

Super Tough Polycaprolactam (PA6)-based Blends with Gas Barrier Properties

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Electronic Supplementary Information

Abstract Polycaprolactam (PA6) is an important engineering plastic known for its excellent strength and processability, making it widely applicable in the automotive and transportation industries. Previous studies have demonstrated that incorporating a small amount of organic-modified montmorillonite (OMMT) can significantly enhance the gas barrier properties of PA6. Based on PA6/OMMT, this study further introduced maleic anhydride-grafted ethylene-octyl copolymer (mPOE) and polytetrafluoroethylene (PTFE). Morphological characterization revealed the successful manipulation of the microstructure within this toughening system, revealing a distinctive tassel bundle morphology in the ternary blend of PA6/mPOE/PTFE. In the quaternary PA6/OMMT/mPOE/PTFE system, scanning electron microscopy (SEM) analysis demonstrated that the special “tassel bundle (TB)” morphology could induce an ordered arrangement of OMMT nanosheets, leading to synergistic improvements in both toughness and gas barrier performance. These findings offer promising potential for applications requiring simultaneously high gas barrier properties and enhanced toughness, particularly in hydrogen storage tanks and related industrial fields.

Keywords Tassel-bundle structure; Toughening; Organic modified montmorillonite; Barrier performance; Polyamide 6

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INTRODUCTION

As a major engineering plastic, PA6 has been widely used in automotive, electrical, electronics, and sports equipment applications owing to its excellent processability, corrosion resistance, self-lubrication, and wear resistance.^[1–5] However, PA6 exhibits a relatively low crack-growth energy (notch sensitivity), leading to inferior notch impact strength, which limits its broader applications. A conventional toughening approach involves the incorporation of elastomers or maleic anhydride-grafted elastomers into PA6.^[6,7] Although this method is effective for impact modification, it inevitably reduces the tensile strength owing to the inherent characteristics of the elastomers. Organic modified montmorillonite (OMMT) is frequently used to enhance the barrier properties of PA6. The introduction of this inorganic filler typically results in a significant toughness reduction, failing to meet the toughness requirements for hydrogen storage tank applications. Consequently, the focus of current research is the synergistic incorporation of OMMT with compati-

bilizers in polymer blends, with the aim of achieving balanced and superior material performance.

Montmorillonite (MMT) is a layered silicate mineral characterized by a fundamental 2:1 phyllosilicate structure, in which an octahedral alumina sheet is sandwiched between two tetrahedral silica sheets, forming layers through shared oxygen atoms. A significant breakthrough occurred in the late 1980s, when Toyota researchers demonstrated that incorporating small amounts of organically modified montmorillonite (OMMT) remarkably enhanced the mechanical properties and barrier performance and reduced the dispersed phase dimensions in polymer composites.^[8–10] Owing to its excellent dispersion and exfoliation capabilities in polymer matrices, OMMT has recently emerged as an effective modifier for PA6.^[11] When incorporated into PA6, OMMT is distributed selectively within the PA6 matrix because of its good compatibility. As the matrix phase, PA6 containing OMMT effectively suppressed the aggregation of dispersed phases, resulting in a more refined phase morphology. Sun *et al.*^[12] prepared PA6/LIC gas cylinders, which demonstrated superior thermal and mechanical properties compared to pure PA6. The hydrogen permeability coefficient of PA6/LIC was reduced by 3–5 times. Wu *et al.*^[13] reported that PA6 filled with 5 wt% OMMT achieved optimal barrier performance, with

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permeability coefficients below 2×10^{-13} mol·m/(m²·s·Pa).

Polyamide has emerged as a promising candidate material for hydrogen storage tanks owing to its strong molecular polarity and hydrogen-bonding interactions. However, most studies have only focused on improving the hydrogen barrier performance while neglecting the requirements for toughness in actual production. Balancing barrier performance and toughness has become a contradictory problem. In our previous work,^[14] we reported a super-toughened ternary blend based on PA6 characterized by a novel “tassel-bundle” (TB) morphology. This blend demonstrates enhanced mechanical properties, exhibiting both stiffness and toughness. In this study, building upon our previous findings, we designed a TB structured quaternary polyamide 6/organically modified montmorillonite/maleic anhydride grafted ethylene-octyl copolymer/polytetrafluoroethylene (PA6/OMMT/mPOE/PTFE) composite system, a three-dimensional energy dissipation network is constructed using nanosheets (OMMT), elastomers (mPOE), and fibrillation (PTFE), instead of relying solely on a single elastomer interface to absorb energy and toughen the core-shell structure. We hope to improve the gas permeability of the material and simultaneously overcome the shortcomings of material brittleness at the same time to meet the requirements of practical applications and processing in areas with good gas barriers and high toughness.

EXPERIMENTAL

Materials

PA6 (trade name: HY-2500) was purchased from the Haiyang Chemical Fiber Company Limited (Co., Ltd.). mPOE (trade name: KT-915), supplied by Shenyang Ketong Plastic Co., Ltd., consists of 20% low-density polyethylene (LDPE) and 80% maleic anhydride grafted ethylene-octyl copolymer (mPOE), with a grafting rate of approximately 1.8%. PTFE (grade X-010) was obtained from KINGFA Technology Co., Ltd. The *n*-hexane solvent was purchased from Shanghai Titan Technology Co., Ltd. and used as received. OMMT was provided by Zhejiang Fenghong New Materials Co., Ltd.

Sample Preparation

PA6, OMMT, mPOE, and PTFE were predried at 80 °C for 12 h before blending. Dried polymers were weighed according to the formulations listed in Table S1 (in the electronic supplementary information, ESI). The components were mixed in a high-speed blender and fed into a twin-screw extruder, where blending was performed at 230–250 °C at a screw speed of 500 r/min. The extrudate was then cooled in water and pelletized. The pellets were vacuum-dried again at 80 °C for 12 h before injection molding into the test specimens or sheets as per the relevant standards. The injection molding process was conducted at 250–270 °C. PA6-based binary blends containing *y*% PTFE were designated as N6F_{*y*}. PA6/mPOE blends containing *x*% mPOE (where *x*=5% increments) were selected as N6T_{*x*}. The PA6/mPOE/PTFE ternary blends containing *x*% mPOE and *y*% PTFE are designated as N6T_{*x*}F_{*y*}. PA6/OMMT/mPOE/PTFE quaternary blends containing *x*% mPOE, *y*% PTFE, and *z*% OMMT were designated as N6C_{*z*}T_{*x*}F_{*y*}.

