Adhesives performance of 3-layer PE pipe coatings: Effects of MAH loading, PE particles size, coating interval time and service temperature

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ABSTRACT

Polyethylene (PE) adhesives used in combination with a PE topcoat and a fusion bonded epoxy (FBE) are one of the most common pipeline corrosion-resistant coating systems used in the oil and gas industry. The role of the adhesive in binding the topcoat to the steel surface is critical to ensuring long term protection against corrosion attack to the pipeline. Consistent with this, it is important to understand how adhesion is optimised by controlling the physical and chemical properties of the adhesive. In this work, adhesives were produced by grafting maleic anhydride (MAH) on to the polymer backbone of an inert polyethylene via free radical chemistries during reactive processing then investigating adhesive performance as function of grafting. The effects of particle size on adhesion performance were also studied for two mean particles sizes of 300 μm and 125 μm. Overall, increasing MAH (along with increasing DBP) concentration enhanced the degree of grafting, as characterised by FTIR spectroscopy, which in turn resulted in enhanced interfacial interaction between the non-polar PE topcoat and polar FBE. However, an intermediate level of MAH was found to produce the greatest adhesion due to a subsequent increase in viscosity, as shown by changes in the melt flow index (MFI) and reduced wetting of the adhesive to the primer at higher MAH concentrations. Thermal analyses using Differential Scanning Calorimetry (DSC) confirmed that functionalization of the PE adhesive disrupted its semi-crystalline structure by reducing melting temperature (T_m) and degree of crystallinity (X_c). Investigation of the effects of particle size and coating interval time revealed that finer particle sizes of $\leq$300 μm produced further improvement in adhesion strength compared to the coarser particles size $\geq$300 μm, while longer interval times degraded the adhesion performance of the coating system. This finding suggests that, apart from grafting efficiency, selection of particle size and coating times are important considerations for achieving optimum coating adhesion performance in three-layer PE coating systems.

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1. Introduction

Polyethylene-based pipeline coating systems provide excellent corrosion protection for a wide range of demanding applications, and as such have remained a dominant pipe coating system in use by the oil and gas industry today [1,2]. Generally, these types of coatings comprise of three layers of materials, as shown in Fig. 1, consisting of an epoxy primer, a polyethylene-based intermediate adhesive layer and a polyethylene topcoat. The epoxy primer (inner layer), often referred to as a fusion bonded epoxy (FBE), affords corrosion protection to the inner steel pipe by providing chemical

resistance and acting as an oxygen barrier. The role of the topcoat (outer layer) is to provide long term protection against mechanical damage arising from the handling, transportation and installation of the pipes in service. The adhesive (sandwiched between FBE and topcoat) is a co-polymer that is normally blended or reactively modified to optimise interaction between the epoxy primer and the topcoat to maintain long term adhesion and thus durability of function. The modification of adhesive is often carried out to enhance interfacial bonding when the three components are brought together in the molten state [3,4].

A wide variety of methods are available for modifying the surface of low energy hydrophobic polyolefin to enhance adhesion or compatibility with other less hydrophobic polymers. One such method, used in the present work, is reactive extrusion which incorporates functionality to an otherwise non-polar,

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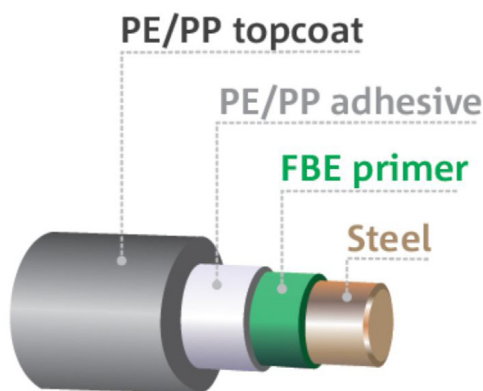 *E-mail address:* shamsul_farid@petronas.com.my (M.S.F. Samsudin).

Fig. 1. Basic configuration of a 3-layer PE pipe coating system.

non-functional and inert hydrocarbon polymer. Without this functionalisation there would result limited interaction or chemical reactions possible with the comparatively polar primer and hence give poor adhesion.

A variety of functional groups can be grafted on to PE via free radical reactions, although maleic anhydride in particular (MAH) in both solution and melt processes has proven to be effective in promoting adhesion between the PE topcoat and epoxy primer [5–8]. The review of the research work and publications on the synthesis of polyolefin graft copolymers including polyolefin with grafted MA, maleates, fumarates, maleimides, etc. by reactive extrusion or other forms of melt phase processing were carried out by Moad [9]. The reaction of free radical in melt phase polymer usually will involve these three processing conditions such as; high processing temperature above than 150 °C, high melt pressure and process in high polymer melt viscosity which in return will lower down the rate of initiator decomposition [9]. Free radical grafting of PE is understood to occur as free radicals generated by the decomposition of initiators which abstract hydrogen atoms from the PE backbone to form macro radicals. MAH is then able to attach itself to the PE backbone through reaction with these macro radicals [10] prior to termination of the free radical process. It is well established that the reactivity and specificity of the initiator's free radical is strongly depend on the nature of the particular initiator itself [11]. Side reactions however, such as crosslinking or homo-polymerisation of the MAH can also occur which reduce the effectiveness of grafting, so it is necessary that for any given system the process must be optimised. Many researchers have studied the effects of chemical parameters, such as monomer concentration, initiator concentration, initiator type and processing parameters, on the efficiency of the grafting and side reactions [5–11]. For example, the effect of initiator on grafting of MAH onto linear low density polyethylene (LLDPE) has been studied by Nazockdast [12] where he found that the degree of grafting initially increased with increasing initiator concentrations but reached a plateau after an optimum concentration. Similarly, research on the effect of varying peroxide content on the changes of LDPE morphology and crystallisation has also been carried out [13–16]. For example, Nilsson et al. [13] reported that DSC studies on the cross-linked LDPE all exhibit considerable impact on thermal properties as the crystallisation temperature (T_C), degree of crystallinity (X_c) and melt temperature (T_m) decrease with increasing peroxide content and crosslinking.

