, followed by a further addition of Tipox (6 ml, 0.01M), and further refluxing over 24hrs under an inert atmosphere. After cooling to room temperature, 100 ml of 5% sodium bicarbonate was added, filtered and the two layers were separated. After evaporating the solvent from the organic layer, the solid product obtained was recrystallized from hexane yielding (~70%) a white solid (M.p.151°C) which was characterised by FTIR and NMR as **AOTP**, **II**.



AOTP, II

2.3. Polymer Processing and Preparation of Stabilised and Crosslinked Polyethylene Samples (PEX_{aL} samples and PEX_a Pipes)

The in-situ free radical grafting reactions of DBPA, AOPP and AOTP on HDPE were carried out under nitrogen atmosphere in the melt using a closed chamber of a Thermo Haake Rheomix torque rheometer (Rheomix 600) in the presence of different concentrations of the AOs and the peroxide T101 (used at different molar ratios to the AOs). Both process temperature and the torque were monitored in-real time using the 'PolyLab' software. The mixing rotor speed (65 rpm) and the processing time (5 or 7 min) were fixed. Thin film samples for testing were prepared by compression moulding (22 kg/cm^2 pressure at 160°C).

The laboratory-made peroxide crosslinked HDPE samples (**PEX_{aL}**) were prepared by compression moulding of formulations containing the polymer, antioxidant and the peroxide **TB** where both crosslinking and, in the case of r-AOs, grafting took place. The formulations were pre-mixed with a small amount of hexane (to aid mixing and distribution of ingredients) which was later removed under vacuum. The formulated mix was spread thinly on P.T.F.E. mats inserts placed between glazed stainless steel sheets to make up the moulding set. This set was initially pressed for 2 min (at 240^{o}C, zero pressure) followed by a further 5 minutes (under 22 kg/cm^2), to produce thin crosslinked film samples (120 µm thick).

Peroxide-crosslinked polyethylene pipes were produced in the presence of 0.5 w/w% of each of the AOs (r-AOs and the conventional hindered phenol Irganox®1076) and the peroxide **TB** by a commercial ram extrusion Engel process (250-265^{o}C, 260 m/h), the pipes produced (dimensions 16.5 x 2 mm) are referred to here as **PEX_{aEng}**. Another set of PEX_a pipes were also produced (dimension of 20 x 2 mm) commercially but by a 'normal' extrusion process (180-250^{o}C) using the peroxide **T145** and, in this case, the polymer was a HDPE pipe grade (trade name BorPex HE1878E, Borealis, Sweden), MFR 10 (190^{o}C, 21.6 kg); these pipes are referred to here as **PEX$_{aHS}$.** Both the r-AOs and the conventional AO combination of Irganox1076 with an unspecified c-HAS were used to stabilise the polymer of **PEX$_{aHS}$**.

2.4. Purification of the Grafted Polymers and Determination of the Extent of Grafting

To establish the grafting level of the **r-AOs** in the un-crosslinked polymer, cut sections (using Leica microtome, see below) of the reactively processed polymer were solvent-extracted (DCM/5% cyclohexane, referred to here as DCM extraction) to remove unreacted and homo-polymerised antioxidant(s) following an accelerated solvent extraction methodology (70^{o}C, 2000psi, 5x30 min cycles) under nitrogen on Dionex ASE200 system (both the r-AOs and their homopolymers are completely soluble in DCM).

To determine the amount of antioxidant retention in the highly crosslinked **PEXa** pipe samples after solvent extraction, the pipes were first microtomed. Pipe sections (1.5 cm each), which were cut out from each 40 m length (for 240 m long pipes, at 2 m intervals) into thin slices (100 µm) using a Leica Ultra cut UCT microtome equipped with a microscope and a stainless steel knife. The slices were subjected to either DCM extraction, as described above, or to a sequential solvent extraction, i.e. DCM extraction by ASE, followed by Soxhlet extraction with xylene (xylene dissolves un-crosslinked PE and swells the crosslinked polymer) under an inert atmosphere. The crosslinked polymer was separated out (in the thimble) as the xylene-insoluble fraction; the xylene-soluble fraction was retrieved as precipitate after dunking the extraction vessel in an ice-cold bath and vacuum filtration. The congealed precipitate, comprising non-crosslinked polymer, free and grafted antioxidant(s) was dried (vacuum oven) and pressed at 150^{o}C (3 min, 10 tonnes) into a 200 µm thick discs using SPECAC/KBr press for further FTIR analysis**.** The xylene-insoluble gel fraction (the crosslinked polymer retained in the thimble) was dried in a vacuum oven (4 h at 80^{o}C), weighed, sliced and pressed into discs (200 µm thick) as described above for further analysis.

2.5. Determination of the Crosslinking of Polymer Samples

Any insoluble gel formed during the melt grafting of r-AO's on PE and the extent of the polymer crosslinking by peroxide were determined according to ASTM 2765-01 method using xylene extraction. Polymer films were cut into small pieces and weighed (w_1), placed in weighed stainless mesh thimbles, and Soxhlet extracted in 150 ml xylene for 50 hrs under nitrogen. After extraction, the thimbles were dried, to constant weight (w2) vacuum oven (8 hrs at 80ºC). The percent gel content, or the extent of polymer crosslinking (in PEXa samples), from duplicates runs, were calculated as 100 (w2/w1).

2.6. Characterisation of the Polymer

Fourier Transfer Infrared (FTIR) spectroscopy was used to characterize the synthesised and grafted antioxidants in HDPE. FTIR measurements were performed on a Perkin Elmer (PE) Spectrum One over the range of 4000-400 cm^{-1} (16 scans, 4 cm^{-1} resolution). The area of the specific ester carbonyl absorption of the antioxidants was determined so that the concentration of grafted antioxidants can be determined by reference to the respective calibration curves. The grafting efficiency, based on analysis of triplicate samples**,** was determined as the ratio of the masses of the grafted antioxidant to that of the antioxidant initially added.

The antioxidant distribution along the length and across the wall thickness of the pipes was determined using a Perkin Elmer (Spectrum GX) FTIR-microscope to run line marker scans. Line scans and line marker scans were performed on microtomed polymer pipe samples (100 µm), where IR-spectra in transmission mode were taken (in the range 800-3600 cm^{-1}) with intervals of 100 µm from the inner to the outer walls of the pipes; 32 scans were set for each spectrum. To obtain the mapping images of the distribution of the antioxidant in the polymer, the ratio of the carbonyl peak area (of the antioxidant ester group centered at 1740 cm^{-1}) over that of a polymer reference peak area (centered at 2019 cm^{-1}) was calculated. The calculations were then presented in the form of coloured maps representing different concentrations of the stabilisers across the pipe thickness.

The amount of the antioxidant homopolymer(s) that may form in the grafting reaction system was quantified using ^{1}H-NMR spectroscopy. NMR experiments were performed on a Bruker Avance-300 spectrometer at ambient temperature using tetramethylsilane (TMS) as internal standard. 1D NMR spectra were recorded using a 5 mm normal dual detection probe and operating at controlled temperatures. The NMR samples were prepared by dissolving 20 mg material in 0.7 ml $CDCl_3$ or DMSO-d6 solvents containing 0.05% TMS. For **^{1}H NMR,** the spectra were recorded at 300.13 MHz using a high-resolution dual (^{1}H ^{13}C) gradients probe. Spectra were recorded using the zg30 pulse program with 32 scans and referenced to an internal TMS standard at 0.0 ppm**.** The ^{13}C chemical shifts were determined from PENDANT ^{13}C NMR spectra obtained at 75 MHz for carbon. The pendant pulse program was used with waltz16 decoupling during acquisition with 2048 scans and phased for CH_3/CH positive and quaternary carbons and CH_2 negative with internal reference TMS at 0.0 ppm. Assessment of the amount of the homopolymer(s) obtained from the extracted (purified) polymer films was obtained by integrations of the ring O-C-H (e.g. H4 proton at 5ppm in AOPP, see Figure 2b later) and any one of the acrylic group protons (9, 8 or 9' at 5.5 ppm, 5.7 ppm and 6.1ppm, respectively). The NMR software was programmed to calibrate all the signals relative to one proton (H4 at 5ppm), used as a reference since this proton is part of the ring structure and does not change in the antioxidant-homopolymers. To calculate the % free AOPP, the value of the calculated integral of one of the double bond protons, (preferably H9 (at 6.1 ppm) which appears as sharp and well resolved signal in the polymer extract, is multiplied by 100.

Oxidative Induction Time (OIT) of film samples prepared from PEX_a pipes and the crosslinked lab-samples (PEX_{aL}) was measured under a stream of oxygen (flow rate of 40 ml/min) at an elevated temperature using DSC 823 (Mettler Toledo) with open pans according to ASTM-D3895. Triplicate samples (4-5 mg) were heated at 20^{o}C/min to 190^{o}C under nitrogen flow before switching to 100% oxygen. Crystallinity of the polymer was determined using DSC (a Perkin-Elmer Diamond Scanning Calorimeter) based on the heat of melting (ΔH) obtained from the second heating cycle (40^{o}C to 190^{o}C at a heating rate of 10^{o}C/min) according to ASTM D-3417-99 (measurements in duplicates).

The long term thermo-oxidative stability (LTTS) of films (150-250 μm) of PEX_a pipes was determined by both accelerated thermal ageing and a hydrostatic pressure test. The accelerated thermal ageing was carried out following extended ageing periods at 125°C under circulating air (85 litres/hour) using a multi-chamber single cell air-circulating (Wallace) oven and determining the time-to-embrittlement, EMT, at which time the polymer film was found to fail on gentle flexing through 180^0 between thumb and forefinger (tests done in duplicates). The hydrostatic pressure test for PEX_{aHS}-pipes was carried out according to **ISO 1167-1973 (**measurements in duplicates). The internal test medium was deionised water and the external medium was air. The antioxidant-containing pipes (lengths of ~1ft) were tested at 115°C and 2.5 MPa pressure. Typically, a pipe should reach a period of at least one year (~8800 h) before failure in this test for it to be considered fit for use in commercial applications.

