1. INTRODUCTION

In view of the rapid resource depletion, the search for alternative engineering plastics and specifically the extensively used polyamides has been in focus to ensure sustainable technocommercial viability. In this regard, biobased polyamides such as polyamide 410 (PA410), have significant advantages over other biobased polyamides (PA), such as PA610, PA11, and PA1010 in terms of an enhanced processing window (due to a high melting point and mechanical properties). PA410 is a new class of biobased polyamide that is obtained from enthalpic measurements and initial degradation temperature indicating thermal stability remained mostly unaffected. A remarkably substantial increase, i.e., ~15-fold enhancement, in the impact strength of the PA410/POE-g-MA blends leading to ultratoughening of PA410 accompanied by a significant increase in tensile strain at breaking is achieved though the elastic modulus (E) and yield strength (σ) decreased with impact modifier content. Thermomechanical analysis revealed a broadening in the loss tangent peak in the temperature range of ~50 to ~30 °C corresponding to the POE phase, whereas the loss tangent peak corresponding to the PA410 phase stayed unaffected.

Conventional theoretical models such as the rule of mixture and foam model were used to analyze the micromechanics of low-strain (<1%) mechanical response (E), and Nikolais–Narkis model and Isahi–Cohen models, for high-strain (>2%) mechanical response (σ). The interdependence of impact toughness, ductility ratio, and domain size of the dispersed rubber phase in the PA410/POE-g-MA blends could successfully be established vis-à-vis the mechanistic role of interparticle distance. Scanning electron microscopy showing domain coalescence of the soft elastomeric POE phase thus reiterated the pivotal role of interdomain distance and domain size in influencing the toughening mechanism of PA410/POE-g-MA blends. The qualitative phase distribution attributes based on atomic force microscopy remained in sync with quantitative parameters, such as domain size, hence reaffirming the mechanism behind ultratoughening of PA410 by POE.

strength, which significantly limits its use in applications that expose it to very high strain rates. Toughening of polyamides using the principles of internal plasticization or by the incorporation of suitable rubbers/elastomers has remained a mechanically effective and commercially viable route due to the extrusion-assisted integrated melt-mixing in combination with filler incorporations. Considering the fact that PA410 has attributes of 10 methylene moieties along the C-axis of the polymer, the blending of an elastomeric component like POE, having 8 methylene moieties in the polymer chain, may lead to a functionally effective interaction scenario that is in tune with the Flory–Huggins thermodynamic criteria for mixing. Such an interaction may efficiently favor reduction in the size of the incorporated rubber domains, which, in turn, may enhance the
intrinsic resistance to crack propagation and hence fracture resistance vis-à-vis resistance to notch sensitivity and strain sensitivity.

Highly flexible polyolefin-type elastomers with a much lower modulus, such as ethylene propylene rubber (EPR), styrene-ethylene-butylene-styrene block copolymer (SEBS), ethylene-propylene-diene rubber (EPDM), poly (ethylene-octene) elastomer (POE), etc., have proven to be commercially feasible as an effective dispersed phase to toughen the matrix polyamide (PA) phase through various reported mechanistic pathways, such as cavitation, crazing, shear yielding, and shear banding mechanisms. The type of rubber, domain size, and interaction with the matrix phase play a crucial role in rubber-induced toughening. Polyamides, due to their inherently high polarity (attributed to amide linkages), limit effective phase interaction with elastomers or any other rubber modifiers, and that, in turn, facilitates enhanced interfacial tension, leading to poor adhesion between the phases and thereby causing inadequate stress transfer. To overcome these issues, conventionally, functionalized elastomers are favored. For example, rubbers grafted with maleic anhydride (-MA) were employed to ensure interaction between anhydride moiety of elastomer and -CONH of polyamide matrix so that stress transfer across the phase interface becomes more efficient. Since larger amounts of free-radical initiator increases the possibility of chain scission and lowers the molecular weight, the content of -MA is therefore kept limited to less than 1%. Such a lower amount of grafting also helps preventing complete miscibility of the two components in the blend and thereby stabilizes the thermal stability, mechanical properties, and crystallinity of matrix polyamide. Reportedly, the use of SEBS/SEBS-MA, EPDM/EPDM-g-MA, and POE/POE-g-MA combinations enhanced toughening of polyamide to the extent of increasing the order of enhancement particularly when functionalized elastomers are incorporated. Besides traditional functionalized elastomers, fluor-elastomer, β-nucleated thermoplastic vulcanizates based on EPDM-g-MA and epoxidized natural rubber (ENR) have also been reported to be used for toughening of PA 6 with a loading percentage of ~30 wt %. Similarly, the incorporation of styrene functionalized POE-g-MA has also been reported to have offered a drastic reduction in domain sizes and improved adhesion with matrix PA 6 compared with neat POE-g-MA.

