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AN OVERVIEW OF TPE-POLYAMIDE BLEND OPTIMIZATION FOR OVERMOLDING TECHNIQUES

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Abstract:
Polyamides (PA) and thermoplastic elastomers (TPE) are foundational polymers, each boasting distinct characteristics. However, their intrinsic incompatibility presents challenges when blending them, particularly in overmolding processes. This review delves into the innovative strategies and interventions explored to improve TPE-PA adhesion, emphasizing the role of reactive molecules such as maleic anhydride and glycidyl methacrylate as potential compatibilizers. Through a comprehensive analysis of various studies, the influence of these compatibilizers, the reaction dynamics, and the resultant mechanical properties of the blends are elucidated. Additionally, the criticality of factors like interfacial temperature in overmolding processes is underscored. The findings provide insights into optimizing TPE-PA blends, unlocking the potential for superior, toughened materials with enhanced applicability in various industries.

Keywords: TPE-Polyamide Blends, Overmolding Challenges, Compatibilizer Strategies, Reactive Molecule Adhesion, Interfacial Temperature Optimization.

Introduction

Thermoplastic elastomers (TPE) and polyamides (PA) are both crucial materials in the realm of polymer science and engineering, each with their unique set of characteristics and applications. While PAs are renowned for their durability and strength, TPEs are celebrated for their elasticity and moldability. A quest has emerged in recent years to combine the strengths of both, aiming to achieve superior materials that can leverage the best attributes of each.

Such blends are not without challenges. The inherent incompatibility between TPEs and PAs has been a significant barrier to producing effective composites, demanding innovative approaches to enhance their adhesion. Various strategies, such as introducing reactive molecules like maleic anhydride and glycidyl methacrylate, have been explored to act as bridges or compatibilizers between these polymers. The interaction dynamics of these modified polymers, their resultant mechanical properties, and the underlying factors affecting their performance have been the subjects of several investigations.

Furthermore, with the rise of overmolding as a favored manufacturing technique—where one material is injection-molded over another already molded part—understanding the intricacies of TPE-PA bonding becomes even more vital. Factors such as interfacial temperature, substrate preparation, and the introduction of specific compatibilizers play pivotal roles in determining the success of overmolding applications.

In the subsequent sections, we delve deeper into various research studies that explore the realms of TPE-PA combinations, elucidating the challenges, innovations, and findings that are shaping the future of this promising material blend.

1. Overview: Blends of Polyamide and Thermoplastic Elastomers

Certain applications demand characteristics that the fusion of EP and PA, while usually more robust than pure EP, might not entirely address. For situations demanding extensive deformation prior to failure, or those necessitating a tactile surface for enhanced tactile feedback and maneuverability, a blend of gentler materials might be more apt. In some scenarios, merging a thermoplastic with an elastomer emerges as a favorable solution.

Elastomers stand out as materials that can withstand extensive deformation compared to conventional engineering polymers. They are primarily constituted of macromolecules that accommodate a high level of strain before breaking. These are combined with a crosslinked structure, either chemically or physically, which combats any permanent change in shape upon the release of any external force. Thermoplastic elastomers (TPEs) are a particular category of elastomers that can be melted and thus offer advantages like easier processing and recyclability. These TPEs often exhibit a phase-distinct microstructure, encompassing alternating rigid and flexible areas. The rigid sections lend structural integrity to the elastic, stretchable sections. On heating, these rigid sections become liquid, allowing the TPE to have a more fluid consistency.

The categorization of TPEs is grounded in the kind of structures shaping their rigid and flexible phases. For instance, Styrenic block copolymers (often referred to as TPE-S or TPS) are characterized by thermoplastic sections of styrene interspersed with elastic segments. Prominent elastic segments in TPS can be butadiene (as seen in SBS) or combinations like ethylene and butylene (as in SEBS). Thermoplastic polyurethanes (designated as TPE-U or TPU) evolve from linear copolymers that oscillate between short and elongated segments terminating in diisocyanate groups. The minimized spacing between these terminal groups in the shorter segments results in highly polar sections, which come together to form rigid, crystalline areas. Lastly, Thermoplastic polyolefins (TPE-O or TPO) are essentially a mechanical amalgamation of thermoplastics and elastomers, sometimes enriched with fillers to optimize the properties of the blend.