Morphological Observations

To investigate the phase morphology of the different blends,

field-emission gun scanning electron microscopy (FESEM) was conducted using a Hitachi S-4800 scanning electron microscope (Japan). According to the purpose of the different sections below, cryo-fractures were prepared from both standard specimens and samples that exhibited internal melt flow in different directions. Prior to imaging, the mPOE phases were selectively etched using *n*-hexane to enhance phase contrast.

RESULTS AND DISCUSSION

The Barrier Performance of PA6 Blends

OMMT exhibited good compatibility with PA6 and was selectively distributed within the PA6 matrix. The incorporation of a small amount of OMMT significantly enhances the barrier properties of the composite material. To evaluate this effect, the hydrogen permeability coefficients of the composites were measured at 3 MPa and 23 °C. The experimental results are shown in Fig. 1. The results demonstrated that the addition of OMMT reduced the permeability coefficients of N6C₂ and N6C₄ by 62% and 67%, respectively, compared to pure PA6. The barrier mechanism can be explained by two factors. First, the impermeable OMMT layers force gas molecules to follow tortuous diffusion paths around the dispersed silicate layers, thereby increasing the effective diffusion path length. Second, the compatibilizer mPOE fills the interfacial gaps between the components, further impeding gas transport. The minimum permeability coefficient of the N6T₅ composite material was 2.1×10^{-16} mol·m/(m²·s·Pa), which was 39% lower than that of PA6. This is because the addition of the compatibilizer mPOE blocks the gaps between some components, which, to some extent, hinders the gas passage. The synergistic effect became more pronounced with the addition of PTFE, leading to an additional 15% reduction in the permeability of N6T₅F₁. After adding 2%–4% OMMT, the permeability coefficient of N6C_{*x*}T₅F₁ decreased significantly. When 2% OMMT was added, the minimum permeability coefficient of the N6C₂T₅F₁ composite material was 0.81×10^{-16} mol·m/(m²·s·Pa). When OMMT was further increased to 4%, the minimum permeability coefficient of the N6C₄T₅F₁ composite material was 0.67×10^{-16} mol·m/(m²·s·Pa), which was 80% lower than that of PA6. However, when 6% OMMT was added, the nanosheets tended to agglomerate, lose their peeled state, and the agglomerates themselves were no

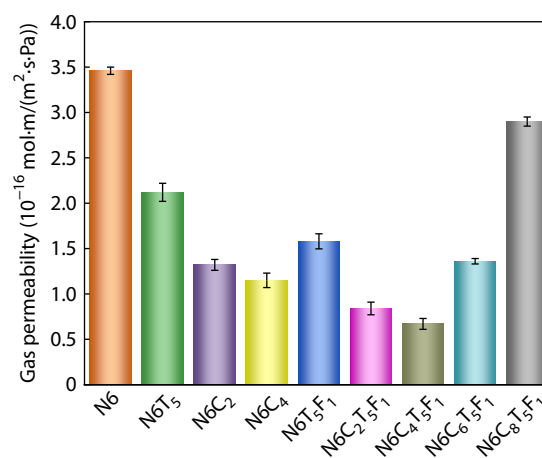


Fig. 1 Hydrogen permeability coefficients of different PA6 blends.

longer effective gas barrier units. Therefore, the minimum permeability coefficient began to increase, and the barrier effect of OMMT added at 6% and 8% began to deteriorate. This remarkable barrier enhancement aligns with our previous findings regarding the unique ability of PTFE to induce an ordered arrangement of components^[14] in melt blends. We propose that in PA6 composites, the PTFE-mediated alignment of OMMT layers creates an optimized tortuous path structure that significantly prolongs the hydrogen diffusion paths, thereby dramatically improving the hydrogen-barrier performance of the material.

For a better comparison, we compared the hydrogen permeability coefficients of some samples with those of toughened PA6 used for hydrogen storage tank liners in foreign patents, as shown in Table S2 (in ESI). The results indicated that the hydrogen barrier properties of the PA6/OMMT/mPOE/PTFE blend system reached or exceeded the level disclosed abroad, and its toughness was significantly better than that of foreign materials.

Relationship Between Izod Impact Toughness and Phase Morphology

The notched izod impact strengths and yield stresses are shown in Fig. 2. Compared to neat PA6, the PA6/PTFE ternary blends exhibited completely brittle behavior, as expected. Owing to the immiscibility between PTFE and PA6, the lack of affinity caused

interfacial detachment at an early stage, resulting in lower yield stress with increasing PTFE content. In contrast, the incorporation of the mPOE phase into the interfacial region caused a remarkable improvement in the impact resistance of the ternary blends, at the cost of a sharp reduction in the yield stress. The improvement seemed to be a certain extent related to the PTFE content, and up to approximately 1% PTFE was necessary to obtain an ideal impact performance. To further elucidate the relationship between the impact toughness and phase morphology, the influence of the rubber fraction on the impact strength of ternary blends with 1% PTFE was studied. It is worth noting that a brittle-tough transition was achieved at a much lower mPOE content in ternary blends as compared to PA6/mPOE binary blends (indicated by the green arrow in Figs. 2a and 2b). Moreover, the improvement was significantly greater for the PA6/mPOE/PTFE ternary blends than that for the PA6/mPOE binary blends at the same mPOE dosage. This finding is consistent with the report in the literature^[15] that the percolated structure of core-shell particles possesses an impact-resistance performance superior to the discrete structure morphology. Fig. 2(d) shows the notched izod impact strength and yield stress upon introducing the fourth component, OMMT, at the same mPOE content. Interestingly, compared to PA6/OMMT/mPOE/PTFE, OMMT synergistically enhanced the toughness, consistent with the barrier performance changes shown in Fig. 1.