The viscosity-to-elasticity ratio of POE is relatively lower than that of EPDM, EPR, and SEBS. POE is preferred over the other elastomers when faster mixing and better dispersion of the components are the aspects critically sought. This is even more pertinent because the viscosity of Polyamide 410 is higher than that of the many conventional polyamides at their melting points. The POE/POE-g-MA-induced toughening in the case of PA 633 and PA 61227,28 is reported to significantly enhance the toughness-to-stiffness ratio. As per the percolation theory proposed by Wu, the interparticle distance and domain size play determining roles in controlling not only the mechanism of toughening but also the extent of enhancement in the toughness. In contrast to high-performance PA 6 and PA 66, PA410 offers better dimensional stability; oil, grease, and salt resistance; and resistance to other chemicals in combination with a low hygroscopic nature. However, the poor notch resistance and strain sensitivity limits the possibilities of such a new class of polyamide from being exploited for several automotive, engineering, and other specialty applications. Therefore, the use of low-modulus and high-flexibility polymer polyolefin elastomer such as POE with a lower viscosity-to-elasticity ratio that ensures not only the domain-dispersed morphology but also minimum compromise in the mechanical attributes of the polyamide 410 (PA410) matrix may be a promising alternative. In this context, the present paper critically explores the toughening efficiency of an elastomeric inclusion like POE-g-MA into the sustainable and biore sourced polyamide like Polyamide 410 that would not only ensure reduction in the strain rate and notch sensitivity but also pave the way to design a fracture-resistant and durable class of polyamide compounds with much less dependency on fossil fuels.

2. RESULTS AND DISCUSSION

2.1. Thermal Characterization. The melting endotherms obtained after second heating and the cooling exotherms of the blends are shown in (Figure 1a,b). The plot clearly shows that the extent of endothermic heat involved in the process remained nearly unaffected irrespective of the compositional variations in the blends. The melting and crystallization behavior as assessed from the differential scanning calorimeter (DSC) peaks and the extent of crystallinity measured from these data is shown in (Table 1). It was observed that the crystallinity remained nearly unaffected with the increase in the extent of incorporation of the elastomeric POE phase. Such an observation in the crystallinity indicates that the incorporation of the POE phase does not interfere with the crystalline microstructure of the PA410 matrix. This may be attributed to the fact that the amorphous phase effectively accommodates the POE phase where both matrix and dispersed phases may
randomly coexist. The thermal stability of the blends is characterized by using thermogravimetric analysis (TGA) curves, as shown (Figure 1c); the blends showed one-stepped degradation behavior, wherein the onset to degradation temperature remained at \(\sim 420^\circ C\) and that is well above the processing temperature of the blends. The absence of any distinct peaks at \(\sim 100^\circ C\) indicates the absence of any absorbed or adsorbed water/moisture. The similarity in the nature of TGA plots also indicated that the degradation behavior is mainly dominated by the matrix phase, i.e., the polyamide (PA410) phase.

### 2.2. Rheological Behavior.

The rheological behavior of the blends is assessed by measuring the variation of complex viscosity \(\eta^*\) as a function of angular frequency \(\omega\) in the range of 0.01–100 rad/s on a parallel plate setup (shown in Figure 2). The flow behavior of these blends is further analyzed by measuring the melt flow index (MFI) data (Table 2). The variation of complex viscosity clearly showed the composition dependence of flow behavior at a temperature above the melting point of PA410, i.e., \(\sim 270^\circ C\). It could be observed from the plot shown in (Figure 2) that the blends showed three distinct types of flow dynamics corresponding to three distinct composition ranges. These are type-I flow in the composition range of 0–5 wt % of POE-g-MA, type-II flow in the composition range of \(\sim 10\) wt % of POE-g-MA, and type-III flow in the composition range of 15–20 wt % POE-g-MA in the blend. The shear thinning tendency increased with the increase in POE content in the blends. This may be attributed to the fact that at higher POE content the melting of the blends becomes too smooth as the elastomer chains become more loose, thereby increasing the tendency of chain slippage and chain movements against each other. Such shear-assisted chain dynamics operating in the blends is attributed to the enhanced extent of phase interactions leading to increased viscosity with increase in elastomeric POE content. These results are also corroborated by the MFI data (Table 2) wherein the decrease in viscosity was attributed to possible interactions between anhydride moiety and amide linkage.