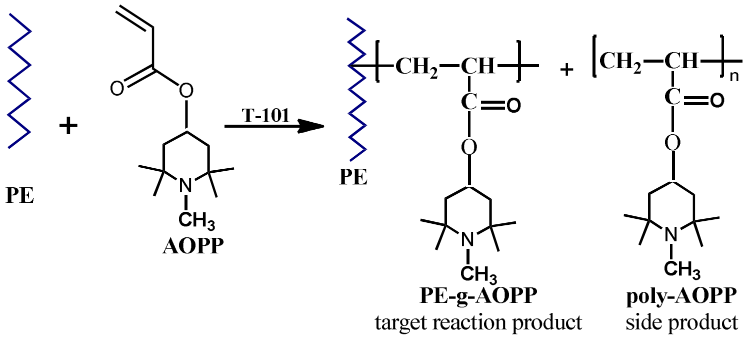
3. RESULTS and DISCUSSION

3.1. Characterisation and In-Situ Melt grafting on HDPE of the Synthesised r-AOs

The synthesised reactive antioxidants were characterised using FTIR and NMR spectroscopy. All three r-AOs show infrared absorptions characteristic of a conjugated carbonyl absorption (maximum around 1725 cm^{-1}; for AATP around1703 cm^{-1}) and an acryloyl double bond absorptions (at around 1408 cm^{-1} and 1635 cm^{-1}) which are the structural characteristics of their polymer-reactive function, see **Figs 1B,2A,3A**. These characteristic structural features are also clearly seen in the ^{1}H and ^{13}C NMR spectra of the three r-AOs, see **Figs. 1-3**.

The synthesised r-AOs (DBPA, AOPP and AOTP) were grafted in the presence of the peroxide T101, as a free radical initiator, on HDPE during melt processing, see **reaction 1** for AOPP. The characteristic signals of the reactive function of the antioxidants showed clear differences when they were grafted on polyethylene. The conjugated carbonyl absorption peak of the r-AOs shifted to a higher frequency (from 1725 to 1733 cm-1) in the FTIR spectra of the polyethylene-grafted antioxidant samples (PE-g-AO). The C=C peak absorptions (at 1408 cm^{-1} and 1635 cm^{-1}) of the free (ungrafted)

AOs, see **Figs. 1B,2A,3A,** appear to be absent in the infrared spectra of the PE-g-AO samples, which confirms the grafting of the r-AOs through their terminal reactive function.



(1)

The extent of the antioxidant grafting reactions on HDPE (not crosslinked) was then characterised by FTIR and ^{1}H-NMR spectroscopy after extensive purification of the polymer samples by solvent extraction in order to remove the main side reaction product, the antioxidant homopolymer, see **reaction 1**, before determining the grafting efficiency**. Fig. 4** shows the effect of the peroxide T101 concentration on the extent of melt grafting of the r-AOs (concentration 3% w/w) and the formation of the main side reaction products (similar trends were observed at 1% and 0.5%, results not shown). It is clear that increasing the peroxide concentration increases the extent of the grafting of all three reactive antioxidants (g-AO) and this is paralleled by a much lower increase in the antioxidant homo-polymer (p-AO) formation. A decreasing amount of gel is also formed at higher peroxide concentrations. An important observation here is that the overall amount of peroxide required to achieve high level of grafting of the reactive hindered phenol DBPA is an order of magnitude higher than that which is required for both of the hindered amines AOPP and AOTP. Under the conditions used here, both AOPP and AOTP were grafted to over 80% at only 0.005 peroxide concentration (expressed as molar ratio of the peroxide to the antioxidant), whereas at the same peroxide concentration, the DBPA did not undergo any grafting and required ten times the amount to achieve about 70% grafting. This is attributed directly to the much higher free radical scavenging efficiency of DBPA, hence the need for the higher amounts of peroxide for its grafting.

The effect of the processing temperature on the extent of grafting is shown in **Fig. 5.** Increasing the temperature increases the extent of grafting of DBPA at all peroxide concentrations. For example, at 0.6 molar ratio of the peroxide T101, the grafting level of DBPA in HDPE increased from 70% to 85% when the processing temperature was increased from 180 to 245^{o}C, **Fig. 5A**. Similarly, the level of grafted AOPP increased with processing temperature up to around 200^{o}C beyond which a slight drop in the level of grafting was observed. This observation is attributable to the highly competitive parallel reaction, i.e. the antioxidant homo-polymer formation, see **Fig. 5B**, hence it is imperative to optimise both chemical composition and the reaction conditions to achieve the target grafting levels of r-AOs.

3.2. The Effect of Free Radical Scavenging Antioxidants on the Extent of Polymer Crosslinking and the Level of their Retention in the PEXa Material

The issue of interference of free radical scavenging thermal antioxidants with the peroxide crosslinking process of HDPE was investigated further. The HDPE polymer samples, both PEX_{aL} and the pipes (PEX_{aEng} and PEX_{aHS}) were peroxide-crosslinked in the presence of 0.5 w/w% concentration of different antioxidants. **Fig. 6** shows that the level of the polymer crosslinking of PEX_{aL} in the presence of all three r-AOs remains very high-with the reactive hindered phenol DBPA giving rise to a slightly lower extent of polymer crosslinking compared to the reactive hindered amine (AOPP and AOTP) antioxidants. This is in line with the earlier results (see **Fig. 5)** where the DBPA was shown to graft to a lower extent than both AOPP and AOTP due to the high free radical scavenging ability of the hindered phenol function. However, it is interesting to note that the conventional hindered phenol, Irganox 1076, which has a similar antioxidant function to DBPA but without the polymer reactive site, interferes with the crosslinking process to a greater extent than that which was observed with DBPA. For example, 74% crosslinking was achieved with Irganox 1076 compared to 80% with DBPA in the PEX_{aL} samples (**Fig. 6A**); this difference was found to be even higher at higher concentration levels of the initially added antioxidant, see **Fig. 6B**.

In order to confirm the laboratory results above, a number of PEX_a pipes (16 or 20 mm diameters and 2 mm wall thickness) were produced in commercial production units using HDPE with both the reactive (graftable) hindered phenol DBPA and with the conventional hindered phenol Irganox 1076; the hindered phenol antioxidants were used in the presence and/or absence of an additional hindered amine stabiliser (DBPA with AOPP or AOTP, and Irganox 1076 with a conventional c-HAS). The effect of these antioxidants on the extent of the crosslinking of the pipe-HDPE polymer was investigated further. Close examination of **Fig. 7** shows that the extent of the polymer crosslinking in pipes containing the reactive antioxidants is higher than in pipes containing the conventional antioxidants (single or in combination), in both sets of pipes (PEX_{aEng} and PEX_{aHS}). This suggests that, in contrast to conventional AOs bearing the same antioxidant function, the r-AOs interfere less with the peroxide crosslinking process in PEX_a pipes produced under the same conditions.

The findings above are corroborated further from the results obtained for the extent of retention of the antioxidants, measured after DCM solvent extraction, in the highly crosslinked PEX_a polymer samples (both the laboratory-prepared and the commercially produced pipes). Examination of **Fig. 8A** reveals that in the PEX_{aL} samples, Irganox 1076 loses over two thirds of its initial concentration (28% retention) after extraction, whereas the r-AOs are retained to very high extent, e.g. 78% retention for DBPA and much higher, over 90%, for AOPP and AOTP. In the PEX_a pipes, an overall higher level of retention of all the antioxidants was generally observed (**Fig. 8B**) although the total amount retained in the pipe containing the conventional antioxidant combination (Irg1076/cHAS) was still slightly lower than in pipes having r-AOs combinations, i.e. DBPA/AOPP or DBPA/AOTP, after the same extraction process. The observed higher overall level of antioxidant retention in the PEX_a pipes compared to the lab-crosslinked PEX_{aL} samples may be attributed to the higher crosslink density network (CLD) achieved in the commercially produced pipes.

To further confirm that Irganox 1076 is susceptible to higher losses (after DCM extraction) when compared to the reactive hindered phenol DBPA, a new set of PEX_a pipe samples were prepared in which antioxidant combinations containing the reactive-antioxidants (DBPA with AOPP or AOTP) had their reactive hindered phenol DBPA replaced by the conventional hindered phenol Irganox 1076. The results obtained (see **Fig. 8B**) show clearly that pipes containing antioxidant combinations with Irg1076 (AOPP/Itg1076 and AOTP/Irg1076) suffer greater antioxidant loss after DCM extraction when compared to pipes produced similarly but where the Irganox 1076 is replaced by DBPA. This is almost certainly due to a higher level of loss of the Irganox 1076 since the level of retention of the r-HAS antioxidants (AOPP or AOTP) in the combination was shown to be very high, see **Fig. 8A**.