The notched impact strength improvement for N6C₄T₅F₁ in

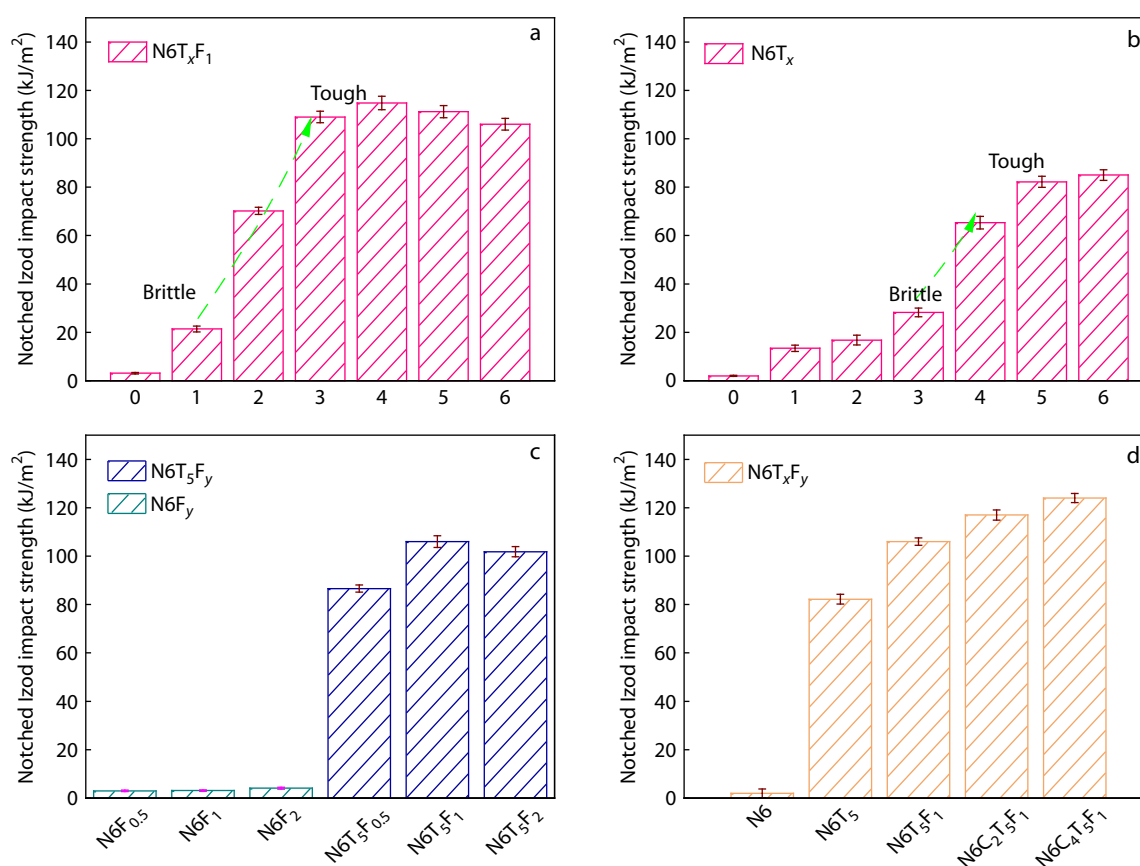


Fig. 2 Notched Izod impact strength for different samples: (a) PA6/mPOE/PTFE ternary blends and (b) PA6/mPOE binary blends with different mass fractions ($x \times 5\%$) of mPOE; (c) PA6/PTFE binary blends and PA6/25% mPOE/PTFE ternary blends with different mass fractions of PTFE; (d) PA6/OMMT/25% mPOE/PTFE quaternary blends with different mass fractions of OMMT.

this study was 58-fold greater than that of neat PA6, surpassing materials with core-shell morphology reported in the literature. Furthermore, the PTFE dosage required to achieve an effect equivalent to that of known core components was only 1%, which is far lower than the reported core-component loadings. This efficient impact improvement can be attributed to the unique toughening micromechanisms, as discussed in later sections. The specific mechanical and barrier properties of the composite materials are compared in Tables S2 and S3 (in ESI). Barrier performance improvements may also enhance the toughness, as demonstrated preliminarily.

The Interlayer Spacing of OMMT in Blends

OMMT and its interlayer spacing in composite materials can be characterized using wide-angle X-ray diffraction (WAXD), as shown in Fig. 3. In previous studies, we found^[14] that PTFE induces component arrangement in molten blends. Therefore, we compared the effects of PTFE on the OMMT arrangement by fixing the mPOE component in the blend. The diffraction peak position of pure OMMT was $2\theta=6.56^\circ$, and the interlayer spacing was calculated to be 1.33 nm according to the Bragg diffraction equation ($\lambda=2d\sin\theta$). As OMMT and PA6 undergo twin-screw blending shear, the interlayer spacing further increases to 6.77 nm ($N6C_4$ in Fig. 3), while $N6C_4T_5$ containing both OMMT and mPOE has a diffraction peak position of $2\theta=1.12^\circ$ and a corresponding interlayer spacing of 7.81 nm. This indicates that increasing the interlayer spacing of OMMT with mPOE may increase the melt viscosity and improve screw shear transfer caused by mPOE. On this basis, further addition of PTFE resulted in the disappearance of the diffraction peak corresponding to OMMT in the $N6C_4T_5F_1$ curve, indicating complete detachment of OMMT at this point. It was speculated that when PTFE was added, the system formed a TB structure, and the fibrous PTFE promoted the complete detachment of OMMT from the resin. This will help extend the diffusion path of hydrogen gas and improve the barrier performance of the material against hydrogen gas.

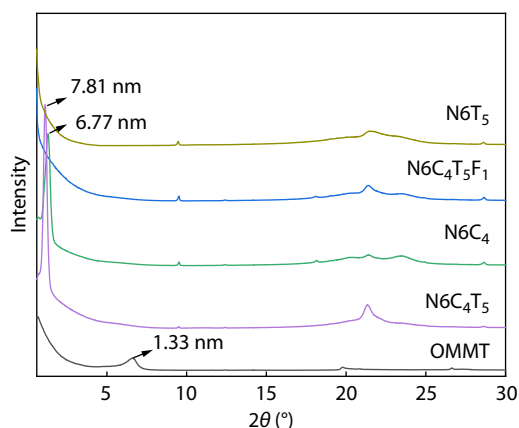


Fig. 3 WAXD patterns of OMMT and different PA6 blends.