Other than the extent of chemical modification, the coating application window is also a critical factor contributing to adhesive performance. Improper selection will jeopardise adhesion and likely lead to the separation of the top coat from the FBE adhered to the pipe. To do this for three layer coating systems, the line speed is adjusted to accommodate the application parameters for the three layers. Based on work by Varughese [17], the FBE has to be gelled and should only be partially cured for the optimum adhesion between the FBE and grafted polyolefin adhesive. If the polyolefin adhesive middle layer is applied to the FBE below about 30% cure conversion, there will be minimal adhesion and pull away from the pipe during application. On the other hand, if the FBE is cured to more than 70% conversion, the FBE will not have enough functional groups available to bond with the grafted polyolefin adhesive layer. Therefore, the application of the adhesive layer at the proper time is critical to optimising adhesion between the FBE and the polyolefin layers.

From an industrial viewpoint, processability, performance and durability are ultimately the critical parameters which control usage, but as industry continues to require materials with better properties, it is important to also have a fundamental understanding of the structure property relationships that affect adhesion. Thus, the present work aims to close this gap by investigating the impact of different concentrations of MAH monomer on the level of grafting of PE, melt flowability, thermal properties and adhesion. The MAH concentration was varied from 1.5 to 3% whilst the relative concentrations of MAH to DBP initiator was controlled at a constant 50:1 ratio. The effect of particle sizes and coating interval times were also carried out to investigate the influence of these two parameters on controlling the melting and wettability of the adhesive layer during the coating process. The work culminates in evaluating a set of peel strength tests carried out at different temperatures on full-size pipes, per industry standard.

2. Experimental

2.1. Materials

LLDPE resin used in this work was supplied by PETRONAS Chemical Polyethylene Sdn Bhd with a melt flow index of 1 g/10 min (190 °C, 2.16 kg load). The initiator used was Di-Benzoyl Peroxide (DBP), and the grafting agent was Maleic Anhydride (MAH), both of which were supplied by Sigma Aldrich. All materials used in this work were in solid form.

2.2. Reactive extrusion compounding

PE adhesive samples were prepared using a Brabender twin screw extruder L/D 40 with an output rate about 3 kg/hour. The extruder temperature was set at a range of between 180–230 °C. The initiator and MAH which are in solid powder form were fed through a micro-twin screw feeder where the two materials were mixed together prior to entry into the extruder to react with PE. This is to ensure a well dispersed MAH/DBP mixture is obtained. The concentration of MAH used were 1.5, 2.5 and 3.0%, and corresponding concentrations of DBP used was based on a constant MAH: DBP ratio of 50:1. The concentrations of MAH and DBP used in each PE adhesive formulation is summarised in Table 1. The resultant PE adhesives were then ground, sieved and segregated into two batches of ≤300 μm and ≥300 μm particle sizes. It was observed through the microscope the ground adhesives have an irregular shape with combination of platy and spherical shape.

Table 1
Concentrations of MAH and DBP in the PE adhesives samples, based on a 50:1 ratio.

Sample	MAH (%)	DBP (%)
S1	1.5	0.03
S2	2.5	0.05
S3	3.0	0.06

2.3. Testing and analysis

2.3.1. Fourier transform infra-Red (FTIR)

Verification of the grafting reaction and the level of grafted MAH in the LLDPE was carried out on a Perkin Elmer FTIR Spectrum 400 using the proprietary spectral analysis software provided by the instrument manufacturer. The presence of MAH was determined using peak intensities of the carbonyl stretches (C–O) at 1790 cm^{-1}, while 1368 cm^{-1} was used as a standard reference peak (C–H). The carbonyl index for the samples was calculated based on the ratio of the peaks at 1790 cm^{-1} to those at 1368 cm^{-1}. Specimen preparation for FTIR analysis involved dissolving the PE adhesive samples in xylene via a refluxing process, which took approximately 3 h. The adhesive was then precipitated in acetone and filtered. The specimens were then dried in an oven at 80 °C for 3 h and pressed into a thin film of about 0.1 mm thick using a hot press set at 200 °C. This procedure was performed to remove any remaining unreacted MAH in LLDPE.

2.3.2. Melt flow index (MFI)

The MFI of the PE adhesive samples were measured in accordance with ASTM D1238 [18]. The temperature was set at 190 °C and a load 2.16 kg was used. The MFI value was recorded based on the average of three readings.

2.3.3. Differential scanning calorimetric (DSC)

The DSC tests were carried out on a DSC Q100 TA instrument with samples of about 5 mg in aluminum pans under nitrogen atmosphere. The samples was heated from 20 °C to 200 °C at a heating rate of 10 °C/min. The melting temperatures and melting enthalpy of the samples were determined from the area of DSC endotherm. The degree of crystallinity was calculated via the total enthalpy method according to the following equation:

$$X_C = \frac{\Delta H_m}{\Delta H_{m100\%}} \qquad \ldots \ldots (1)$$

where X_C is the degree of crystallinity, ΔH_m is the enthalpy of fusion and $\Delta H_{m100\%}$ is the enthalpy of fusion for 100% crystalline polyethylene. The value for $\Delta H_{m100\%}$ is taken as 288J/g as reported in the literature [19,20].