This finding, however, has raised a question: is it possible that some of the antioxidants could remain trapped in the tightly crosslinked network of the pipe polymer and would appear as 'retained' to high levels after DCM extraction? Is it possible also that under these conditions DCM is not a strong enough solvent to remove any 'mobile' antioxidant(s) from the crosslinked network? To answer these questions, the pipe samples were subjected to a sequential solvent extraction protocol where the polymer was subjected first to DCM extraction followed by extraction in a higher boiling solvent, xylene, which dissolves any un-crosslinked polymer as well as swelling the polymer so as to ensure that all mobile and un-trapped antioxidant(s) are totally removed from the system. Results from PEX_a pipes containing the conventional antioxidant combination, Irg1076-cHAS, were then compared with those of pipes containing the **r-AO**s combinations. **Fig. 9A** depicts the extent of retention of the antioxidants after extraction with DCM only and after the sequential DCM/xylene extractions. It is clear, see **Fig. 9A**, that more than half of the initial amount of the conventional AO-combination Irganox 1076/cHAS used in the crosslinked pipes is lost after the sequential solvent extraction. By contrast, analogously crosslinked pipes containing the graftable-AO combinations (DBPA/AOPP and DBPA/AOTP), show a very high level of retention (of over 85%) when subjected to the same exhaustive sequential extraction regime (for the extent of crosslinking of these pipes see **Fig. 7B**). This was also the case with the laboratory-prepared PEX_{aL} samples (results are not shown here). **Figs. 9B** and **9C** show the changes in the infrared ester absorption peak of the antioxidants after DCM extraction and in the soluble and insoluble-polymer fractions after the sequential xylene extractions. The much higher level of reduction of the antioxidant ester peak (in the case of Irg1076/cHAS combination) compared to that of the reactive DBPA/AOPP combination reflects the lower extent of retention of the conventional antioxidants in the PEXa pipes.

Hindered phenols are known to be highly effective free radical scavengers [20] and are expected, therefore, to interfere with the peroxide-initiated crosslinking process concomitant with their sacrificial chemical loss. The above results indicate this very clearly for Irganox 1076 (similar findings, not shown here, were obtained also for Irganox®1010). However, in the case of both the reactive- hindered phenol and hindered amines, they may become grafted on the polymer chains during the crosslinking process and thus clearly overcoming the problem of loss, reflected in the very high level of their retention even after an exhaustive sequential DCM/xylene extraction process which removes any mobile antioxidants (ungrafted unreacted, oligomers, homopolymers).

The reason for the much lower extent of interference with the crosslinking process by the same AO-functional group (e.g. hindered phenol function) when present in the grafted form is not fully clear yet. It is suggested here that in the case of the reactive antioxidants, since the grafting process is taking place in the polymer melt, the antioxidant becomes distributed throughout the whole polymer network and that some of the chemically grafted-antioxidant may well remain in the crystalline region (when the polymer solidifies) and may affect the polymer degree of crystallinity. On the other hand, in the case of the conventional more mobile antioxidants, these are excluded from the crystalline region and are located almost entirely in the amorphous region and can more easily interfere with the crosslinking reaction of the macromolecular free radicals and are, therefore, more easily consumed chemically, in addition to some physical losses. The crystallinity of both pipe samples were calculated (from DSC) and results showed that the pipe containing the graftable antioxidant DBPA has a lower (42%) crystallinity than that containing Irganox 1076 (48%) which is in accord with the above suggestion.

3.3. The Stabilising Performance of the Antioxidants in PEX_a polymer

The long-term thermal stability (LTTS) of highly crosslinked PEX_a pipes is affected by a number of factors including the materials, both polymer and antioxidants, the contact environment, normally air and water, as well as the loading and temperature [21]. The type of antioxidant used plays a critical role, not only in terms of the extent of their retention in the pipes after the crosslinking process, as antioxidant depletion results in loss of protection against thermal oxidation, but also the uniformity of their distribution across the wall thickness and the length of the pipes. To examine the uniformity of distribution of the reactive and the conventional antioxidants, samples of PEX_a pipe were cut from different length runs, microtomed and examined by FTIR microscopy. **Figs. 10 and 11** show FTIR-microscopy colour contour images representing the differences in the intensity of the ester carbonyl peak index of reactive (**Fig. 10**) and conventional (**Fig. 11**) antioxidant combinations which reflects the antioxidant distribution, across the thickness and the different lengths of the pipes. The contours and the line scans at all the different lengths of the PEX_a pipe containing the r-AO combination DBPA:AOTP show clearly (**Fig. 10**) a highly uniform antioxidant distribution not only across the thickness of the pipe but also at all lengths measured up to 240 meters of the extruded pipe. In contrast, the conventional antioxidant combination of Irg1076:cHAS in the PEX$_a$ pipe shows a much less uniform AO's distribution.

The higher level of retention of the more uniformly distributed r-AOs found in the PEX$_a$ pipes, as shown earlier, would be expected to result in better protection of the pipes compared to their conventional analogues. The long term thermal oxidative stability of the PEX$_a$ pipes was, therefore, examined using three different methods. **Fig. 12** shows the retention of the oxidative induction time (OIT) measured after DCM extraction in laboratory-crosslinked samples (**Fig. 12A**) and after ageing at 125^{o}C for 42 days in PEX$_{aEng}$ pipes (**Fig. 12B**) as well as the time to physical embrittlement (by flexing to180 degrees) after ageing at 125^{o}C of PEX$_{aEng}$ pipes (**Fig. 12C**). The results of all these tests show that the reactive hindered phenol DBPA, alone or in combination with the r-HAS (AOPP), significantly outperforms the stabilising effect obtained by Irganox 1076 in PEX$_{aEng}$ pipes which were produced and treated under the same conditions.

To further evaluate and compare the performance of the r-AOs with that of their conventional analogues in the PEX$_a$ pipes, a hydrostatic pressure testing was applied. Such dynamic tests are typically conducted under specified internal and external environments (e.g. air or water), at different pressures and temperatures followed by recording of the time to failure [22]. **Fig. 13A** shows a schematic representation of a typical PEX pipe stress rupture showing three failure stages [23]: the pipe fails mainly in a ductile manner under mechanical overload during stage **I**, initiation of micro-cracks in the pipe wall occurs in Stage **II**. However, in Stage **III**, a brittle failure occurs under low stress level which was shown to be mainly due to a chemical degradation process caused by the loss and consumption of the antioxidants. PEX$_a$ pipes that have a 'normal' degree of crosslinking of >70% were shown to display mainly stages **I** and **III** failures [14, 15, 24, 25] .

Two highly crosslinked (>80%) PEX$_a$ pipes, one containing the conventional antioxidant combination (Irg1076/c-HAS) and one containing a combination with similar antioxidant functions but is based on the r-AOs (DBPA/AOPP), were subjected to a hydrostatic pressure test with water inside and air outside at 115^{o}C under pressure of 2.5 MPa. **Fig. 13B** shows that the pipe containing the conventional antioxidant combination failed in just over one year, whereas the pipe containing the graftable AOs failed after much longer time. The final failure of these pipes occurred mainly by a chemical degradation process (shown clearly for one of the pipes here in **Figs. 13 C and D**) through the build-up of oxidation products (this is reflected in the IR signature of carbonyl- and double bond- containing products) which accumulate on the fractured surfaces of the pipes. This occurs, almost certainly, due to the depletion of the AOs and the initiation of the thermo-oxidative degradation of the pipes (chemical changes) which leads to their ultimate brittle fracture.

The high level of retention of the graftable AOs in the PEX$_a$ pipes, their highly uniform overall distribution across the length and wall thickness of the pipes and the lower extent of their interference with the crosslinking process are supporting evidences for their much improved LTTS performance observed and compared to pipes containing similar but non-graftable conventional AO systems. This has been validated by the three performance tests, discussed above (results shown in **Fig. 12** for extent of OIT retention after solvent extraction, the EMT from accelerated thermal ageing in an air-circulating oven, and the traditional hydrostatic pressure test of pipes, **Fig. 13**). These reactive antioxidant systems, therefore, present a great potential for future use in potable water pipe applications.

4. CONCLUSIONS

The results achieved in this work demonstrates clearly the feasibility of reaching high levels of grafting of the synthesised reactive antioxidants (r-AOs) on polyethylene. Specifically, the extent of their retention in highly crosslinked polymers (PEX$_a$ polymer and PEX$_a$ pipes), after a stringent solvent extraction process, is very high (>85%), and and exceeds significantly that of samples prepared in the same way (e.g. in PEX$_{aL}$) with conventional (non-reactive) antioxidants with the same antioxidant functions. The level of interaction of the r-AOs, e.g. the Chain-breaking donor hindered phenol DBPA, with the free radical polymer crosslinking process was found to be lower (i.e. higher level of crosslinking was maintained) compared to that of PEX$_a$ polymer containing Irganox 1076, and that the difference in the extent of crosslinking increases substantially with increased antioxidant concentration. The distribution of the r-AOs (e.g. DBPA:AOTP) in PEX_a pipes was found to be much more uniform throughout the length (tested up to 240 m lengths) and across the walls of the pipes compared to similar pipes containing Irg1076:cHAS. The higher extent of retention and more uniform distribution of the r-AOs (e.g. DBPA:AOPP) in PEXa pipes was reflected in a significantly higher long term stabilising performance, both before and after DCM extraction, when compared to pipes containing conventional antioxidants with similar functions based on Irg1076:c-HAS. These results clearly demonstrate the advantages of using reactive (graftable) antioxidants in peroxide crosslinked polymers including PEX_a pipes