Crystallization Behavior in Blends

The gas-barrier properties of polymers are closely related to their crystalline and amorphous regions. In the crystalline region, the molecular chains are densely packed, making them nearly impermeable to the gas molecules. Conversely, the amorphous region served as the primary pathway for gas diffu-

sion, facilitating permeation. Consequently, crystallinity is a critical factor influencing the polymer barrier performance. An increase in crystallinity can reduce the probability of gas molecules passing through, thereby lowering the hydrogen permeation performance. Using differential scanning calorimetry (DSC), according to the formula $X_c(\%) = \frac{\Delta H_f}{\Delta H_f^*} \times 100\%$ [16]

(where X_c is the crystallinity, ΔH_f is the melting enthalpy, and ΔH_f^* is the melting enthalpy of the sample when the crystallinity is 100%), the crystallinity can be quantified by comparing the melting enthalpy of the crystalline phase (ΔH_f^*) with that of a 100% crystalline reference sample.

The DSC curves in Fig. 4 reveal that the crystallinity values of PA6, PA6/mPOE, PA6/mPOE/PTFE, and PA6/mPOE/PTFE/OMMT were 21.32%, 25.68%, 30.21%, and 40.30%, respectively. Notably, PA6/mPOE/PTFE/OMMT exhibited the highest crystallinity, approximately 40.30%. These results demonstrate that OMMT enhances the cold-crystallization ability of PA6. Consequently, higher polymer crystallinity makes it more difficult for gas molecules to permeate, resulting in improved gas barrier performance.

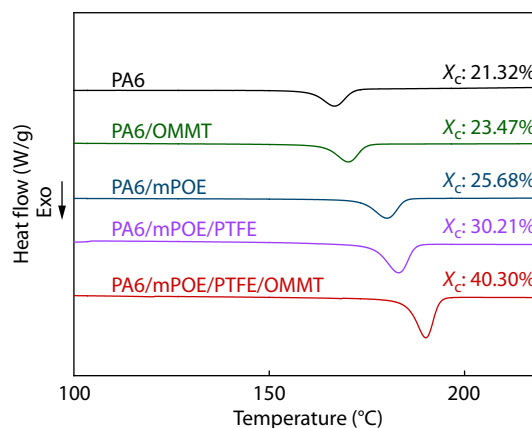


Fig. 4 DSC thermograms of PA6 and PA6 composites (20 °C/min).

Dispersion of mPOE Phases in PA6/mPOE/PTFE Blends

To explore the special structure formed by the addition of PTFE and its induction mechanism, the morphology of the $N6T_xF_y$ composites was analyzed using scanning electron microscope (SEM). The $N6T_xF_y$ series exhibits two distinct mPOE phase distributions. The conventional “sea-island” structure, where discrete mPOE droplets are uniformly dispersed within the PA6 matrix. The small mPOE droplet size suggests low interfacial tension between the phases, likely due to chemical interactions between maleic anhydride groups (mPOE) and amino-terminal groups (PA6) during compounding. This interaction reduces the interfacial tension and inhibits dispersed phase aggregation.^[17] The fibrillar morphology arises from PTFE’s fibrillation behavior of PTFE and ternary phase interactions. Cryo-fractured $N6T_xF_y$ specimens showed aligned fibril bundles oriented perpendicular to the melt flow direction, with dark voids remaining after the rubber-phase etching.

The TB structure emerges when mPOE coats the PTFE fibrils and clusters, creating the distinctive morphology shown

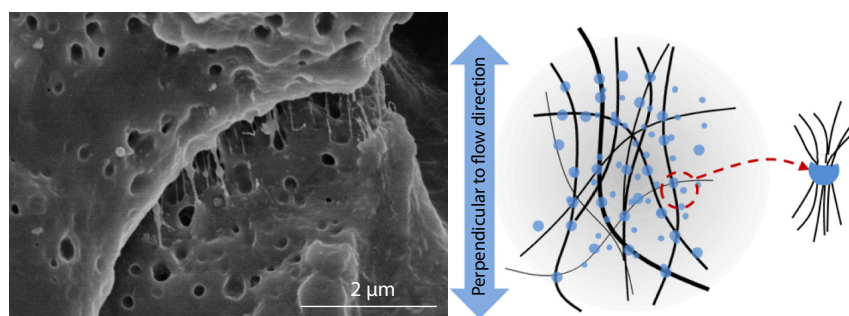


Fig. 5 SEM image of cryo-fractured surface of PA6/mPOE/PTFE blends with non-reactive mPOE etched by using *n*-hexane and schematic diagram of the tassel-bundle structure.

in Fig. 5. This structure is driven by the reduced interfacial tension and enhanced adhesion between the PTFE fibrils and PA6 matrix. The residual material observed on the fibril surfaces and within clusters suggests encapsulation by the POE-g-MA-PA6 copolymer. Nanoscale fibrils embedded in the mPOE phase, visible in cryo-fracture sections, further confirmed the formation of the TB structure.

Influence of ‘Tassel-Bundle’ Structure on the Morphology of PA6/OMMT /mPOE/PTFE Blends

The evolution of phase morphology is well documented to play a crucial role in the mechanical properties of multiphase polymer blends, which are strongly influenced by several factors, including interfacial tension,^[18,19] interfacial reactions,^[20,21] viscosity differences,^[22,23] and elasticity differences^[24] between phases. Thus, it is essential to study the microstructure and dispersion state of the minor components of the composite before discussing its macroscopic performance.