2.3.4. Peel adhesion strength

The peel adhesion test used for the present work was based on ISO 21809 [21] using an Instron 5569. Basically, the test is performed by pulling and debonding a 3-layer coating from its steel substrate by subjecting to a constant peel rate. The test coupons comprised 3 mm thick of steel plate with a nominal coating thickness of 2.45 mm. The peel rate was set at 10 mm/min, and the test was terminated when 100 mm of the coated length has been debonded. The average peel strength was recorded for every interval of 20 mm. The first and last 10 mm interval value will be
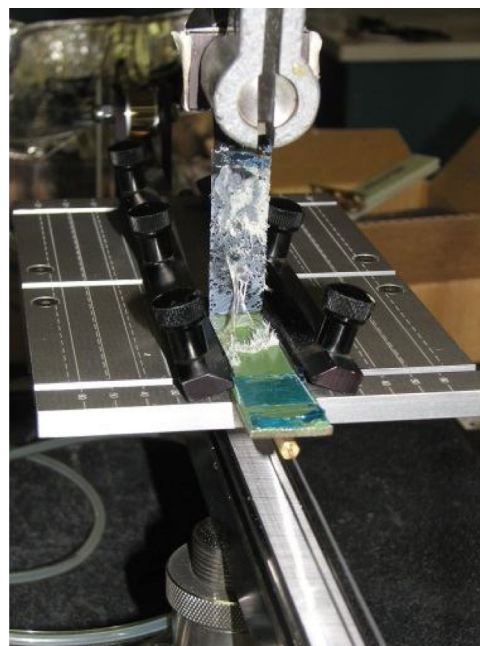

Fig. 2. Setup of the laboratory peel adhesion test.

discarded. The test was repeated two times for each test parameter applied. Fig. 2 shows the setup of the peel adhesion test, while the test coupons dimension and thickness of the coating layers applied is represented in the Fig. 3.

The flowchart in Fig. 4 summarises the steps taken to fabricate the peel adhesion test coupons. In summary, flat steel samples measuring 3 mm by 25 mm by 120 mm steel were grit blasted to achieve a consistent quality equivalent to SA 2.5, per ISO 8501 [22]. The plates were then heated to approximately 200 °C after which it is spray-coated with FBE, followed by the application of the PE adhesive (under study) and finally the PE topcoat. To facilitate studying the effects of coating interval time, the time elapsed between steps 4 and 5, in Fig. 4, was varied for (only) the adhesive with 1.5% MAH (and 0.03% DBP), i.e. sample S1, from the standard used in this work of 10 s to 20 s, and then to 30 s.

Peel adhesion tests were also carried out on full size pipes that had undergone the coating process in an industrial coating plant. A number of deposition temperatures as well as inter-coat deposition interval times were studied for their effect on the peel adhesion performance of the coating system. The peel adhesion tests used on the pipes were in principle the same as that used on the flat coupons, and were also based ISO 21809. Due to commercial sensitivities, details of the production coating is not disclosed in this
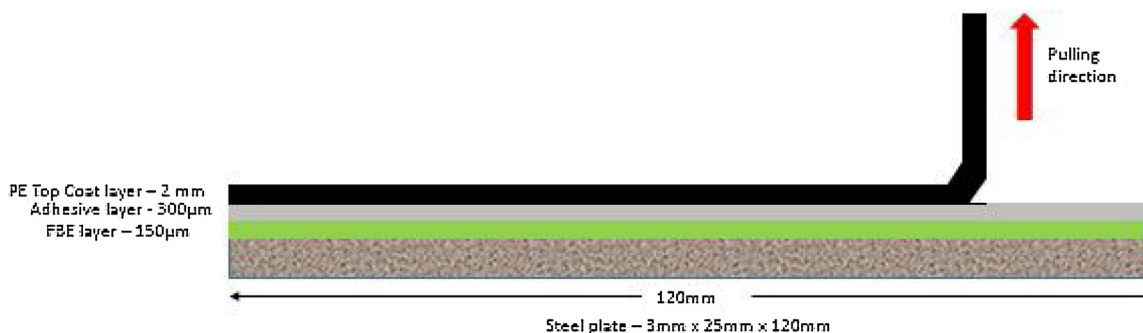

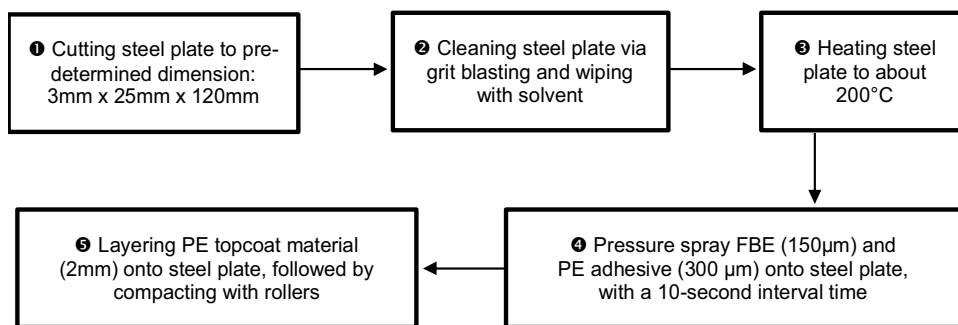**Fig. 3.** Schematic diagram of the peel adhesion test specimen.