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FIGURES

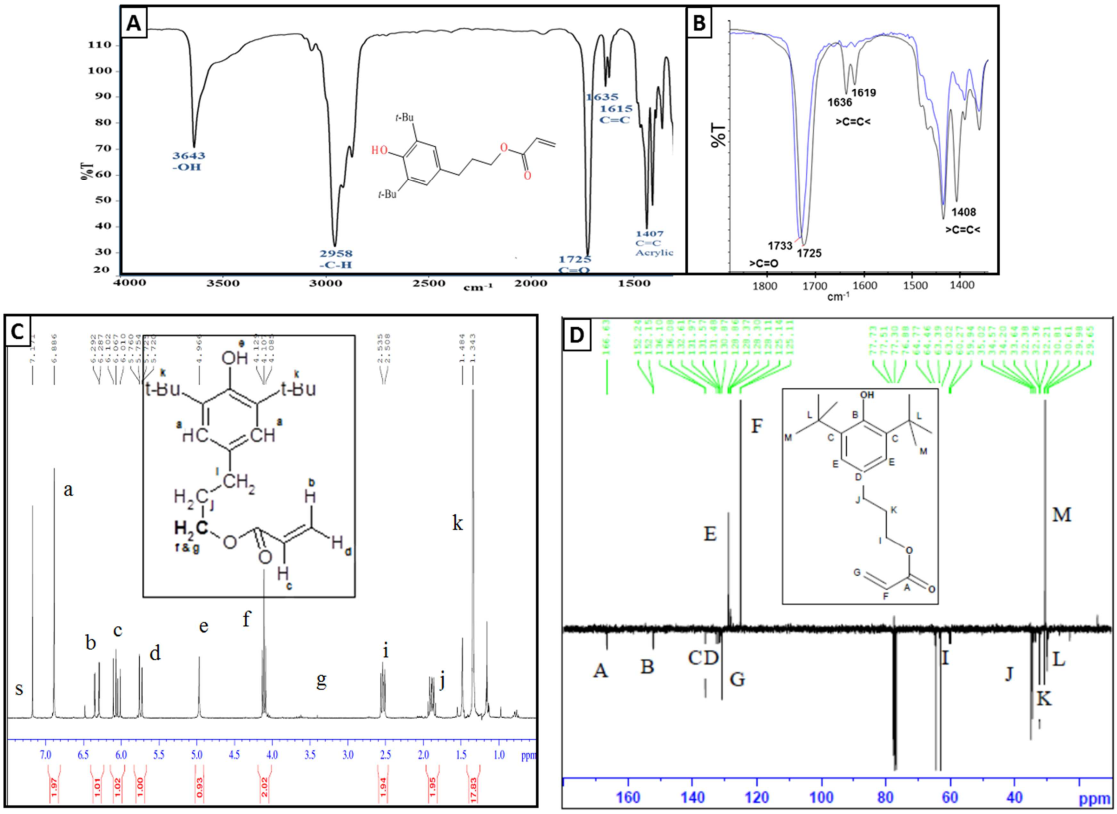

Figure 1: Spectral characteristic of DBPA: (A) FTIR; (B) FTIR in the carbonyl and double bond region (black) compared to that of PE-g-DBPA in blue; (C) and (D) are the 1H- and 13C- NMR spectra of DBPA, respectively.

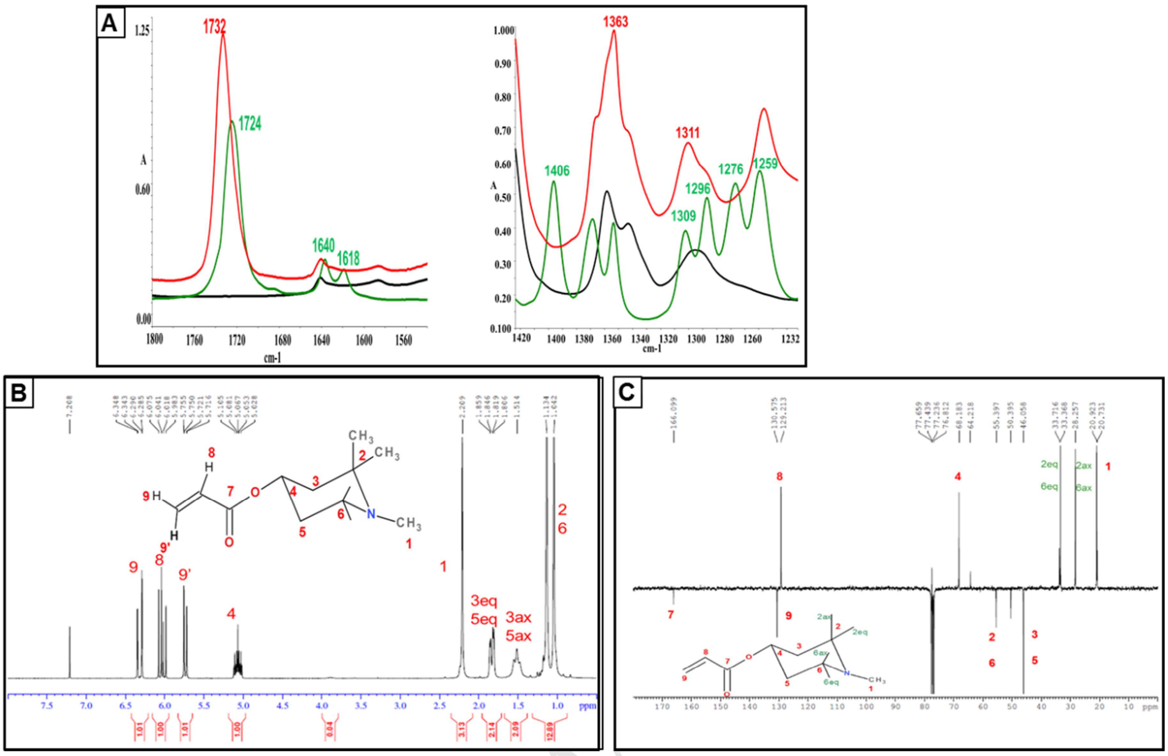

Figure 2: Spectral characteristic of AOPP: (A) FTIR in the carbonyl and double bond region (green) compared to that of PE-g-AOPP in red; (C) and (D) are the 1H- and 13C- NMR spectra of AOPP, respectively.

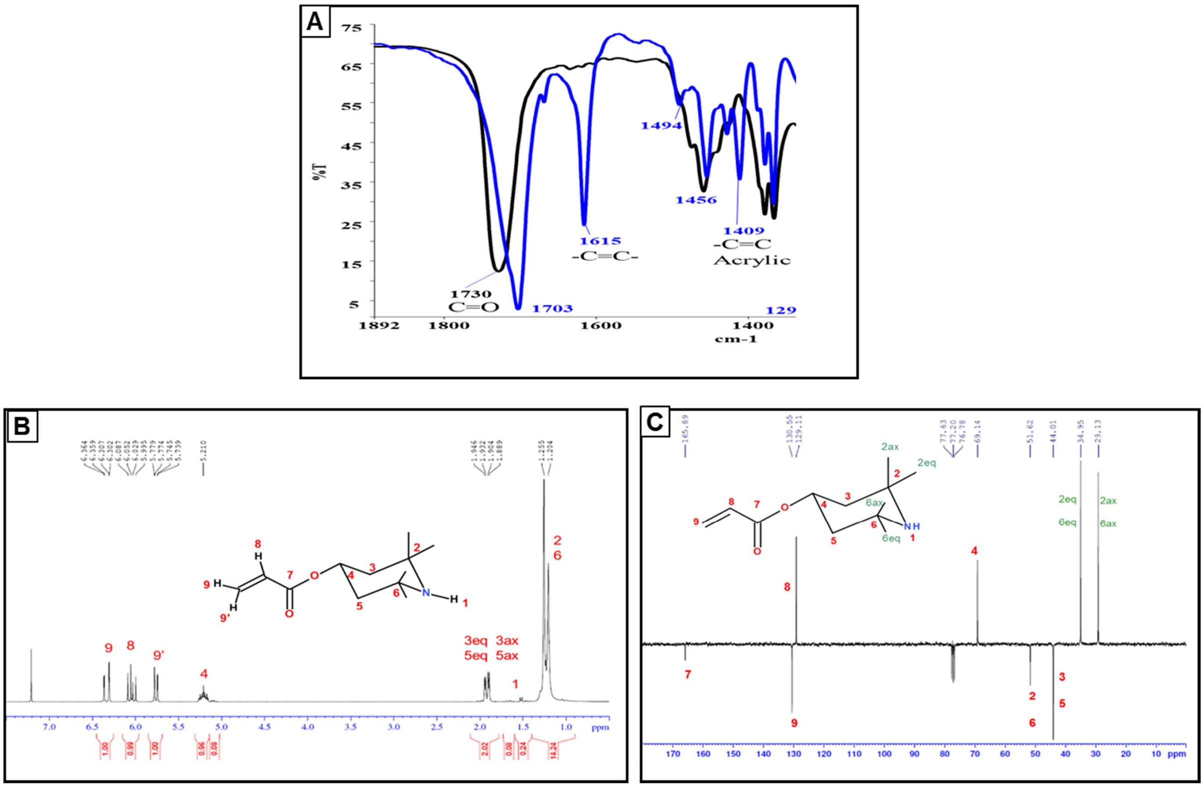

Figure 3: Spectral characteristic of AOTP: (A) FTIR in the carbonyl and double bond region (blue) compared to that of PE-g-AOTP in black; (C) and (D) are the 1H- and 13C- NMR spectra of AOTP, respectively.