Figs. S1(a)–S1(c) (in ESI) show SEM images of the PA6/mPOE/PTFE ternary blends, revealing the influence of the PTFE fibrils on the morphological evolution of the mPOE phases. Compared to the binary blends, the mPOE phase domains transitioned from a uniform spherical shape to a deformed ellipsoidal shape. This phenomenon became more pronounced with increasing mPOE volume fraction. For instance, while N6T₆ and N6T₆F₁ contain the same mPOE volume fraction, N6T₆F₁ exhibits a distinct morphology in which the mPOE domains are ellipsoidal, with their long axes uniformly aligned in the flow direction. Close examination of the etched voids in the micrographs revealed an interpenetrating structure, suggesting that the dispersed phase domains tended to agglomerate or percolate in the PA6/mPOE/PTFE ternary blends. This resulted in deeper etching sites with sharper margins, as shown in Figs. S1(a)–S1(c) (in ESI). Fig. S1 (in ESI) also compares the cryo-fractured surfaces of the PA6/mPOE/PTFE ternary blends and the PA6/mPOE binary blends after mPOE extraction. The N6T₆ (Fig. S1d in ESI), exhibited excellent dispersion, with finely and uniformly distributed mPOE domains and indistinct interfacial regions with the PA6 matrix. This can be attributed to the *in situ* formation of the POE-g-PA6 copolymer at the PA6/mPOE interface.

The evolution of phase morphology in ternary component systems, particularly the formation of encapsulation structures, can be predicted using the interfacial values between components.^[20,25–33] In the spreading coefficient concept, Hobbs *et al.*^[34] reformulated Harkin’s equation by replacing the surface tension with the interfacial tension to predict the

morphology of ternary blends. The spreading coefficient λ_{CB} , is defined as:

$$\lambda_{CB} = \alpha_{BA} - \alpha_{CA} - \alpha_{BC} \quad (1)$$

Among them, λ_{CB} is the spreading coefficient, α_{BA} is the interfacial tension between components B and A, α_{CA} is the interfacial tension between components C and A, and α_{BC} is the interfacial tension between components B and C. When λ_{CB} is positive, it indicates that component C will spread on the interface between components A and B, forming a structure where C coats B. Conversely, components B and C will form independent phases.

In this study, the interfacial tension values were calculated from the surface tensions obtained *via* the contact angle method. The contact angles of PA6, mPOE, and PTFE with water and diiodomethane are presented in Table S4 (in ESI). The surface energy of each component was calculated using the geometric mean method, which relates the contact angle to the surface energy.^[35] The surface energy of the components can be calculated using the geometric mean method:

$$(1 + \cos\theta_{H_2O}) \gamma_{H_2O} = 2\sqrt{\gamma_{H_2O}^d \gamma^d} + 2\sqrt{\gamma_{H_2O}^p \gamma^p} \quad (2)$$

$$(1 + \cos\theta_{CH_2I_2}) \gamma_{CH_2I_2} = 2\sqrt{\gamma_{CH_2I_2}^d \gamma^d} + 2\sqrt{\gamma_{CH_2I_2}^p \gamma^p} \quad (3)$$

where γ is the surface energy, $\gamma = \gamma^d + \gamma^p$, γ^d and γ^p are the dispersion and polar components, respectively. θ_{H_2O} and $\theta_{CH_2I_2}$ are the contact angles of the material with water and diiodomethane, respectively. Here, the numerical values were taken from the literature^[36,37] $\gamma_{H_2O}^d = 22.1 \text{ mN} \cdot \text{m}^{-1}$, $\gamma_{H_2O}^p = 50.7 \text{ mN} \cdot \text{m}^{-1}$, $\gamma_{CH_2I_2}^d = 50.4 \text{ mN} \cdot \text{m}^{-1}$, $\gamma_{CH_2I_2}^p = 0.4 \text{ mN} \cdot \text{m}^{-1}$.

Because the surface energy is determined at ambient temperature according to the contact angle method, the use of interfacial tensions requires extrapolation of the surface energy to the melt mixing temperature based on its variation with temperature ($-d\gamma/dT$) and polarity ($x_p = \gamma_p/\gamma$).

The values of the surface energy, dispersion, and polar components at ambient temperature, the temperature dependence of the surface energy, and the extrapolated surface energy values at high temperature are listed in Table S4 (in ESI).

The interfacial tension between the components was calculated using the harmonic mean equation (Eq. 4),^[38] the results are presented in Table S5 (in ESI).

$$\alpha_{AB} = \gamma_A + \gamma_B - \frac{4\gamma_A^d\gamma_B^d}{\gamma_A^d + \gamma_B^d} - \frac{4\gamma_A^p\gamma_B^p}{\gamma_A^p + \gamma_B^p} \quad (4)$$

According to the data outlined in Table S5 (in ESI), the interfacial tension values varied significantly with different polymer pairs in the PA6/mPOE/PTFE ternary blend. It should be noted that the interfacial tension was obtained by extrapolation from the ambient temperature, without considering chemical or physical reactions at elevated temperatures. However, the reaction of the anhydride group of rubber with the amino end groups of PA6 significantly changed their interfacial tension. Fleischer *et al.*^[39] reported that the interfacial tension decreased by up to 70% when *in situ* interfacial modification was performed using an end-functionalized agent. In other words, by considering the reaction of mPOE and PA6 during the dynamic melt mixing procedure, the actual interfacial tension of the PA6/mPOE pair should be much less than 4.39 mN·m⁻¹ as reported in Table S5 (in ESI). The interfacial tension of the PA6/PTFE pair was much higher than those of PA6/mPOE and mPOE/PTFE. This can be ascribed to the fact that PA6 is a polar polymer, and PTFE is a nonpolar polymer that is immiscible.

The data demonstrate that it is feasible to predict the morphology through a theoretical calculation of the spreading coefficient. It is clear that the morphology predicted using the spreading coefficient is consistent with the morphologies observed in Fig. 5. For the PA6/mPOE/PTFE ternary blends, the spreading coefficient values in Table S5 (in ESI) suggest that the mPOE phases would spread along the interface of PA6 and PTFE, and led to an encapsulation morphology with PTFE fibrils as the core component and mPOE droplets as the shell component. Given the fibrillation capability of PTFE during dynamic melt mixing, the shear stress transformed the PTFE component into a continuous fiber network with partial physical cross-linking. Moreover, even at a relatively low dosage, PTFE forms a fibrous structure with nanoscale diameters. As shown in Fig. 5, the long axis of most nanofibrils aligned in a uniform direction, which is consistent with the flow direction of the melt. The encapsulation mechanism and fibril framework caused rubber phases to adopt an ellipsoidal shape with their long axes aligned in the flow direction (FD). As a result, the conventional “core-shell” structure evolved into a new TB structure, in which the encapsulated morphologies were not

discrete but continuous and oriented. As shown in Fig. 6, for the ternary blends, the rubber particles on the same or adjacent fiber bunches gradually increased in size and number with increasing volume fraction of mPOE, which subsequently merged the rubber particles to form a percolated structure.