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┌─────────────────────────┐     ┌─────────────────────────┐     ┌─────────────────────────┐
│ ❶ Cutting steel plate    │     │ ❷ Cleaning steel plate   │     │ ❸ Heating steel          │
│   to pre-                │ ──▶ │   via grit blasting and  │ ──▶ │   plate to about         │
│   determined dimension:  │     │   wiping with solvent    │     │   200°C                  │
│   3mm x 25mm x 120mm     │     │                          │     │                          │
└─────────────────────────┘     └─────────────────────────┘     └─────────────────────────┘
                                                                              │
                                                                              ▼
┌─────────────────────────┐     ┌─────────────────────────┐
│ ❺ Layering PE topcoat    │     │ ❹ Pressure spray FBE     │
│   material (2mm) onto    │ ◀── │   (150µm) and PE         │
│   steel plate, followed  │     │   adhesive (300 µm) onto │
│   by compacting with     │     │   steel plate, with a    │
│   rollers                │     │   10-second interval time│
└─────────────────────────┘     └─────────────────────────┘
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Fig. 4. Procedure used to fabricate the peel adhesion test coupons.
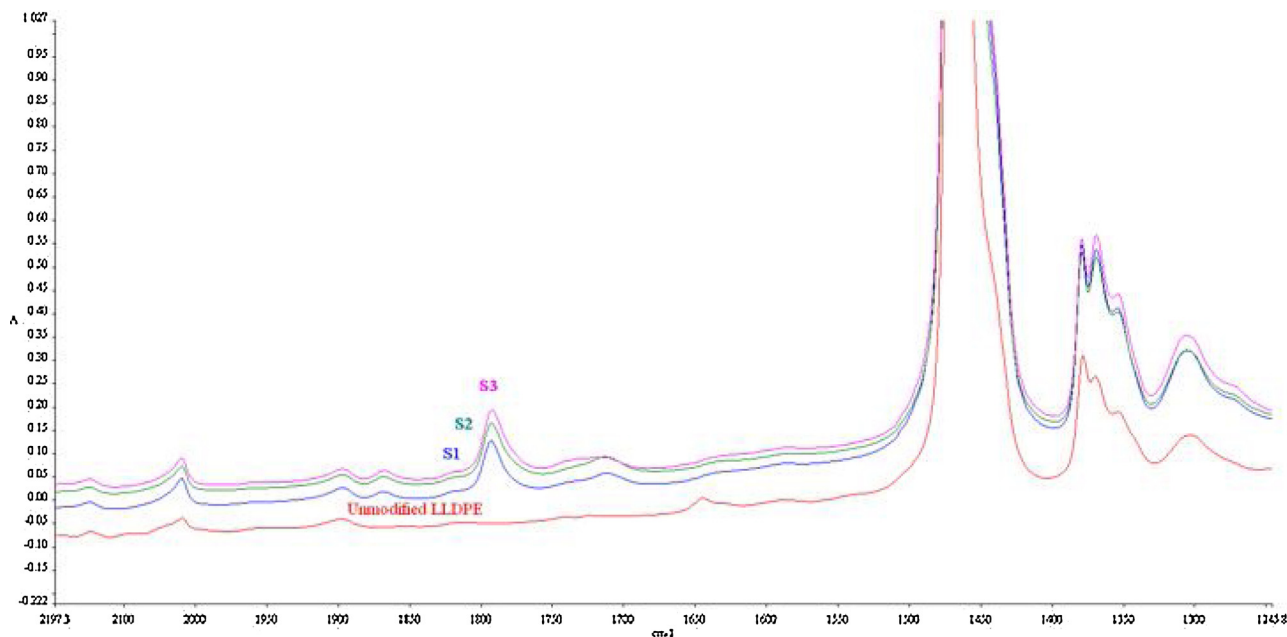
Fig.5. Representative FTIR spectrum of the PE adhesives with different concentration of MAH.

3. Results and discussion

3.1. Degree of grafting versus MAH loading

FTIR analysis was used to confirm the presence and the relative amount of grafted MAH in the LLDPE chain. Representative FTIR spectra of the PE adhesive samples under study are shown in Fig. 5. The absorption band at $1790\,cm^{-1}$ for the three MAH grafted adhesives provide evidence that grafting had taken place onto the PE backbone and can be attributed to the carbonyl group originating from the ester linkage of MAH. Important to note also, the complete absence of any carbonyl peak in the virgin unmodified PE. Increasing MAH concentration increases the probability of LLDPE macro-radicals reacting with the monomer, as evident by correspondingly higher carbonyl index. The carbonyl index for each adhesive was calculated based on the ratio of the peak intensities at $1790\,cm^{-1}$ and at $1368\,cm^{-1}$, and presented in Table 2. This result is consistent with the findings of Gaylord and co-workers [23] on grafting of MAH on HDPE at the melting stage. In addition, increasing of DBP concentrations is expected to generate more radical sites for the grafting reaction to take place.

Table 2
Carbonyl indices of the different PE adhesives.

Sample	Peak Intensity @ $1790\,cm^{-1}$	Peak Intensity @ $1368\,cm^{-1}$	Carbonyl Index (1790/1368)
S1	0.2242	0.6269	0.35
S2	0.2735	0.7315	0.38
S3	0.2568	0.6076	0.42

Table 3
MFI value of PE adhesives at different concentration of MAH (and DBP).

Sample	MFI (g/10 min)
LLDPE	0.89 ± 0.01
S1	0.78 ± 0.02
S2	0.65 ± 0.01
S3	0.64 ± 0.02

3.2. Flow viscosity versus MAH loading

The MFI measurements were carried out to study the melt flow behaviour of the adhesives as a function of (grafted) MAH concentration. The indices measured for each of the three adhesive samples are summarised in Table 3, alongside the value for the virgin LLDPE. Comparing with the virgin LLDPE, which has an MFI of 0.89 g/10 min, the adhesives have MFI values ranging from 0.78 to