### 2.3. Morphological Characteristics.

The xylene-etched cryofractured surface morphologies of PA410/POE-g-MA blends are shown (Figure 3). The micrographs show the uniformly distributed voids/cavities scattered and embedded on the surface of the matrix phase. These cavities indicate the void space created by the dislodging of the dispersed POE phase upon dissolution and swelling in hot xylene. Thus, the cavities indicate the size of the elastomeric domains. The randomly scattered white globules on the surface indicates loosely adhered and swollen elastomeric particles that are dislodged from the PA410 matrix phase. The size and size distribution of the domains dispersed in the matrix phase have been measured by using Image J software. The number average domain size \(\left(D_n\right)\), interfacial area \(\left(A_i\right)\), and interparticle distance \(\left(r\right)\) were measured by using Wu's percolation theory. The various parameters defining the domain-related attributes are given in (Table 3). The micrographs in general show characteristics of partial miscibility. The domain sizes increased with the increase in the POE contents in the blend, and in consequence the interdomain distance decreased. Such two-phase domain-dispersed morphology remained not only distinct but also the domain sizes remained nearly uniform for a given blend composition. These observations indicate that the shear sensitivity of the droplet break-up process remained directly proportional to the amount of elastomeric inclusions. The increased domain sizes of the POE phase apart from acting as effective stress concentrators also reportedly facilitate the process of stress dissipation through reduced interdomain distances.

To understand the realistic distribution of the elastomeric phase, the atomic force microscopy (AFM) images of sliced specimens were recorded in lateral force mode. The AFM images (shown in Figure 4) reveal the dispersed POE phase in the lighter contrast. It can be clearly seen that the elastomeric phase tends to be more continuous above \(\geq 20\) wt % POE-g-MA content. At the concentration \(\geq 10\) wt % POE-g-MA content, the elastomeric phase tends to coalesce, tending to become more continuous in terms of its phase distribution. The AFM images thus corroborate the observation from SEM, and the quantitative measurements (domain sizes and interparticle distance) remain well in accordance with the qualitative attributes exhibited by AFM.

### 2.4. Mechanical Response.

The uniaxial tensile response of the blends is shown in the stress–strain \((\sigma–\varepsilon)\) diagrams (Figure 5a). The tensile modulus \((E)\) and tensile (yield) strength \((\sigma)\) of the blends showed a consistent decrease on increasing the POE-g-MA content (Figure 5b). For example, the tensile modulus and yield strengths decreased by \(\sim 24\) and \(30\%), respectively in the blend with 15 wt % POE-g-MA compared to that of PA410 matrix. This may be attributed to the systematic reduction in the extent of bulk rigidity due to the rubber-based soft phase inclusion. Such phases when

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**Table 1. Crystallization and Melting Temperature of PA410/POE-g-MA wt % Melt-Mixed Blends**

| system | \(T_c\) (°C) | \(T_m\) (°C) | crystallinity (%) |
|--------|-------------|-------------|------------------|
| NE-00  | 229.95      | 246.66      | 24.54            |
| NE-05  | 229.78      | 246.84      | 24.97            |
| NE-10  | 229.75      | 246.44      | 24.43            |
| NE-15  | 229.74      | 246.26      | 24.21            |
| NE-20  | 229.62      | 246.38      | 24.31            |

**Table 2. Melt Flow Index (MFI) of the PA410/POE-g-MA Blends**

| system | NE-00 | NE-05 | NE-10 | NE-15 | NE-20 |
|--------|-------|-------|-------|-------|-------|
| MFI (g/10 min) | 30.25 | 24.16 | 19.54 | 8.87  | 7.2   |

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**Figure 2. Complex viscosity vs angular frequency.**

**Figure 3.** Cryofractured surface morphologies of PA410/POE-g-MA blends at different POE-g-MA contents. The dark contrast reveals the dispersed elastomeric domains in the polymer matrix. The void spaces created by the dislodging of the dispersed POE phase upon dissolution and swelling in hot xylene increase with POE-g-MA content. The interdomain distance decreases with increasing POE-g-MA content due to the increased domain sizes. The AFM images thus corroborate the observation from SEM, and the quantitative measurements (domain sizes and interparticle distance) remain well in accordance with the qualitative attributes exhibited by AFM.

**Figure 4.** AFM images of POE-g-MAcryofractured surface morphologies of PA410/POE-g-MA blends. The AFM images reveal the dispersed POE phase in the lighter contrast. It can be clearly seen that the elastomeric phase tends to be more continuous above \(\geq 20\) wt % POE-g-MA content. At the concentration \(\geq 10\) wt % POE-g-MA content, the elastomeric phase tends to coalesce, tending to become more continuous in terms of its phase distribution. The AFM images thus corroborate the observation from SEM, and the quantitative measurements (domain sizes and interparticle distance) remain well in accordance with the qualitative attributes exhibited by AFM.