Relationship Between Tensile Properties and Phase Morphology

Tensile and notched Izod impact tests were conducted to determine whether OMMT addition disrupted the macroscopic mechanical behavior of the blend and the effect of the TB structure on the toughness. Fig. S2 (in ESI) shows the typical stress-strain curves of the neat PA6, PA6/mPOE binary blends, PA6/PTFE binary blends, PA6/mPOE/PTFE ternary blends, and PA6/mPOE/PTFE quaternary blends. Neat PA6 exhibited semi-ductile behavior, yielding, and unstable post-yield deformation. The addition of PTFE significantly affected the tensile properties of the PA6/PTFE binary blends. As shown in Fig. S2 (in ESI), necking was suppressed and the yield strength decreased slightly with increasing PTFE content. This effect stemmed from PA6/PTFE immiscibility, which is linked to their poor interfacial interactions. In contrast, the PA6/mPOE binary blends exhibited lower yield stress and more stable post-yielding deformation with necking propagation than neat PA6, as shown in Fig. S2(b) (in ESI). Because mPOE has a lower yield stress and higher elasticity than PA6, the reduced yield stress and enhanced elasticity likely result from the strong interfacial bonding between mPOE and PA6. This is supported by the indistinct interfacial region in the phase morphology shown in Fig. S1(d) (in ESI).

Interestingly, Fig. S2(c) (in ESI) shows that the PTFE addition improved the ternary blend toughness, with the extent of improvement scaling with the PTFE content. N6T₅F_{0.5} exhibited a 14% increase in elongation at break, whereas N6T₅F₁ and N6T₅F₂ showed a 2-fold increase compared to N6T₅. Despite immiscibility, this suggests that the PTFE/PA6 interface enabled phase morphology optimization for toughening, rather than performance degradation due to poor interfacial interactions.

Fig. S2(d) (in ESI) further reveals that PA6/mPOE/PTFE blends displayed pronounced strain hardening and significantly higher toughness than PA6/mPOE binary blends at varying mPOE loadings. Grafting PA6 chains onto maleic anhydride functionalized rubber compatibilized PTFE with the

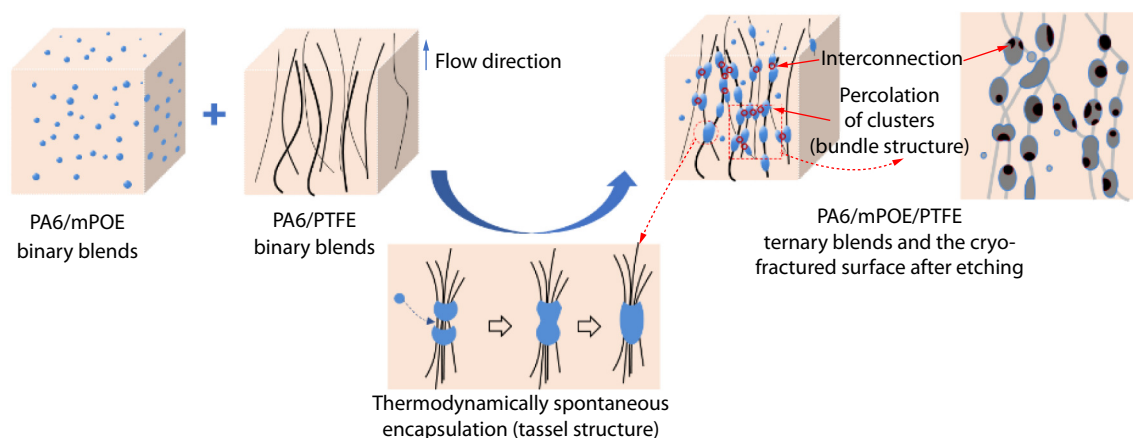


Fig. 6 Schematic illustration of the morphology evolution from in ternary blends to PA6/mPOE/PTFE ternary blends.

PA6 matrix while balancing toughness and rigidity. At high mPOE loadings, PA6/mPOE/PTFE ternary blends exhibited lower yield stress than PA6/mPOE blends. Stress and tensile strength in polymer blends are well-documented to depend on phase morphology and interfacial affinity between dispersed domains and the matrix. Thus, the percolated/agglomerated rubber phases in the TB structure likely intensified stress concentration, promoting interfacial void formation (early stage) and plastic deformation (later stage), explaining the lower yield stress and higher ductility.

Fig. S2(e) (in ESI) explores the synergistic effect between toughening agent PTFE and gas barrier component OMMT in the PA6/OMMT/mPOE/PTFE quaternary blends. The synergistic toughening effect of the TB structure and OMMT's gas barrier properties (with fixed mPOE content) resulted in tensile strengths for N6C₄T₅F₁ and N6C₂T₅F₁ that were about 2.3 times and 2.2 times higher than that of N6T₅, and about 1.19 times and 1.15 times higher than that of N6T₅F₁, respectively. OMMT addition preserved system toughness while synergistically enhancing both toughening and gas barrier properties compared to the ternary system. Fig. S2(f) (in ESI) compares the typical stress-strain curves of the blend at low temperatures under the same composition as Fig. S2(e) (in ESI). Notably, tensile strength at −40 °C showed no significant reduction compared to 23 °C. While elongation at break decreased substantially, values remained within acceptable application limits, suggesting viability for extreme conditions. Furthermore, the specific tensile properties of composite materials are listed in Table S3 (in ESI).