Many TPEs exhibit non-polar and non-reactive characteristics, making them incompatible with polar entities such as PA. Nonetheless, there exist methods to enhance TPE's miscibility with these molecules, predominantly through the introduction of compatibilizers or co-reactive agents. This commonly involves the integration of reactive entities to TPE molecular chains, facilitating enhanced miscibility and creating avenues for covalent crosslinking between TPE and PA. Previous research has provided insights into the reaction mechanisms between PA and enhanced TPEs, and the resulting mechanical properties of their combinations.

While the macroscale integration of PA and TPE has been less explored, well-documented processes like hybrid injection molding for other thermoplastic-TPE combinations exist. A deep understanding of PA's interaction with enhanced TPEs paves the way for innovations, such as hybrid molding TPE onto PA bases.

2. Combinations of Polyamide and Elastomers

Research by Naeim abadi et al [1] highlighted that when SBS is grafted with maleic anhydride (SBS-g-MA), it can develop formidable interfacial bonds with PA12, despite the known immiscibility of unaltered SBS with PA. It was discerned that bonding occurred through hydrogen and covalent interactions between maleic anhydride and PA12's amide group nitrogen atom. PA12, with its wider intermolecular spacing among polar amide groups compared to PA6 or PA6,6, displays lesser polarity and better compatibility with non-polar entities like SBS, hinting at enhanced molecular intermingling. Nevertheless, the dual bonding approach seems feasible for all PA variants when combined with maleated TPE.

Further details of the PA and MA interaction are provided by Van Duin et al [2], as depicted in Figure 2.20. Their findings indicate that the primary reaction centers around the imide group at a PA chain's terminus and MA's core oxygen atom. The subsequent water molecule, which arises from this interaction, might hydrate an amide unit further down the PA chain, bisecting the chain and revealing another imide group ready to engage with MA. This interaction fosters a strongly interconnected interface between the two polymer phases, which, over prolonged durations, could lead to PA degradation.

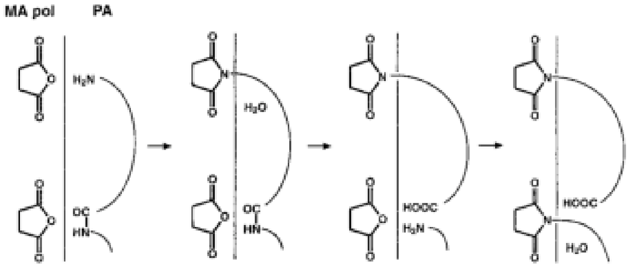

Figure 3.1. Reaction between PA imide group and maleic anhydride, followed by hydrolysis of amide group. From Van Duin et al [2].

Tomova and Radusch [3] developed blends using PA6, PA6,6, and maleated rubber (EO-g MA). They observed that due to the monofunctionality of PA6, the blend exhibited reduced interfacial tension between the PA and rubber. This led to the formation of smaller rubber particles compared to those in PA6,6 blends where a higher interfacial tension was noticed.

Ebrahimi Jahromi et al [4] ventured into creating ternary blends of PA6, nanoclay, and acrylonitrile butadiene rubber (NBR). They experimented with and without glycidyl methacrylate (GMA) as a compatibilizing agent. While the nanoclay moderately influenced the mechanical properties, the incorporation of GMA as a compatibilizer significantly bolstered both tensile and impact strength. This boost in blend properties is credited to the enhanced bonding between PA6 and NBR-g-GMA compared to the bond between PA6 and NBR.

Kim and colleagues [5] focused on discerning the influence of maleic anhydride concentration in PA6/rubber mixtures. Their findings revealed that with the surge in MA content, the rubber particles that formed in-situ were tinier. This owes to the better phase compatibility, which diminished the energy needed to craft PA/rubber interfaces. Furthermore, they noted that as the bonding between PA6 and the modified rubber intensified, there was a commensurate increase in the blend's impact strength.

Huang and his team [6] discovered that a heightened content of SEBS-g-MA in PA/SEBS-g-MA binary blends drastically lowered the yield strength. However, incorporating a modest amount of SEBS-g-MA, roughly 10wt%, resulted in remarkably toughened blends. Beyond this concentration, there were no noticeable advances in Izod impact performance with augmented TPE content. Additionally, a reduction in SEBS-g-MA particle size enhanced the elongation at break but was inconsequential for the yield strength or impact performance within the tested range.