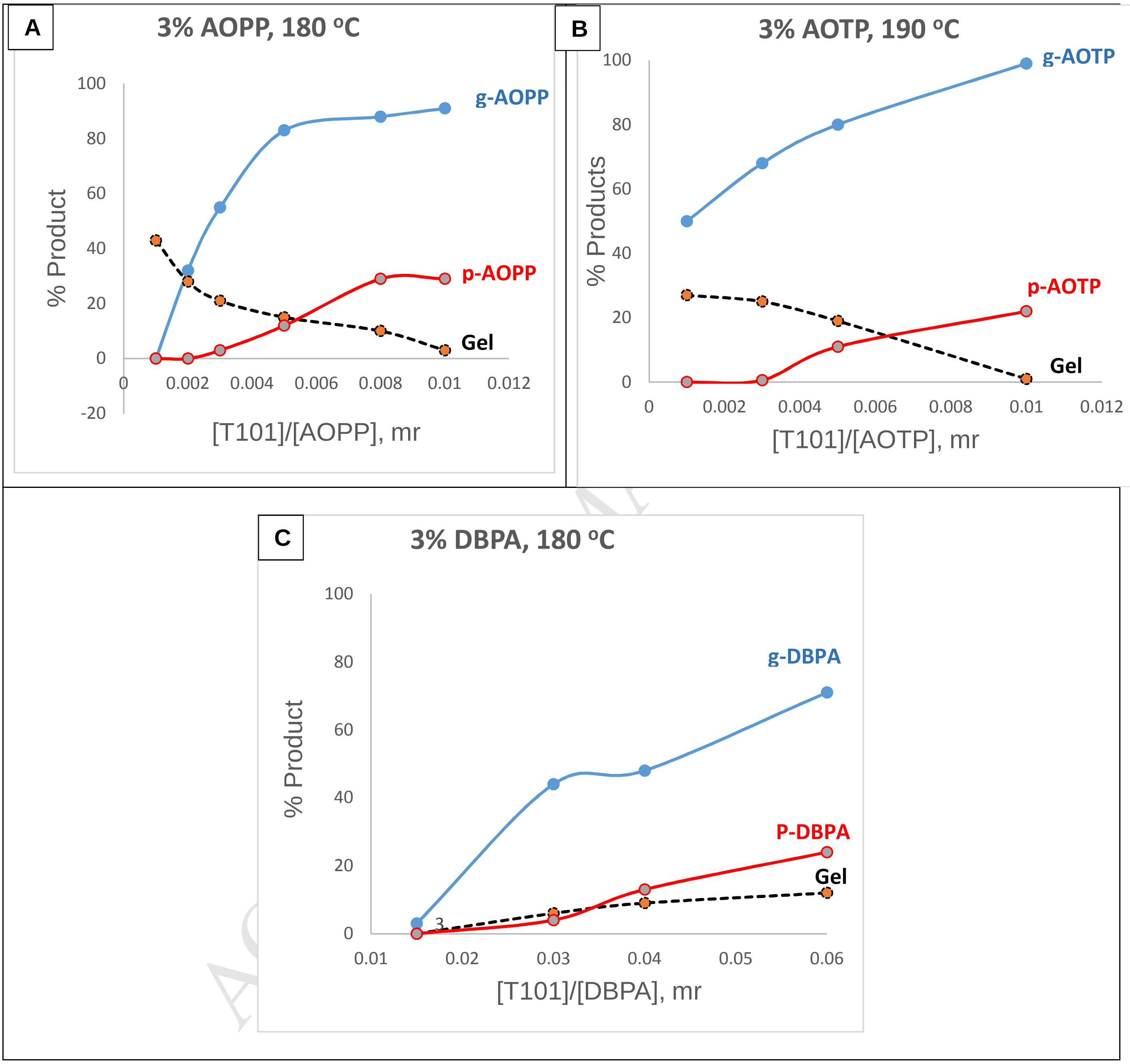

Figure 4: Effect of peroxide concentration on the grafting efficiency on HDPE of: AOPP (A), AOTP (B) and DBPA (C), and on the formation of their homopolymers (p-AO) and the polymer gel.

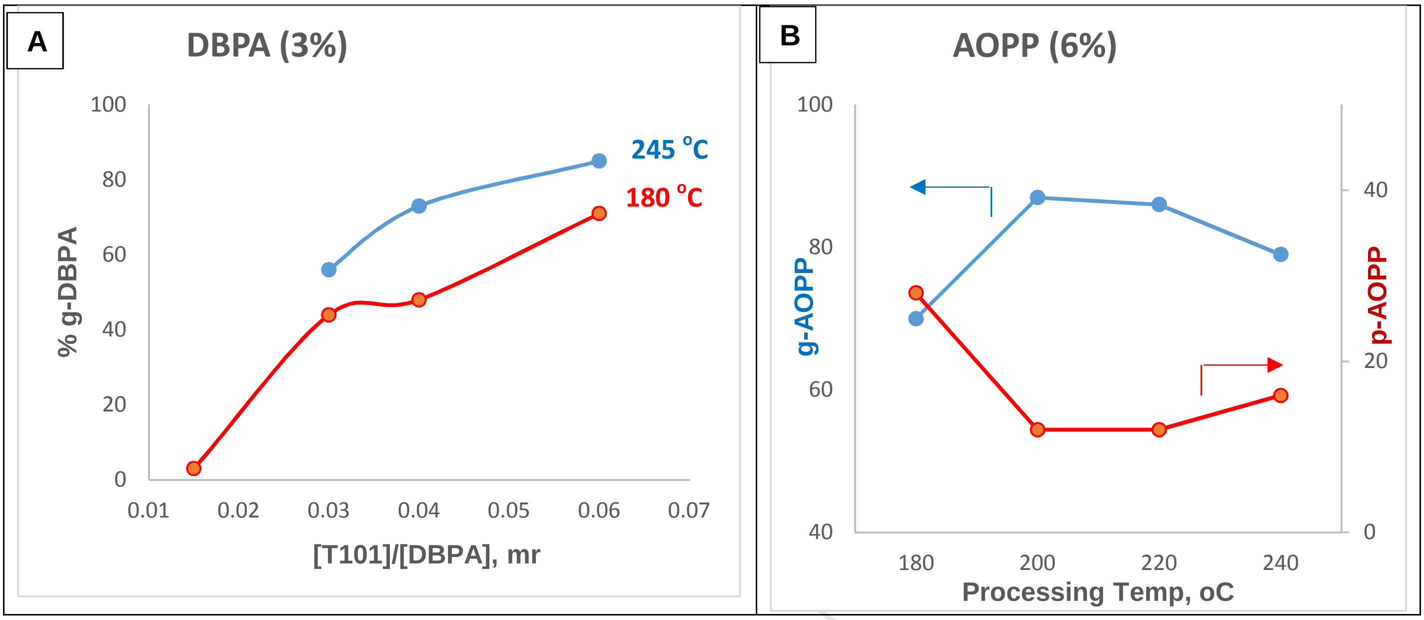

Figure 5: Effect of processing temperature on the extent of DBPA grafting at different peroxide concentrations (A), and on the grafting of AOPP and formation of p-AOPP at a fixed peroxide concentration of 0.005 molar ratio (to the antioxidant)

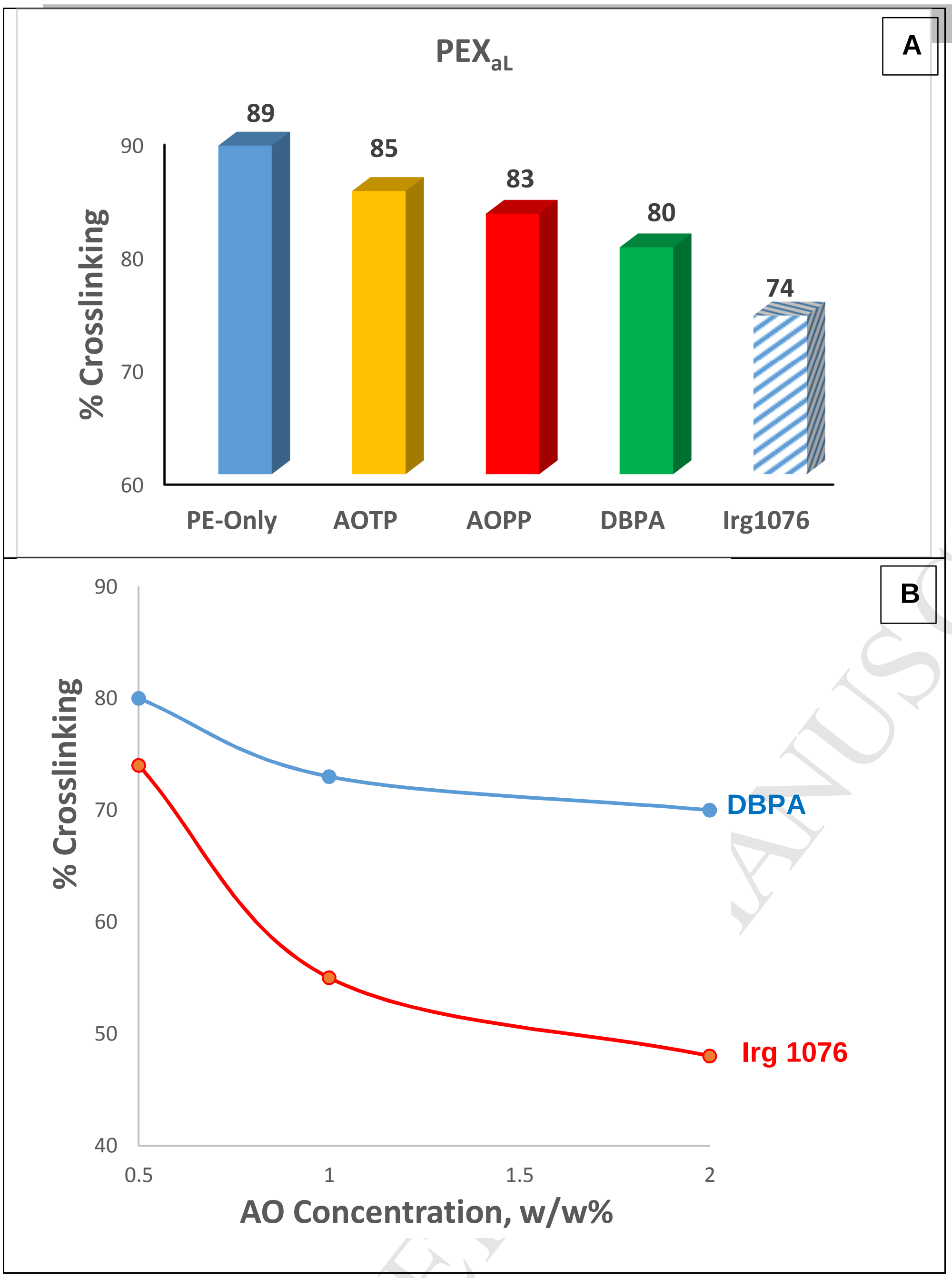

Figure 6: The effect, on the extent of HDPE crosslinking, of 0.5 w/w% reactive antioxidants (DBPA, AOPP, AOTP) and conventional hindered phenol antioxidant Irganox 1076 (A), and of different concentrations of the hindered phenol antioxidants (B).