Impact-fractured Surface Analysis and Toughening Mechanism of Blends

The SEM images in Fig. 7 show the microstructures of the impact cross sections of PA6/mPOE, PA6/OMMT/mPOE, and PA6/OMMT/mPOE/PTFE. Fig. 7(a) shows that the impact cross-section of PA6/mPOE is rough, and the cavitation of the rubber phase forms obvious pores. In contrast, PA6/OMMT/mPOE in Fig. 7(b) has a smoother and flatter impact cross-section owing to the addition of OMMT, and there is almost no sign of plastic deformation in the substrate. The impact section roughness of PA6/OMMT/mPOE/PTFE in Fig. 7(c) significantly increased, exhibiting typical toughness characteristics. The voiding of the rubber phase left obvious holes in the cross section (indicated by the yellow dashed circle), accompanied by extensive plastic deformation of the PA6 matrix. In addition, as a toughening feature of the TB structure, nanofibers were found in the pores formed by energy absorption. Rubber particles form micropores during the shear-yielding process, absorbing and dissipating stress energy, thereby preventing the formation and propagation of cracks. The appearance of the fibers further proves the existence of the TB structure. Owing to the voiding of the rubber phase, the fibers originally embedded inside the rubber phase undergo deformation, stretching, and exposure along with the rubber phase. Fig. 7(d) shows an enlarged view of the hole in Fig. 7(c), clearly showing the presence of a large number of PTFE fibers with a diameter of approximately 10 nm around the hole. Most of the fibers fractured owing to energy absorption deformation and voiding of the rubber phase (indicated by the yellow arrows in Fig. 7d).

The stress field distribution in multiphase polymer materials is crucial for energy dissipation and absorption mecha-

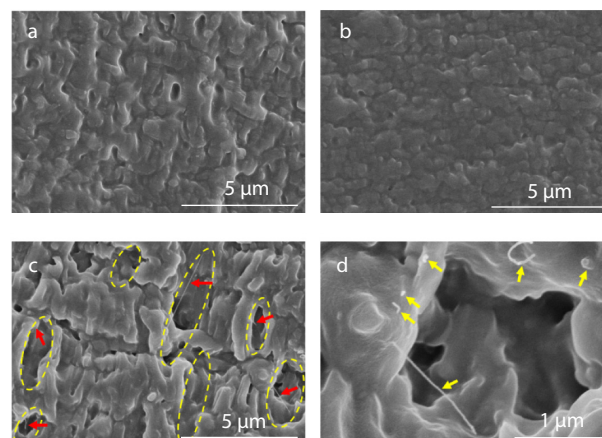


Fig. 7 SEM micrographs of impact-fractured surface of PA6/mPOE (a: N6T₅), PA6/OMMT/mPOE (b: N6C₄T₅), PA6/OMMT/mPOE/PTFE (c and d: N6C₄T₅F₁) blends.

nisms. The TB structure can improve the brittleness problem caused by OMMT owing to its special rubber morphology, which directly affects the stress field distribution of the polymer. In PA6/OMMT/mPOE, the dispersed phase of the mPOE rubber presents a discrete sea island structure. Owing to the effects of the reaction capacity expansion and rubber volume fraction, the overlap of the local stress fields is limited. Simultaneously, the interface between OMMT inorganic rigid particles that have not been fully peeled off and agglomerated with the PA6 substrate becomes the stress concentration point, accelerating the propagation of cracks and leading to premature material failure. In PA6/OMMT/mPOE/PTFE, the nanofiber network formed by PTFE fibrosis occupies the compatibilizing copolymer at the interface with the PA6 substrate, forcing unreacted mPOE to agglomerate into larger particles and spread on the surface of the PTFE fibers to share the compatibilizing area, thereby reducing the free energy of the system. This dispersion mechanism forms rubber particles with higher aspect ratios and even continuous rubber phases that penetrate the structure, giving the material a preliminary overlapping stress field before strain. However, the TB structure leads to a significant increase in melt viscosity, which facilitates shear transfer and achieves complete detachment of OMMT, reducing the problem of stress concentration points in ternary blends. Therefore, considering the aforementioned advantages, PA6/OMMT/mPOE/PTFE can effectively prevent crack propagation when subjected to tension or impact, complete voiding of the rubber phase, triggering large-scale plastic deformation of the matrix, and consuming more energy before fracture. The two aforementioned mechanisms are illustrated in Fig. 8.

Gas Permeability Mechanism

The dispersion effect of OMMT has a significant impact on the gas barrier properties. WAXD analysis showed that the interlayer spacing of OMMT in the PA6/OMMT/mPOE blend (N6C₄T₅) was 7.81 nm, whereas in the PA6/OMMT/mPOE/PTFE blend (N6C₄T₅F₁), OMMT was completely peeled off. The hydrogen permeability coefficients of N6C₂T₅F₁ and N6C₄T₅F₁ containing OMMT and TB structures were much lower than those of hydrogen-containing OMMT and TB structures at different times. The

TB structure significantly prolongs the diffusion path of small molecules through the sample by improving the dispersion effect of OMMT while maintaining the same amount of OMMT added, thereby enhancing the barrier performance against small-molecule hydrogen gas. This is consistent with the conclusion in reference^[40] regarding the barrier mechanism of extending the path of small gas molecules through the layered fillers.

During melt blending of PA6/mPOE/PTFE/OMMT, PTFE undergoes fibrillation to form a high-viscosity fibrous network,

acting as "anchor points," which impedes local melt flow. As the melt passes through the fibers, the streamline is disrupted, generating stronger local shear and tensile flow fields and forcing the OMMT layers to align parallel to the flow direction. During the cooling stage, the PTFE fiber network solidifies first due to its high melting point, forming a rigid skeleton that "locks" the oriented OMMT layers in an ordered position, inducing and maintaining their highly ordered arrangement in Fig. 9.

