THEORETICAL RATIONALE FOR MODIFYING FILM-GRADE POLYETHYLENE WITH ALCOHOLYSIS PRODUCTS OF SECONDARY POLYETHYLENE TEREPHTHALATE

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Abstact. *The accumulation of post-consumer polyethylene terephthalate (PET) waste and the demand for higher-performance polyolefin films create a scientific rationale for converting secondary PET (sPET) into functional polymer modifiers rather than treating it solely as waste to be disposed of or mechanically re-melted. This paper substantiates, on theoretical grounds, the feasibility of using an oligoester alcoholysis product (PAPET) - obtained from sPET and diethylene glycol (DEG) - as a reactive modifier for high-pressure film-grade polyethylene (PE). The structural prerequisites of PE, the chemistry of PET glycolysis/alcoholysis, the mechanisms by which polar oligoester fragments interact with a non-polar PE matrix, and the analytical framework (FTIR, thermal and mechanical testing) required to verify such modification are analysed. The work argues that partial retention of ester and hydroxyl functionalities in PAPET is the key structural feature enabling limited compatibilization and property modification in PE, and outlines the theoretical basis for the experimental programme reported in the parent dissertation.*

Keywords: *secondary polyethylene terephthalate, alcoholysis, PAPET, polyethylene modification, oligoester modifier, polymer compatibilization, circular economy of plastics.*

Introduction and Relevance. Global polyolefin and PET production continues to grow, and with it the volume of post - consumer PET packaging waste, most of which is chemically inert toward conventional recycling routes based on simple re - extrusion. At the same time, high - pressure (low - density) polyethylene used for blown-film production is one of the largest - volume polymer materials in the packaging, agricultural and construction sectors, and is subject to continuous demand for improved tensile strength, environmental stress - crack resistance (ESCR) and thermal stability. Bridging these two problems - sPET utilisation and PE film performance enhancement - through chemical modification is a scientifically and environmentally justified direction of polymer materials science, directly aligned with circular-economy principles for plastics.

Structural and Chemical Basis of the Research. Polyethylene is a non - polar, semi - crystalline hydrocarbon polymer whose film - grade (high - pressure, branched) varieties combine moderate crystallinity with the flexibility required for blown-film processing; their mechanical and barrier performance is governed primarily by molecular weight distribution, branching degree and crystallite morphology. PET, in contrast, is a polar polyester whose ester linkages are susceptible to solvolytic depolymerisation. Glycolysis/alcoholysis of secondary PET with a diol such as diethylene glycol cleaves the ester bonds of the PET macrochain, yielding shorter oligoester chains terminated by hydroxyl and residual ester/carbonyl groups - the product referred to as PAPET. The proportion of these functional groups, and consequently the average molecular weight and reactivity of PAPET, is governed by the VPET:DEG molar ratio used in synthesis (this study considers 1:0.1 and 1:0.2).

When such an oligoester is introduced in small quantities into a PE matrix during melt compounding, three theoretically expected effects arise: (i) the polar carbonyl/hydroxyl groups can act as localized polar centres that alter chain packing and crystallization behaviour of PE near the interface; (ii) at low concentrations, the oligoester can function analogously to an internal lubricant/plasticizing agent, influencing melt flow index and processability; (iii) beyond a critical concentration, phase incompatibility between the polar oligoester domains and the non - polar PE matrix is expected to introduce stress - concentration sites, which is anticipated to reduce impact resistance and elongation at higher PAPET loadings. This concentration-dependent duality - property enhancement at low loadings versus embrittlement at higher loadings - is the central working hypothesis theoretically justified in this thesis and subsequently verified experimentally.

Comparative Analysis of Modification Approaches. review of the literature on polyolefin–polyester compatibilization identifies several established reactive-modification routes: grafting of maleic anhydride (MA) or glycidyl methacrylate (GMA) onto polyolefin backbones, use of isocyanate-functional coupling agents, and peroxide-initiated radical grafting. Comparative studies on recycled - PET-based film systems have reported tensile - strength gains on the order of 29–38% and compatibility-index improvements of roughly 1.7-2.1-fold when GMA - and MA - type reactive compatibilizers are used, at the cost of additional reagent expense and, in the case of peroxides, the risk of uncontrolled chain scission or crosslinking during processing. These routes generally require either a separate grafting reaction step or the purchase of specialty functionalized polyolefins.