paper. Suffice to say that the process remains as that outlined in Fig. 4 except at a more industrial scale.
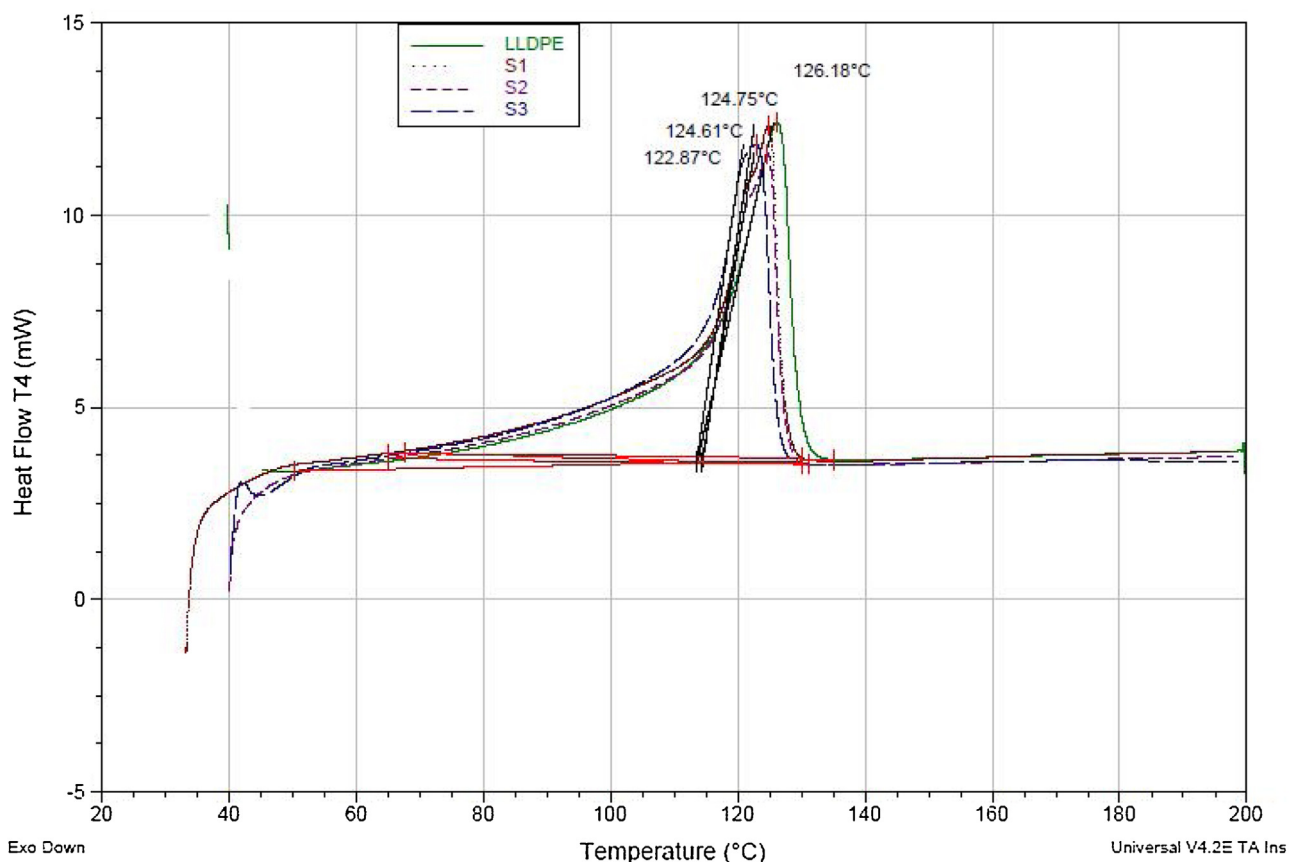
Fig. 6. Representative DSC thermogram of PE adhesives with different concentrations of MAH.

0.64 g/10 min, *i.e.* a maximum reduction of some 30%, corresponding to the sample with the highest MAH loading. The reduction in flowability with increased grafting of MAH is believed to be due to a combination of side reactions such as crosslinking in the LLDPE and/or homo-polymerisation. According to Moad [9] PE is susceptible to undesired crosslinking or branching when it is grafted with a monomer which leads to gel formation, increased torque during mixing and reduced flow. Reduction in MFI (i.e higher melt viscosity) is foreseen to cause a deleterious impact upon processability by reducing wetting when applied to the FBE and hence reducing adhesion. The viscosity effect can be correlated to the epoxy primer flow where the primer required to flow smoothly before it gel in order to have intimate contact with the steel substrate [17]. Increased crosslinking due to greater presence of PE-MAH macro radicals, as inferred above, may also embrittle the primer/adhesive interface thus leading to inferior adhesion.

3.3. Melting temperature versus MAH loading

The DSC analysis of PE adhesives was carried out for the samples with different concentrations of MAH to understand the effect of the grafting process on melting temperature (T_m) and on the crystallisation behaviour of LLDPE. In the present work, the latter is characterised by the degree of crystallisation, X_c, which is calculated per Eq. (1). The endotherm melting peak of the three PE adhesives samples are presented in Fig. 6.

It can be observed that the melting temperature decreased with MAH concentration, albeit only marginally. Between the three samples, the T_m only changed slightly from 126 to 122 °C, but the changes nevertheless suggested that the crystal structure of the PE adhesive had been disrupted as the MAH and DBP concentrations increased. In addition the degree of crystallinity summarised in

Table 4
Melting point and degree of crystallinity of PE adhesives at different concentrations of MAH.

Sample	T_m(°C)	X_C
LLDPE	126.18	0.37
S1	124.75	0.35
S2	124.61	0.35
S3	122.87	0.34

Table 4, demonstrated a similar trend where the X_c value decreased marginally as MAH concentration increased. The trend suggests that the formation of chain crosslinking from the grafting side reaction that directly influences the crystallisation structure of LLDPE. As the level of crosslinking increases, the crystallisation of LLDPE reduces [24]. The crosslinks impede the folding of macromolecular chains and thus the crystal size remains small which consequently reduces the X_c [13–16].