The TB structure formed by the PTFE fibers and orderly ar-

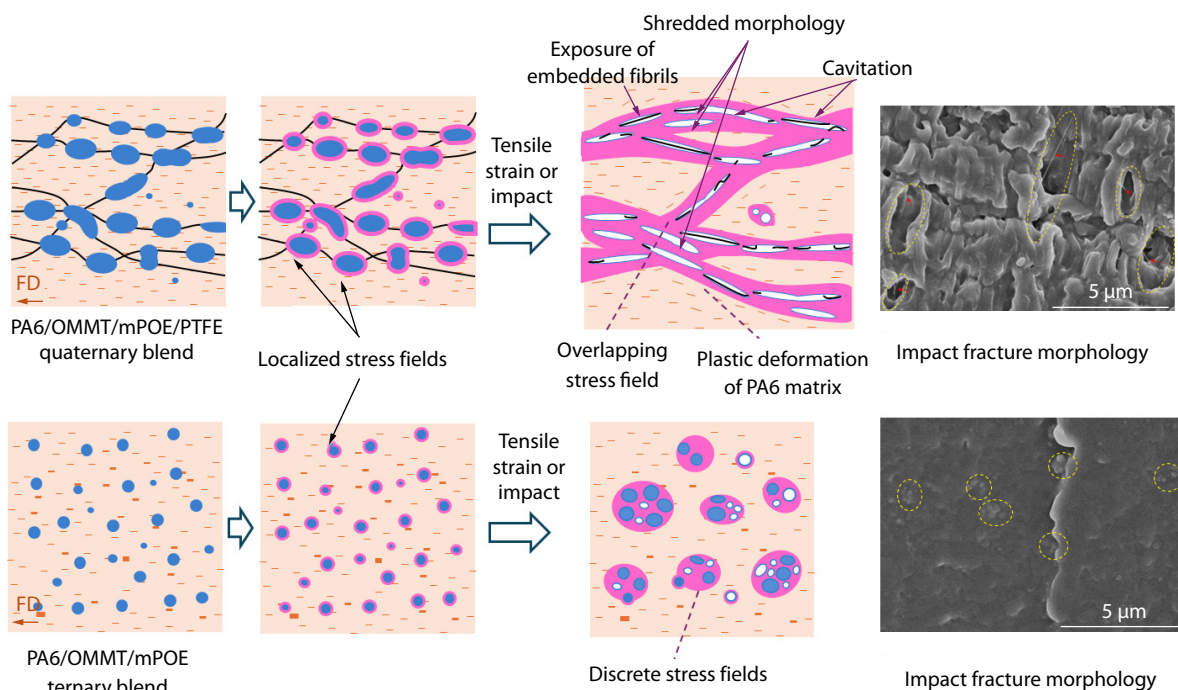


Fig. 8 Comparison of the toughening mechanisms between Tassel-Bundle (TB) structure and traditional toughening structures in OMMT-Modified PA6.

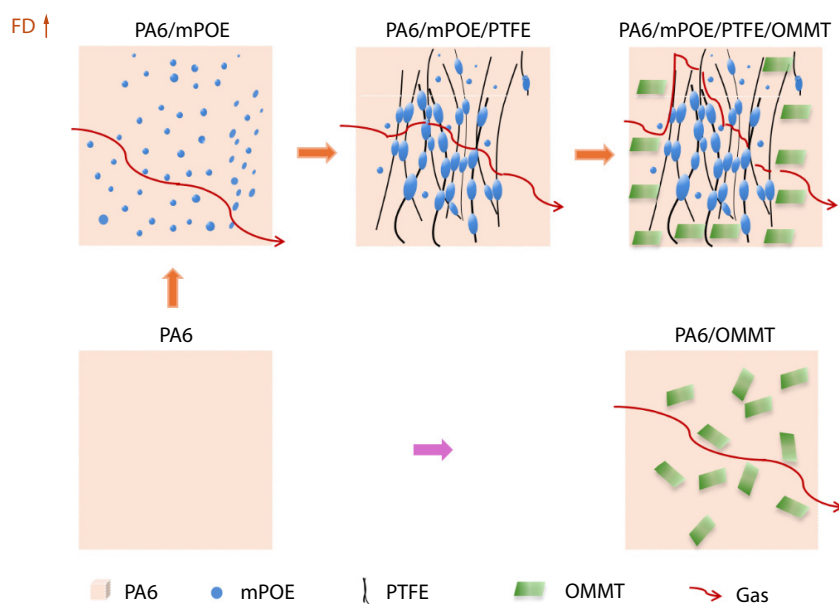


Fig. 9 Gas barrier mechanism model.

ranged OMMT platelets synergistically optimized both the toughness and gas-barrier properties of the material. The PTFE microfiber network efficiently absorbed impact energy through mechanisms such as crack bridging, fiber pull-out, and stress dispersion. The PTFE fiber network effectively mitigates the stress concentration caused by rigid OMMT particles. Mechanisms such as crack bridging and fiber pullout prevent both the initiation and propagation of cracks near these particles. Consequently, while substantially enhancing the gas barrier performance, it also preserves and even improves the toughness of the material. In contrast, PTFE microfibrils serve as physical supports that induce a highly ordered alignment of OMMT platelets while stabilizing and maximizing their gas-barrier efficiency. Simultaneously, mPOE improves compatibility and provides additional toughening, whereas the processing shear force simultaneously promotes PTFE fibrillation and OMMT delamination orientation. The high shear force during processing simultaneously promoted the fibrillation of PTFE and the delamination and orientation of OMMT. This multi-scale structural design not only enhanced the toughness but also significantly improved the barrier performance, achieving synergistic optimization of the comprehensive performance of PA6/mPOE/PTFE/OMMT.

CONCLUSIONS

In this study, guided by the calculation of the diffusion coefficient, we investigated the melt blending modification of nanomontmorillonite OMMT, traditional toughening agent mPOE, and fiber-reinforced PTFE using PA6 as the substrate and constructed PA6/OMMT/mPOE/PTFE nanocomposites with excellent toughness and gas barrier properties. The special "bundle" (TB) structure constructed using mPOE and PTFE significantly improved the toughness and gas barrier properties of the material. The elongation at break reached 83.5%, which is 1.1 times that of the pure PA6. Its toughness is significantly higher than that of foreign hydrogen storage materials (the elongation at break is approximately 9.6%). The gas permeability coefficient reaches 0.69×10^{-16} mol·m/m²·s·Pa, which is 80% lower than that of pure PA6. Its hydrogen barrier properties have reached or exceeded the level reported abroad (0.8×10^{-16} – 2.27×10^{-16} mol·m/m²·s·Pa). These findings indicate potential applications in high-toughness hydrogen storage bottles.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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Data Availability Statement

Data supporting the findings of this study are available from the corresponding author upon reasonable request. Author's con-

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