Tjong and his collaborators conducted extensive research on short glass fiber-reinforced PA6,6, which was toughened using SEBS-g-MA particles [7]–[9]. They ascertained that introducing maleated SEBS significantly augmented the impact performance, particularly when the glass fiber concentration was on the lower side. In the absence of glass fibers in the blends, the energy absorption mainly occurred through cavitation of the rubber particles and matrix shear yielding [7]. Conversely, when glass fibers were incorporated, mechanisms like fiber delamination and pull-out were predominant.

3. Overmolding of TPE onto PA

Braüer et al. [10] investigated the influence of an adhesion promotor, specifically 4,4’-diphenylmethane diisocyanate (MDI), on the bond between PA6 and overmolded TPU. The adhesion promotor enhanced bond strength by approximately 50%, driven by covalent bonding between the MDI and PA6 amide groups.

Pompe et al. [11] delved into the impact of processing conditions on the adhesion of PA6 and TPU overmolded with an adhesion promoter. Utilizing a multi-material injection molding procedure, they concluded that optimal adhesion is attained when a temperature gradient exists between the initial and subsequent material. Nonetheless, the primary material must retain adequate warmth to allow the overmolded material to marginally heat the bi-material interface, facilitating interface annealing.

In a related study, Persson et al. [12] examined the effects of processing conditions on multi-material injection molded components, consisting of PA12 integrated with different glass fiber proportions, overmolded with TPE optimized for PA adhesion. They identified trends analogous to those highlighted by Pompe [12], noting that elevating the TPE overmolding and substrate temperatures augmented adhesion by heightening the interfacial temperature. They also discerned that an increased glass fiber content in the PA12 substrate negatively impacted bond strength.

While overmolding has proven effective for TPE and PA combinations, there's a demand for more in-depth exploration regarding the processing and mechanical attributes of these blends.

4. Overmolding with Other Thermoplastic/TPE Combinations

Insights derived from overmolding TPE onto alternative thermoplastics can illuminate strategies for designing and fabricating components from TPE overmolded onto PA. According to Weng et al. [12], overmolding TPE onto a thermoplastic substrate involves:

1. Wetting the substrate using TPE melt.
2. Interaction between TPE and thermoplastic polymers, which could encompass interdiffusion or bonding.
3. Solidification, potentially encompassing specific crystallization parameters.

Arzondo et al. [14] explored the overmolding of solid polypropylene (PP) using molten TPE. They deduced that robust interfacial bonding can manifest even if the interface temperature resides substantially below PP's melting point. The primary contributor to this adhesion was speculated to be molecular motion within the TPE overmold.

Candal et al. [14] established that for PP overmolded with thermoplastic vulcanate (TPV), the molten TPE's temperature played a pivotal role in bond strength. In contrast, mold temperature and hold pressure were lesser determinants within the tested boundaries.

Rossa-Sierra et al. [15] emphasized that heightening the TPU overmold temperature considerably bolstered bond strength. However, the most effective strategy to amplify the bond strength between a thermoplastic substrate and TPU overmold was to enhance the substrate's surface roughness. The flow rate's influence on bond strength was marginal, hinting that the TPU melt viscosity reduction's potential improved substrate wetting didn't significantly alter bond strength.

On a different note, Chandran et al. [15] discerned that, when overmolding TPE onto isotactic polypropylene (iPP), the mold temperature was the most influential factor affecting bond strength. They also observed adhesion at temperatures below the iPP melting point, partly ascribed to a localized melt temperature decrease at the surface, likely resulting from the TPE melt's plasticizer migrating into the iPP.

5. Recapitulation of Findings

The adhesive quality between TPE particles and the PA matrix has a direct bearing on the material's impact performance. Even though there's a general incompatibility between PA and TPEs, the introduction of reactive molecules, such as maleic anhydride and glycidyl methacrylate, into TPE chains can function as effective compatibilizers. A comprehensive body of research sheds light on the dynamics of PA and TPE combinations, touching on aspects like the role of compatibilizers, underlying reaction mechanics, and modes of failure. The primary mechanisms for toughening PA blends using TPEs seem to be TPE particle cavitation and PA shear yielding.

Regarding overmolding procedures, the pivotal element in fortifying adhesion appears to be the interfacial temperature between the substrate and the TPE overmold. An excessively cool temperature hampers the molecular mobility of both the overmold and substrate, limiting their interactive capacity across the boundary. Elevating this interfacial temperature—achieved by adjusting the overmolding melt's temperature, the substrate's temperature within the mold, or both—can lead to enhanced bond strength. This is especially true when a pronounced thermal gradient is maintained across the interface, enabling a melting and subsequent solidification process at the juncture.

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BIOGRAPHIES

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