3.4. Peel adhesion strength versus MAH loading, adhesive particle size, and coating interval time

3.4.1. MAH loading

The adhesion strength between the PE topcoat and the FBE primer is the most important measure of the PE adhesive performance for pipe coatings, and is determined using a form of peel test. A representative selection of raw data traces showing the improvement in strength versus MAH concentration are shown in Fig. 7, and the average of measured strength values for each adhesive sample are presented in Table 5. Similarly, plots of peel strength versus particle size are shown in Fig. 8, and the average of measured strength values for each adhesive sample is presented in Table 6. Note that
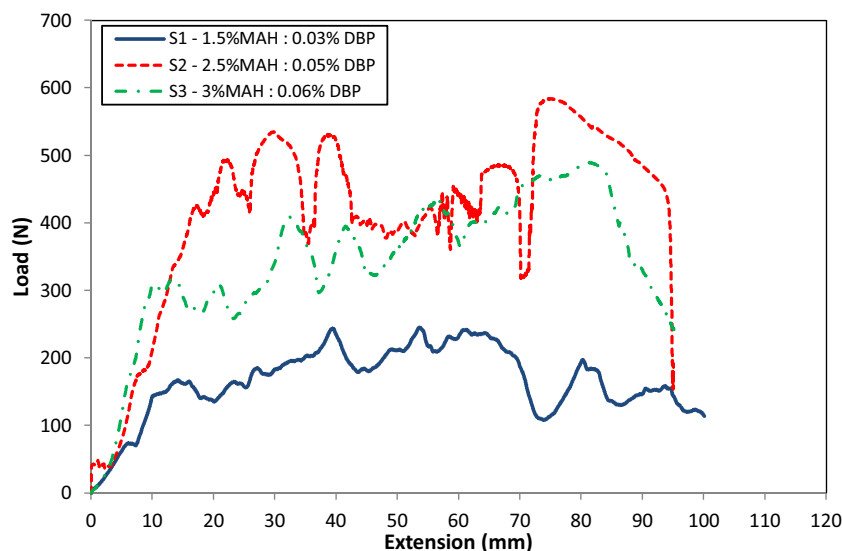
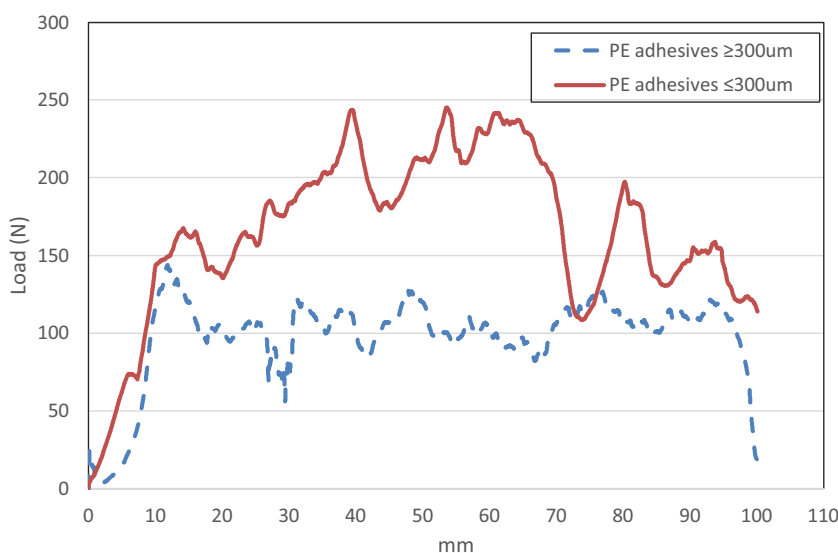**Fig. 7.** Peel strength of PE adhesives with different concentrations of MAH.

Fig. 8. Peel strength results for PE adhesives having particles sizes of $\leq 300\,\mu m$, and of $\geq 300\,\mu m$.

Table 5
Peel adhesion performance versus different concentrations of MAH.

Sample	Peel strength (N)
S1	193 ± 34.2
S2	465 ± 43.2
S3	372 ± 63.2

Table 6
Peel adhesion performance versus adhesive particles size.

Particle size	Peel strength (N)
$\leq 300\,\mu m$	193 ± 34.2
$\geq 300\,\mu m$	107 ± 7.5

these test results are all based on flat specimens prepared according to the procedure illustrated in Fig. 3.

It can be seen that the peel adhesion strength showed notable improvement as the MAH concentration is increased. Note is that there was no adhesion at all for un-modified PE reflecting the importance of grafting. The tests recorded a more than two times improvement in strength when MAH concentration was increased from 1.5% to 2.5%. However, at 3% MAH concentration, the adhesive strength, despite being still relatively high, and certainly well above that achieved with 1.5% MAH concentration, was lower than the value 2.5% MAH concentration. This implies there are competing factors such as the increase in side reactions affecting the adhesive strength of the coating as discussed earlier i.e increasing of viscosity due to crosslinking of LLDPE.

3.4.2. Adhesive particle size

Based on the adhesive sample with 1.5% MAH (and 0.03% DBP), *i.e.* sample S1, it was shown in this study that by applying coarser particle size $\geq 300\,\mu m$, the peel adhesion strength could be degraded by some 50%, as seen from Table 6. It is believed that, as for finer particle size $\leq 300\,\mu m$ due to its increased surface area, it enable more even and faster melting of the adhesive as it contacts the heated surface of the substrate, thus facilitating easier flow and better wetting. Coarser particle is expected to impede the heat transfer and as a result require longer time to melt and fuse the adhesive particles to achieve uniform coverage. Fig. 8 shows load
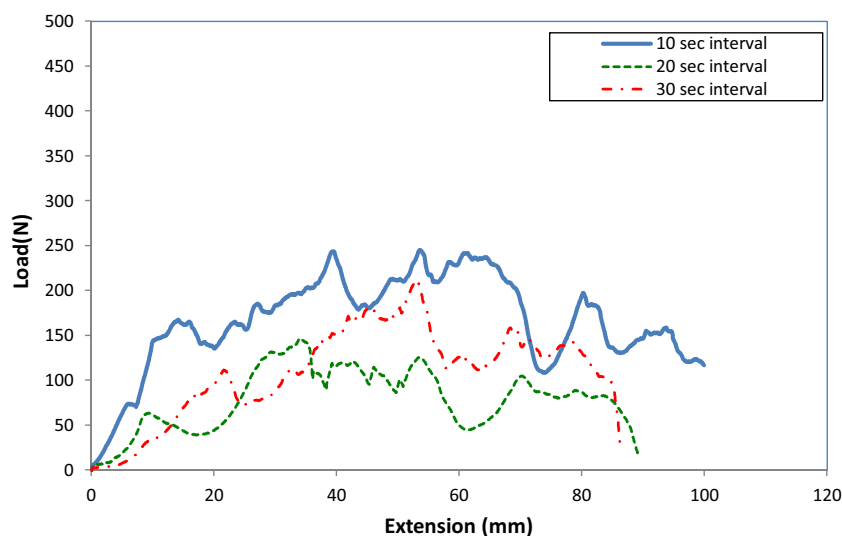
Fig. 9. Peel strength performance versus different coating interval times.

extension curves for the two samples of differing particle size illustrating this improved adhesion for smaller particle sizes. Coarser particle size specimen demonstrated both cohesive and adhesive failure in the adhesive FBE interface.

3.4.3. Coating interval time

Only the adhesive with 1.5% MAH (and 0.03% DBP), *i.e.* sample S1, was considered for studying the effects of coating interval time. The coating interval time, in the present context, refers to the time elapsed between the first application of the adhesive and that of the topcoat, *i.e.* from steps 4–5 in Fig. 4. This study was carried out to simulate the different pipe conveyance speed used in actual pipe coating setup. Varying the traverse speed is a normal practice for optimising coating conditions with respect to substrate temperature, homogenous application of materials and uniform curing and solidification.