The PAPET approach analysed in this thesis differs qualitatively from the above routes in that the modifier itself is derived directly from waste PET via a single-step alcoholysis reaction, requiring no additional grafting chemistry and no virgin

functionalized polyolefin. From a theoretical standpoint, PAPET's mode of action is expected to combine two mechanisms simultaneously found only separately in conventional compatibilizers: (a) an interfacial, polarity - bridging mechanism analogous to that of MA/GMA grafts, arising from PAPET's residual ester and hydroxyl groups; and (b) a plasticizing/lubricating mechanism at low loadings, arising from the relatively low molecular weight of the oligoester relative to the PE matrix. This dual mechanism is the theoretical basis for the hypothesis that PAPET can achieve meaningful property modification at markedly lower cost than conventional grafted compatibilizers, while simultaneously valorising a waste stream.

Theoretical Compatibility Considerations. From the standpoint of polymer thermodynamics, PE and PET are fundamentally incompatible in the melt, owing to their large difference in solubility-parameter and the absence of favourable specific interactions between a purely aliphatic hydrocarbon and an aromatic polyester. Classical Flory - Huggins - type reasoning predicts that direct blending of PE with unmodified PET (or high-molecular-weight PET oligomers) would yield strongly phase-separated, poorly adherent domains, with adverse effects on mechanical properties. The theoretical rationale for using a low-molecular-weight alcoholysis product rather than PET itself is that reducing the oligomer's molecular weight and increasing its concentration of polar end-groups relative to its non-polar backbone segments narrows the effective interfacial energy mismatch, allowing the oligoester to reside preferentially at the PE crystallite boundaries and amorphous - phase interfaces rather than forming large, poorly bonded macro-domains. This is consistent with the concentration - dependent duality (enhancement at low loading, embrittlement at higher loading) identified in Section 2, and provides the theoretical justification for testing PAPET at graded concentrations (0.5, 3 and 8 wt.%) rather than at a single arbitrary loading.

Analytical Framework for Verification. Confirmation of chemical incorporation of PAPET into the PE matrix requires spectroscopic evidence, since physical blending alone does not guarantee retention of the oligoester's functional groups after processing. Fourier-transform infrared spectroscopy (FTIR) is theoretically the most direct method, as successful incorporation is expected to manifest as a carbonyl (C-O) absorption band in the 1714 -1745 cm^{-1} region, absent or negligible in unmodified PE. Complementary methods - differential scanning calorimetry (DSC) for crystallinity and melting behaviour, scanning electron microscopy (SEM) for phase morphology, and standardized physical-mechanical tests (tensile strength and elongation at break, Izod impact strength, Vicat softening point, heat deflection temperature, and environmental stress-crack resistance) - together constitute a coherent structure –

property evaluation methodology. This multi-technique framework is necessary because no single method can independently establish both the chemical mechanism of modification and its practical consequence for film performance; FTIR alone, for instance, can confirm chemical incorporation without indicating whether the resulting morphology is beneficial or detrimental to mechanical performance, which is why the framework deliberately spans chemical, thermal, morphological and mechanical scales of observation.

Expected Theoretical Significance for the Dissertation Programme.

The theoretical framework presented here is intended to serve three functions within the broader dissertation. First, it defines testable, falsifiable hypotheses - specifically, the existence of an optimum PAPET loading and its dependence on VPET:DEG ratio - rather than treating the experimental programme as purely exploratory. Second, it identifies the minimum analytical toolkit required to distinguish genuine chemical modification from simple mechanical blending, guarding against the common methodological error of attributing property changes to a mechanism that spectroscopic evidence does not support. Third, it situates the specific PE grades and PAPET synthesis conditions used in the dissertation (Chapter II) within the broader theoretical landscape of polyolefin - polyester compatibilization, allowing the dissertation's experimental findings (Chapters III-IV) to be interpreted as a specific, verifiable instance of a generalisable modification strategy rather than as an isolated empirical result.

Scientific Novelty and Conclusion. The novelty of the theoretical approach substantiated here lies in treating an alcoholysis product of secondary PET - rather than virgin compatibilizers such as maleic anhydride or glycidyl methacrylate grafts - as a reactive, low-cost modifier for film-grade PE, thereby simultaneously addressing PET waste utilisation and PE property enhancement within a single chemical process. The theoretical framework developed identifies the VPET:DEG molar ratio and PAPET loading as the two governing synthesis - processing variables, predicts a non-monotonic (optimum - exhibiting) dependence of mechanical properties on PAPET content, and defines the analytical protocol required to verify these predictions. This provides the scientific foundation for the subsequent experimental chapters of the dissertation and is proposed as a generalisable approach for the chemical valorisation of secondary PET in polyolefin modification, with direct relevance to circular-economy strategies for both the polyolefin-film and PET - packaging industries.

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