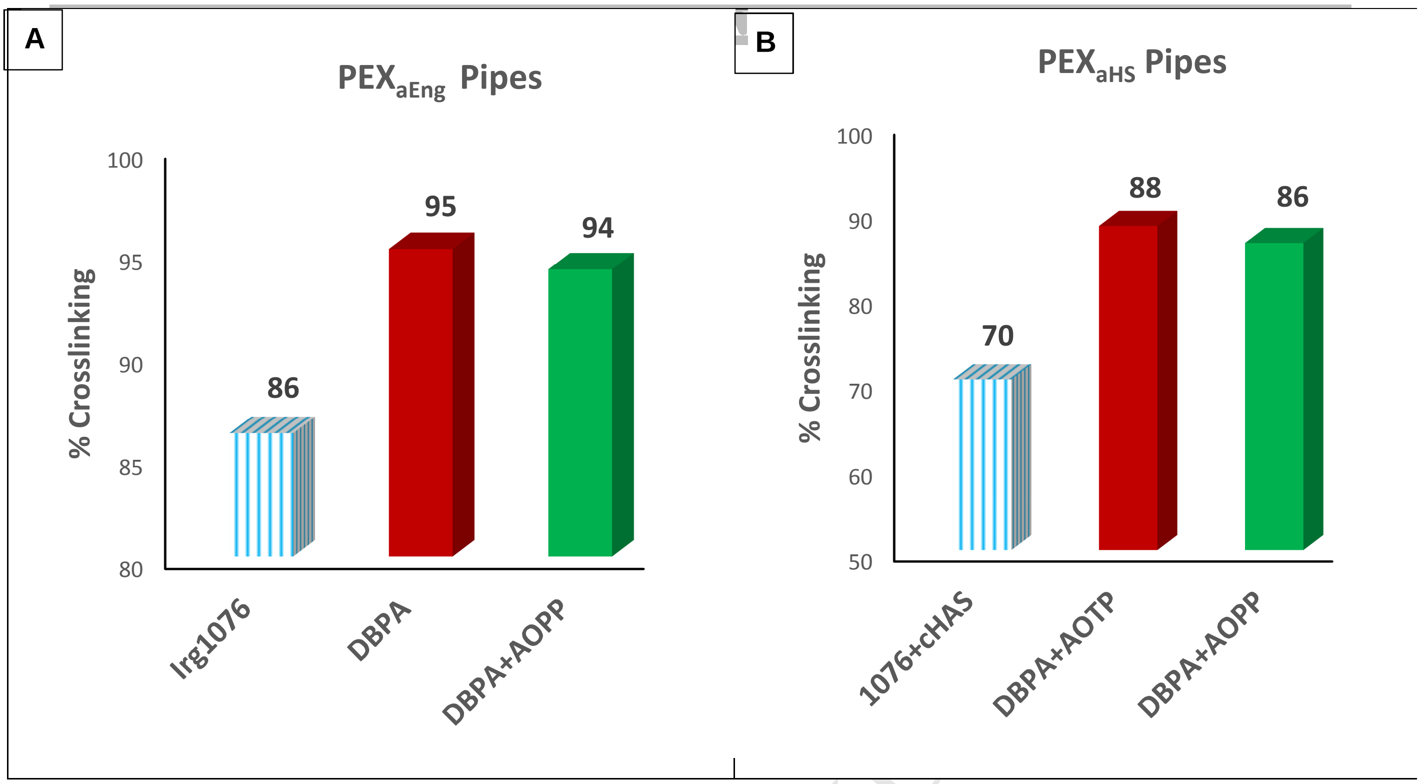

Figure 7: Effect of antioxidants on the extent of HDPE crosslinking in commercially produced PEX$_a$ pipes

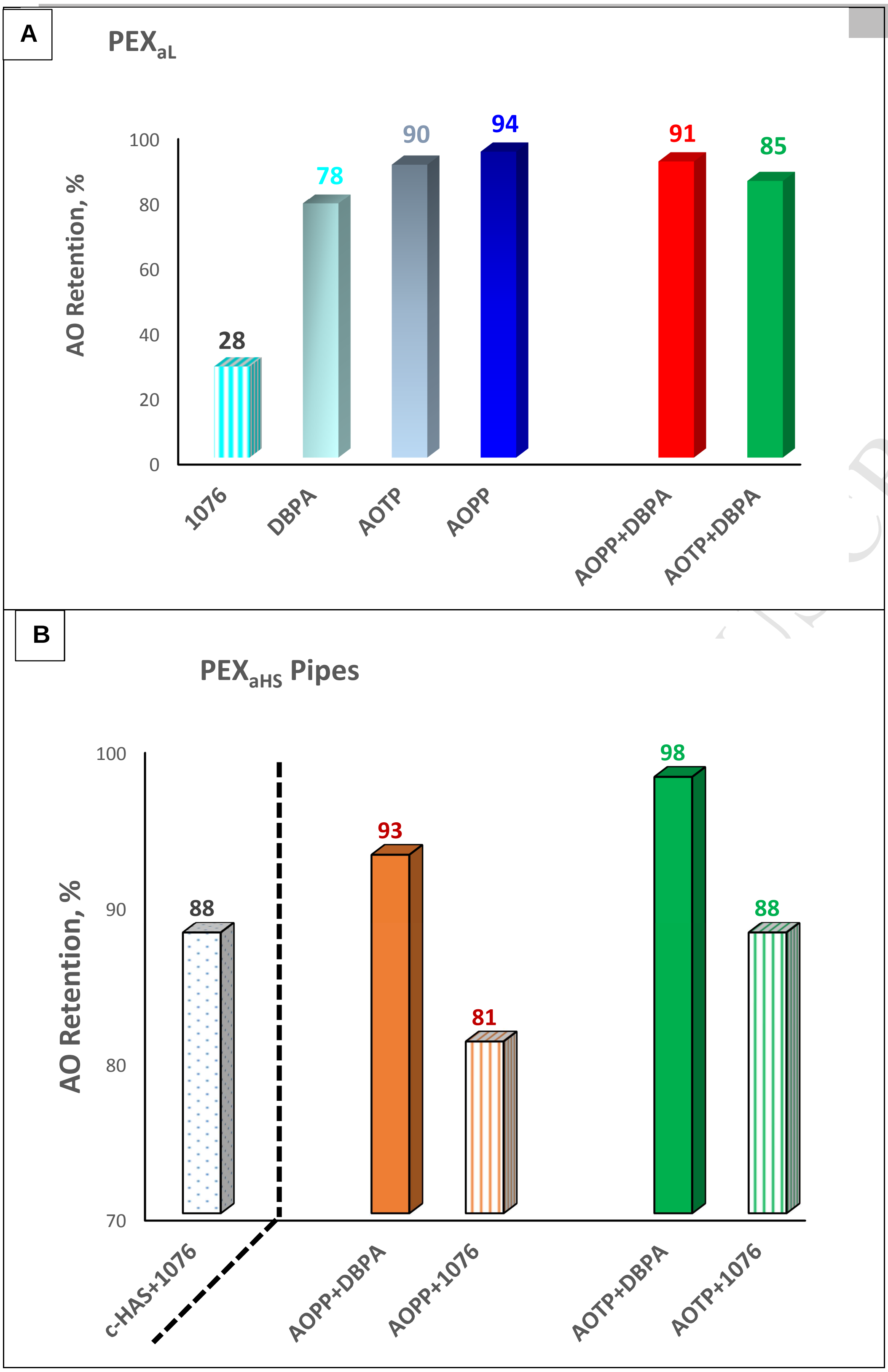

Figure 8: The extent of antioxidant retention after DCM extraction in crosslinked HDPE samples, PEX$_{aL}$, (A) and PEX$_{aHS}$ Pipes (B)