The peel strength plots for different interval times are presented in Fig. 9. The average strength values were determined based upon the guidelines of ISO 21809, and summarised in Table 7. The peel strength is observed to decrease as the interval time is extended from 10 s to 20 s and finally to 30 s. While a longer interval time may have been expected to produce better surface wetting and at the same time allow more time for chemical interaction between the coating layers, this unexpected reduction in adhesion is proposed to be due to the increasingly crosslinked structure of the epoxy primer. As the primer approaches gelation and curing stages a three dimensional intractable network starts to form that reduces polarity, compatibility, polymer flow and molecular reactivity, all of which would reduce or impede interaction with the adhesive. Even though there is an increment of peel strength moving from 20 s to 30 s, the value at 30 s is still lower than the optimum 10 s interval time. Thus in this case the reduction in adhesion at longer coating intervals is likely due to higher degree of FBE crosslinking, which supports the work done by Varughese [17] that claimed FBE had to be completely gelled but only partially cured for the best adhesion between FBE and adhesive. Higher degree of FBE curing will further

Table 7
Average peel strength versus coating interval times.

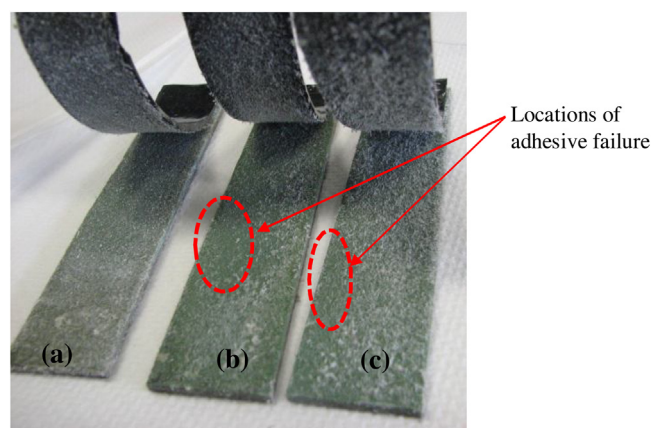| Interval time	Peel strength (N)
10 s	193 ± 34.2
20 s	101 ± 41.5
30 s	134 ± 28.0

Fig. 10. Failure surface of the adhesion peel test coupons for (a) 10 s, (b) 20 s, and (c) 30 s.

reduce the functional groups available to bond with adhesive layer. Fig. 10 shows the failure surfaces for both a well-bonded adhesive, *viz.* the 10 s sample, which exhibit complete cohesive failure (in the adhesive layer), compared with the ones where adhesive failure has partially occurred (in the adhesive-FBE interface), *viz.* the 20 s and 30 s sample.

3.5. Peel adhesion strength versus test temperature

Fig. 11 shows the adhesion peel test used to qualify mill-applied coatings on pipes. Like the laboratory peel adhesion test, this test involves measuring the force necessary to detach the coating from its substrate when subjected to a constant rate of pull (*viz.* 10-100 mm min^{-1}, depending on specification). A purpose-built test rig that can be rotated over the pipe surface is used, see Fig. 11(a), whereby a peel strip (or, 'tongue') is gripped and pulled at 90° to the tangent of the pipe surface. The strip is of a pre-determined width (typically 25 mm), see Fig. 11(b), which is formed by carefully cutting and chiseling into the coated pipe. Industry standards, such as ISO 21809, generally recommend that the test be carried out at different temperatures, covering the field conditions of room/ambient, low and high temperatures, although the exact recommended temperatures may vary somewhat between different
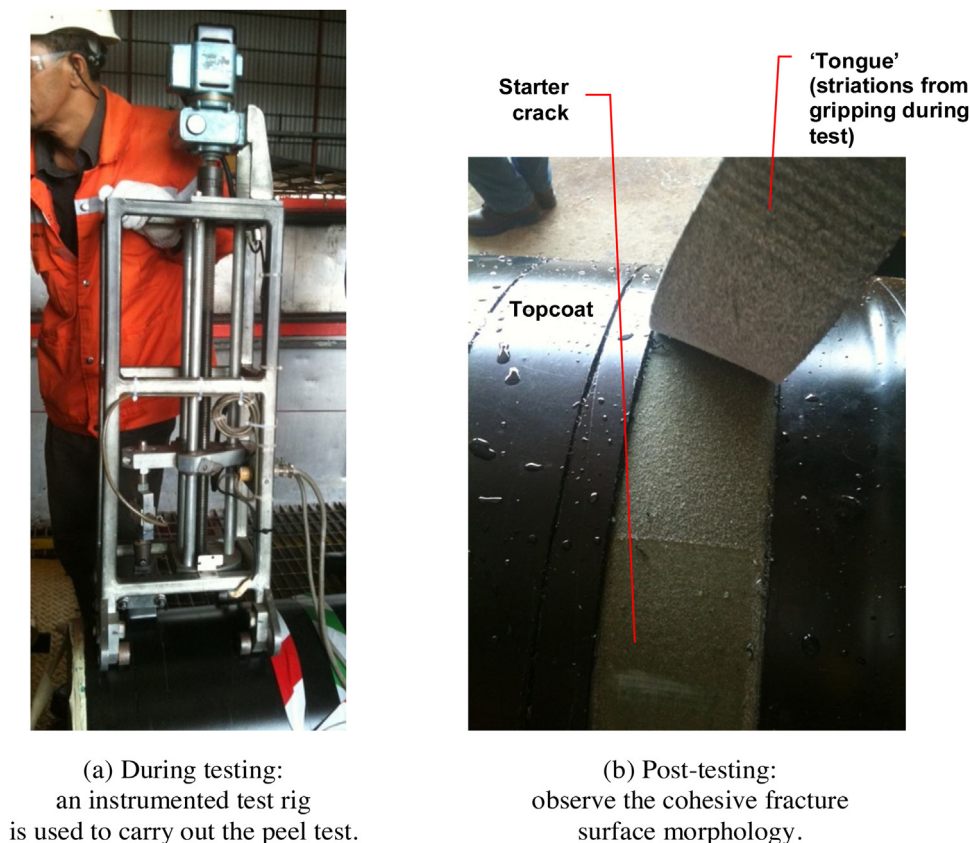
(a) During testing:
an instrumented test rig
is used to carry out the peel test.

(b) Post-testing:
observe the cohesive fracture
surface morphology.

Fig. 11. The peel adhesion test is used as a standard pass-fail assessment tool for three-layer pipe coatings.

standards. The test requires cohesive failure in the adhesive layer for test values to be deemed valid.

The effectiveness of the S1 adhesive (*i.e.* the adhesive with 1.5% MAH (and 0.03% DBP)) at various temperatures was assessed using mill-coated pipe specimens (rather than flat coupons). Fig. 12 shows the result for tests carried out at 23 °C, 50 °C, 70 °C, 80 °C and 90 °C. It can be seen that peel adhesion strength decreased with temperature, dropping from 17 x to 6 x over the temperature range considered. The magnitude of strength reduction is around 15–20% for each test temperature. However the value is still higher than the minimum ISO 21809 standard requirement which is ≥30 N/cm at 80–90 °C. This observation is not unexpected, and concurs with the work of Miyajama et al. [25], which is primarily due to increased mobility of PE chains with temperature. Increasing temperature also leads to expansion in free volume that makes the PE chains slip more easily across/over each other and subsequently disrupt the adhesion between the coating layers. It is also understood that when the test temperature is near to the FBE glass transition temperature (T_g), which is around 105 °C, the FBE glassy structure will start to diminish thus contributing to the deterioration of peel strength.

4. Summary and conclusion

This paper describes and discusses the results of work undertaken to develop a MAH-grafted polyethylene adhesive for a three-layer polyethylene (3LPE) pipe coating system. In specific, the effects of the following, *i.e.*

- MAH loading used during adhesive synthesis;
- adhesive particles size and coating interval time used during the coating process and

- service temperature

on the adhesion performance of the 3LPE coatings have been systematically investigated. It has shown that these parameters have inter-related influences on the overall adhesion behaviour of the PE adhesive and, hence, the ultimate performance of the final 3LPE coating.

Based on the MAH concentrations studied in this work, *viz.* 1.5%, 2.5% and 3.0%, the degree of grafting increased with MAH loading, but there appeared to be an optimum level of adhesion achievable at between 1.5% and 3% MAH concentration. The increased level of grafting produced a modest reduction in the melting temperature of the adhesive which in turn improved the efficient of the coating process. However the accompanying reduced flow of the adhesive that is expected to be detrimental to good wettability and homogenous spreading of the adhesive over the pipe surface during the coating process resulted in reduced adhesion. This highlights the importance of optimising the reactive extrusion processby minimizing side reactions during grafting in order to enhance adhesion. Due to the various competing effects, as a result, the maximum peel strength in this work was achieved for the 2.5% MAH sample.

Other factors such as particle size and coating interval times between deposition of adhesive and topcoat were also investigated. Whilst only two particle sizes were considered in this study, *i.e.* ≤300 μm and ≥300 μm, it was clear that a smaller particle size advantageous for a higher peel adhesion strength. This is due to the higher surface area of finer particles thus leading to more even melting and hence better flow and enhanced wetting.

In terms of coating interval time, based on the 10 s, 20 s and 30 s conditions studied in this work, shorter times were found to be overall better for adhesion performance. It is believed that the maximum adhesion was a result of balancing two competing
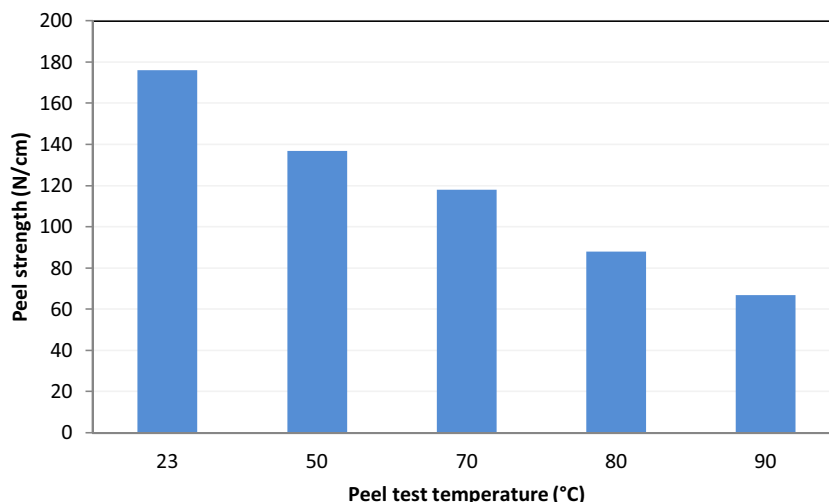
Fig. 12. Peel adhesion strength as a function of test temperature.

factors – a shorter coating interval ensures that higher degree of curing is avoided thus increasing the availability of reactive functional groups, while a longer time enables sufficient surface wetting and time for chemical reactions between the adhesive and the PE topcoat to take place.

By taking all the above findings into consideration, despite not having the highest level of adhesion between the topcoat and the primer, the adhesive with 1.5% MAH content was selected for factory trials to coat 10" steel pipes using a commercially available topcoat and FBE primer. The peel adhesion tests per ISO 21809 was then carried out on the coated pipes for a series of temperatures, namely 23 °C, 50 °C, 70 °C, 80 °C and 90 °C, to gauge its service temperature performance. It was found that peel adhesion degraded as temperature increased, with an estimated drop in strength of 15–20% per 10 °C, over the temperature range considered. It is noteworthy though that the peel adhesion strengths measured in the factory have at least met with the requirements specified in the industry standard ISO 21809.

This work clearly highlights how a good understanding of the inter-related factors affecting the properties and behaviour of PE adhesives is critical to facilitate the selection of processing conditions for three-layer PE coating system. The right selection of these parameters have a direct bearing on the efficiency of the processing, while at the same time ensuring the most optimum 3LPE coating performance that fulfils the requirements of industry standards is also be attained.

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