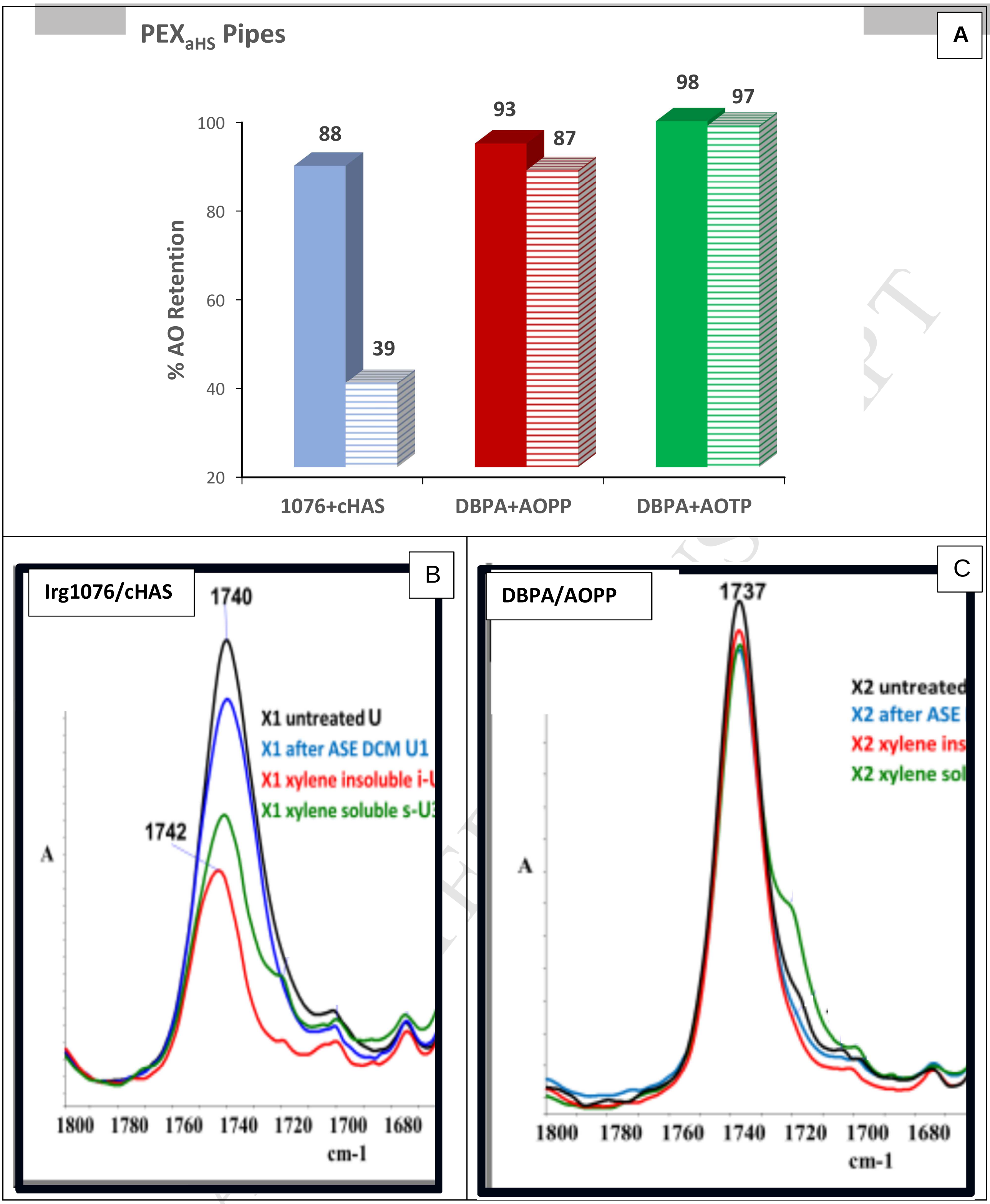

Figure 9: Effect of DCM extraction (solid histograms) and sequential DCM/xylene extraction (lined histograms) on the extent of retention of the antioxidants in PEXa pipes (A). The changes in the ester absorption peak of the antioxidant combination Itg1076:cHAS (B) and that of DBPA:AOPP (C) is shown for the polymer before extraction and after DCM and xylene extractions both in the soluble and insoluble fractions of the xylene fraction

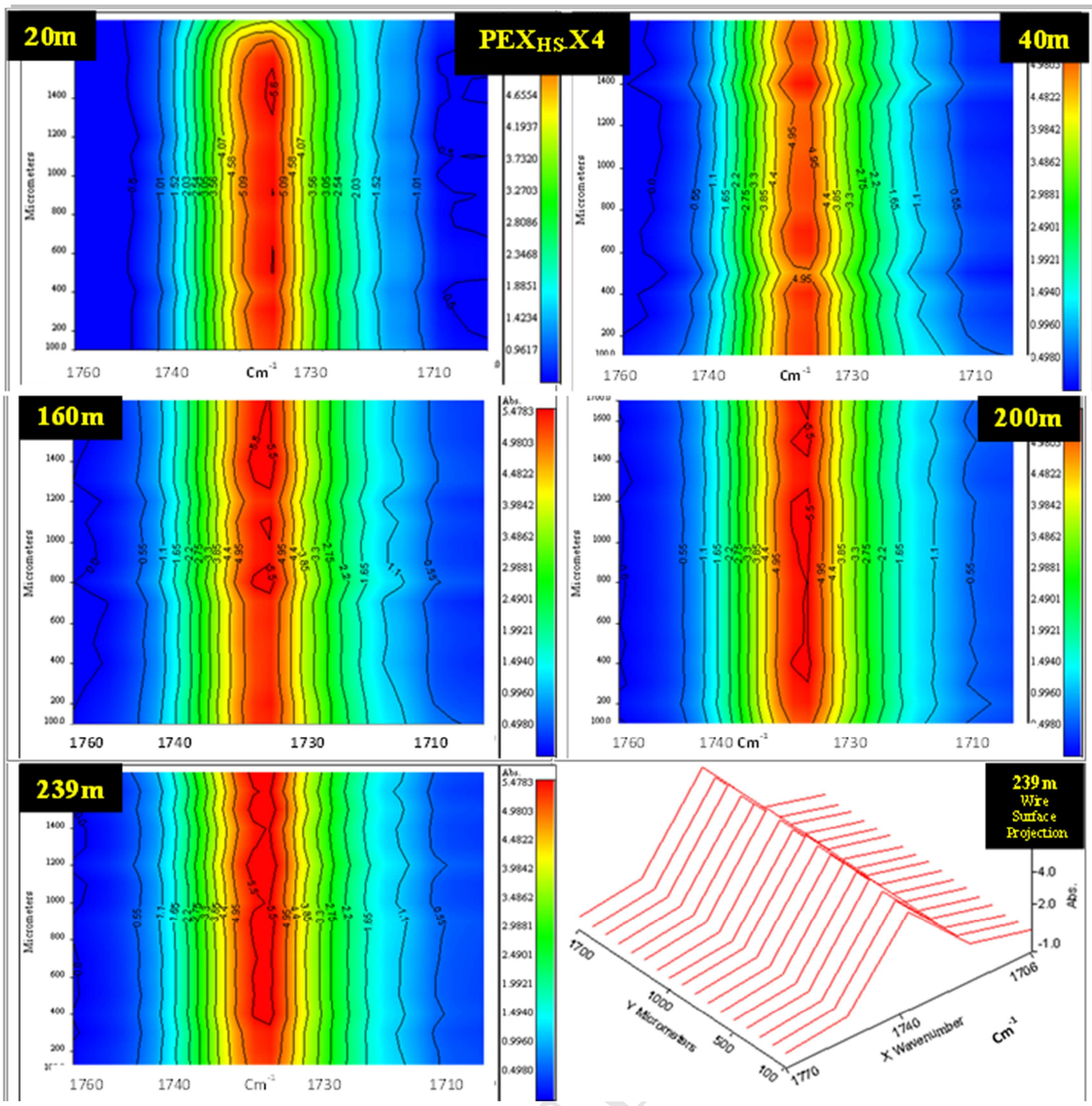

Figure 10: FTIR-microscopy showing colour contours and a line scan (the latter measured at pipe length of 239 m) of the ester carbonyl index of the antioxidant combination DBPA:AOTP present in PEX$_{aHS}$ pipe and measured at different lengths of the pipe. The numbers on the contours are the length of the pipe in meters where the measurements were taken

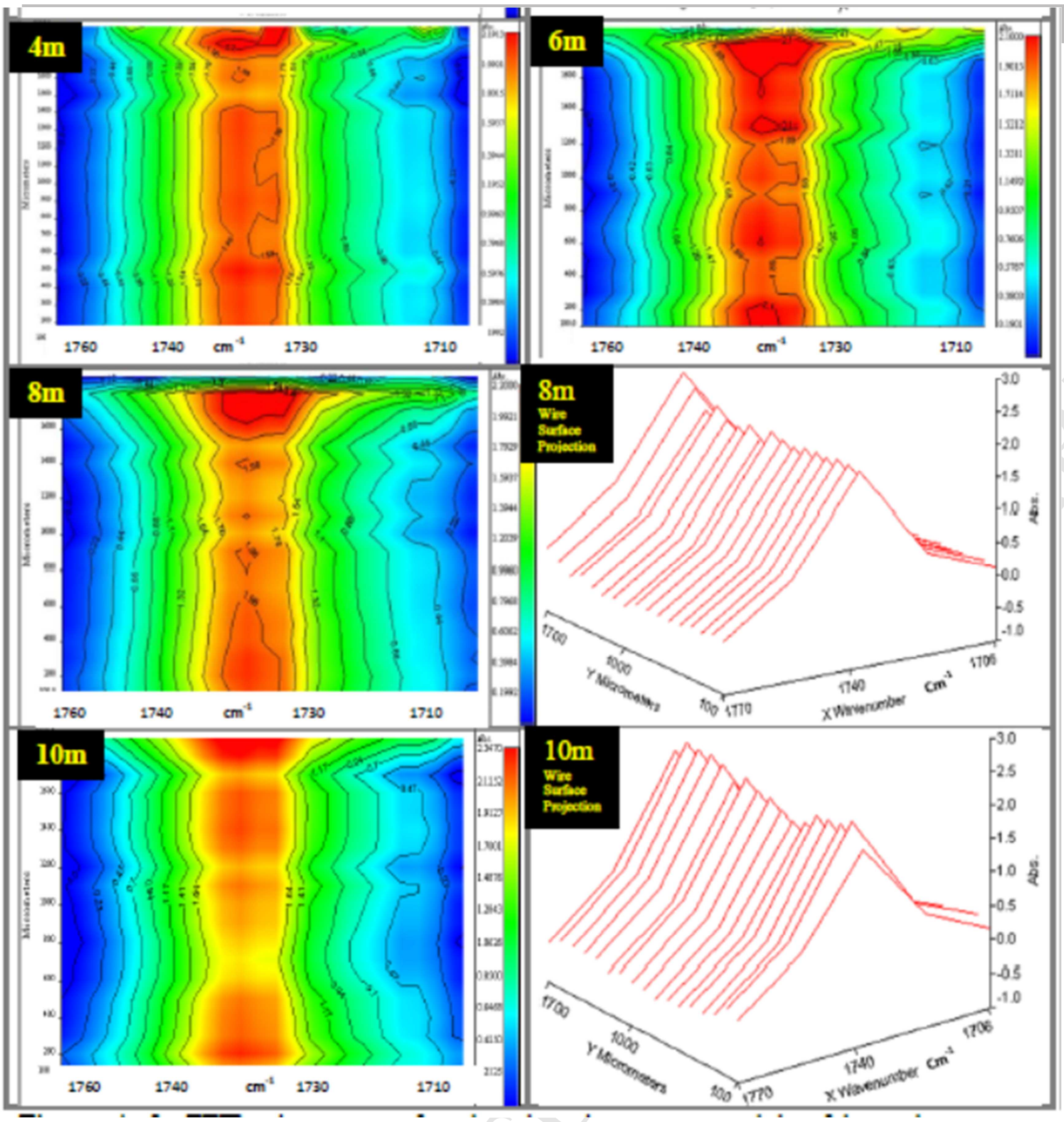

Figure 11: FTIR-microscopy showing colour contours and a line scan (the latter measured at pipe length of 10 m) of the ester carbonyl index of the antioxidant combination Irg1076:cHAS present in PEX$_{aHS}$ pipe and measured at different lengths of the pipe, the numbers on the contours are the length of the pipe in meters where the measurements were taken

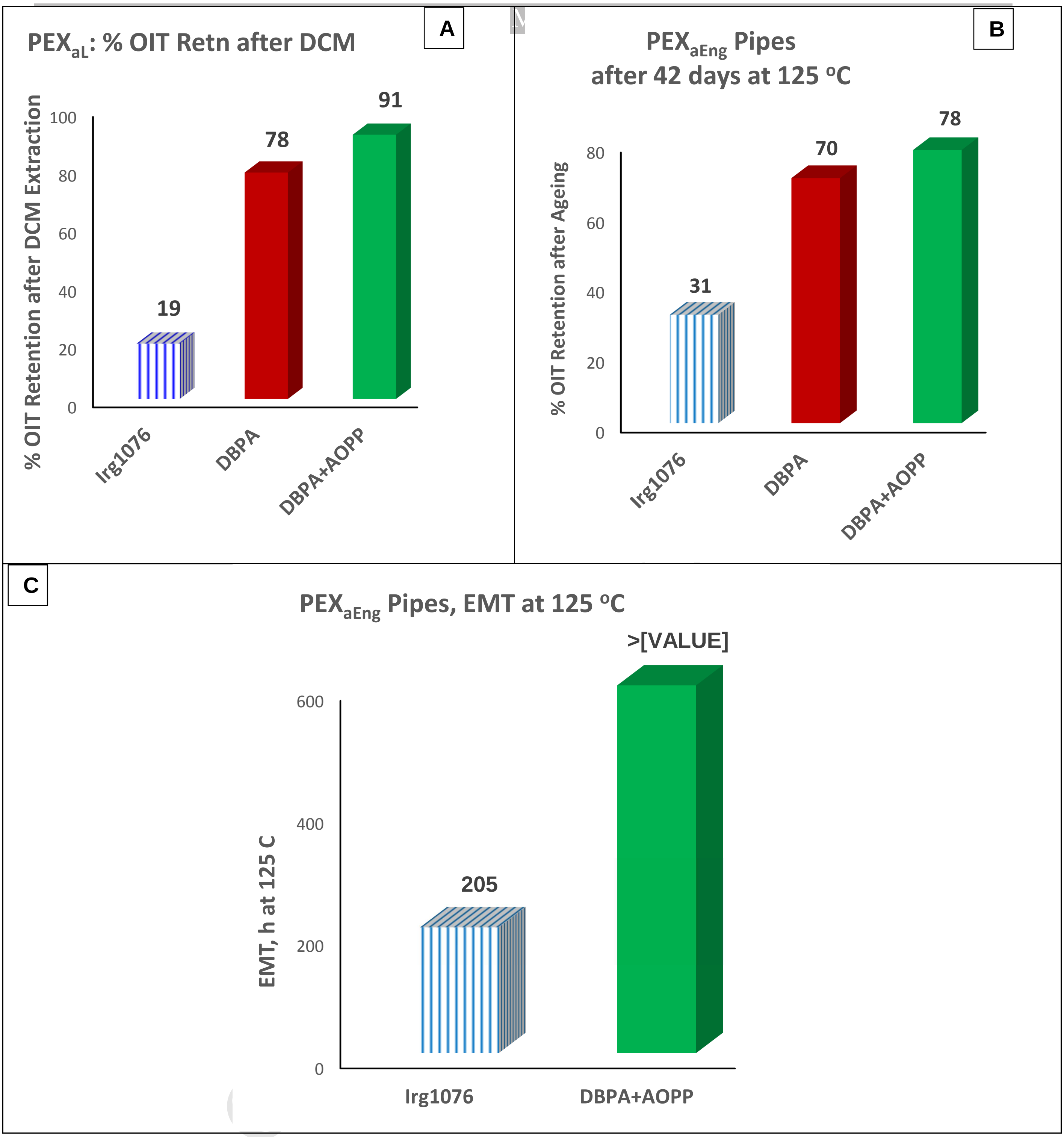

Figure 12: The extent of OIT retention after DCM extraction of PEXa pipes containing antioxidants (A); the thermal stabilising performance (measured by OIT retention) of the antioxidants in the pipes (B) and the time to embrittlement (C) after thermal ageing at 125°C with circulating air for 42 days

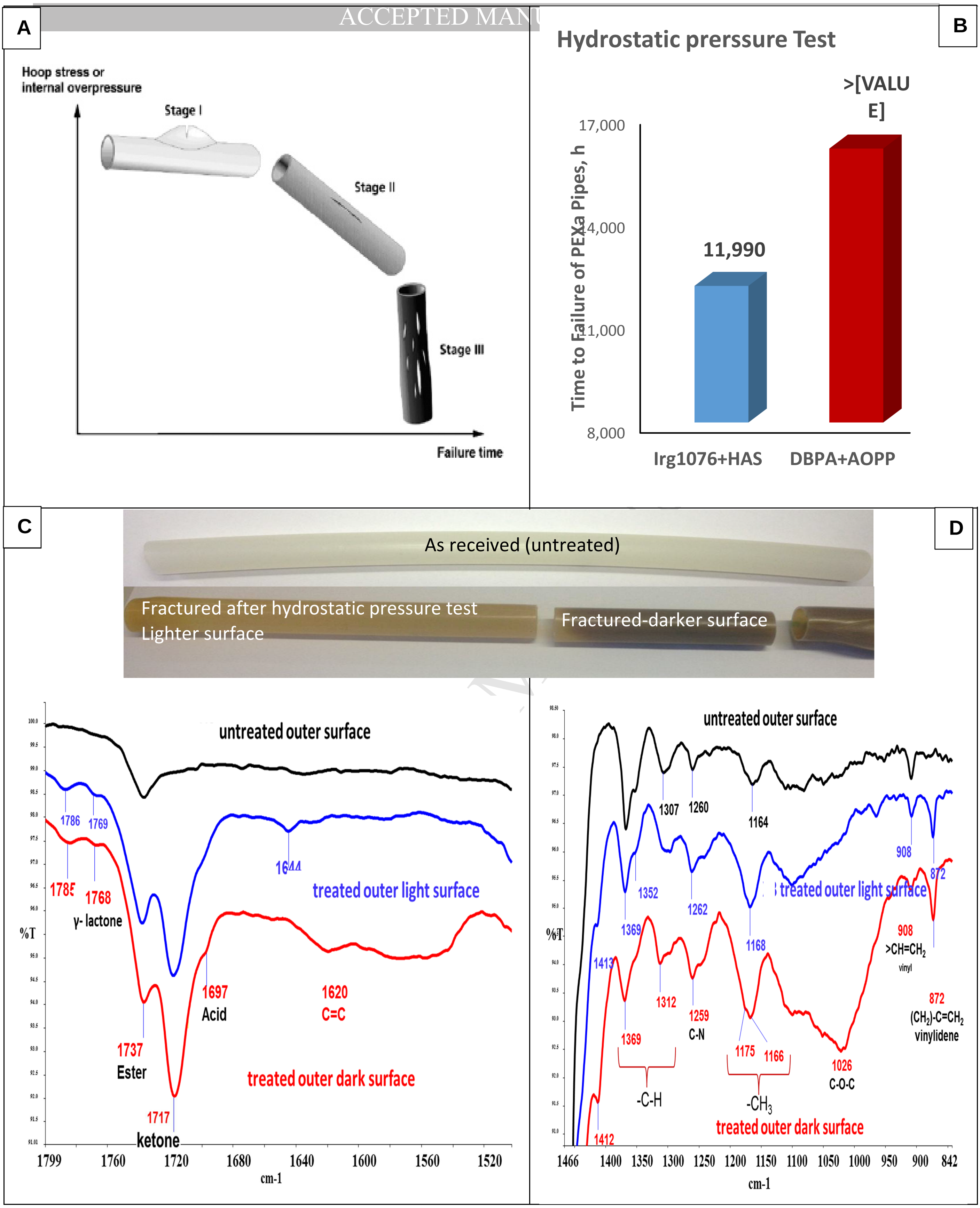

Figure 13: Schematic of PEXa pipe failure under hydrostatic test (A); time to failure of PEX$_{aHS}$ Pipes containing conventional and reactive antioxidant combinations under Hydrostatic Pressure test (B); formation of oxidation products (carbonyl and double bond formation-infrared absorptions) from a PEXa pipe containing Irg1076/c-HAS (C).