**Figure 5.** Stress–strain \((\sigma–\varepsilon)\) diagrams of PA410/POE-g-MA blends. The tensile modulus \((E)\) and tensile (yield) strength \((\sigma)\) of the blends show a consistent decrease on increasing the POE-g-MA content. For example, the tensile modulus and yield strengths decreased by \(\sim 24\) and \(30\%), respectively in the blend with 15 wt % POE-g-MA compared to that of PA410 matrix. This may be attributed to the systematic reduction in the extent of bulk rigidity due to the rubber-based soft phase inclusion. Such phases when
incorporated in to polyamide matrix may lead to interference with the overall packing of the polymer chains of PA410 in a rigid three-dimensional entanglement space. Similarly, in flexural mode also, the blends showed continuous reduction in the flexural moduli (∼34% in the blend with 15 wt % POE-g-MA compared to that of PA410 matrix) and strengths (∼50% in the blend with 15 wt % POE-g-MA compared to that of PA410 matrix), indicating the bulk material response under mechanical loading remained unaffected irrespective of the kind of loading/stressing and thereby indicating the isotropic and homogeneous nature of the blends from structural and micromechanics point of views (Figure 5c). The significant extent of increase in the strain at break (ε) for the blends with increase in the POE-g-MA content indicates the deformation mode of the blends to be shifting gradually from semiductile to distinctly ductile modes. This is clearly inferred from the registered strain (strain at break) value of ∼>50% (distinctly ductile) in the blends with ∼15−20 wt % POE-g-MA to ∼20% (semiductile) in PA410 matrix. Such observations correspond to the fact that the toughness of the blends becomes more dominated by the yielding and necking related phenomena whereas in the neat polyamide matrix the toughness value

### Table 3. Morphological Parameters of PA410/POE-g-MA Blends

| sample designation | Dn (μm) | A (μm) | IPD (μm) |
|--------------------|--------|-------|---------|
| NE-00              | 0.2427 | 1.529333 | 0.25183 |
| NE-05              | 0.296 | 2.476972 | 0.18469 |
| NE-10              | 0.3339 | 3.253605 | 0.14173 |
| NE-15              | 0.3848 | 3.719003 | 0.11522 |
| NE-20              | 0.4356 | 4.129003 | 0.10123 |

Figure 3. Etched (cryofractured) scanning electron microscopy (SEM) micrographs of PA410/POE-g-MA blends.

Figure 4. Schematic of lateral force mode AFM and AFM images of PA410/POE-g-MA blends.
remained grossly controlled by the tensile yield strengths ($\sigma_y$). Interestingly, due to the inherent notch sensitivity of polyamides, the toughness measured in quasistatic uniaxial tension modes may actually be indicative from general assessment of material point of view. However, the Izod impact strength data showed (Figure 5d) significant enhancement (≈400% increase) in impact strengths in the composition range of $\sim$10–15 wt % POE-g-MA. Such an increase reiterates the high-strain energy dissipation ability of the blends that is fundamentally controlled by an optimum size of the domain of the dispersed elastomeric phase as a morphological parameter. It is thus quite evident that the energy dissipation ability of the blends with 0–10 wt % POE-g-MA remains primarily matrix-controlled whereas the same remains domain size controlled when the POE-g-MA content exceeds 15 wt %. To understand the intrinsic toughness-to-stiffness response of these blends in a combined manner as the response to both low-strain and high-strain deformations, the impact strength data is normalized with Young’s moduli (elastic modulus), (Figure 5d). It is found that the impact strength to the Young’s modulus ratio resembles the trend of absolute impact strength values measured for the various blends. These observations qualitatively indicate that the bulk mechanical response of the blend systems is mainly controlled by the attributes of the elastomeric phase, viz., domain size and interparticle distance.

To further assess the micromechanical aspects responsible for such materials, various theoretical models are reported to be useful.15 Two of these theoretical models that most convincingly are based on two extreme assumptions are (a) simple rule of mixture considering the fact that the attributes of the two components may be quasilinear and (b) foam model proposed by Isahi–Cohen that renders the dispersed domain phases in a noninteracting and noncontributing phase, such as in foams or voids. The rule of a mixture is inherently based on considerations that blend systems are ideal with perfect bonding between the two phases and without any residual stress or voids while overruling the possibility of the presence of any defects at the interface either due to the processing or due to any possible interaction between the two phases. Since in polarity-grafted elastomer-induced toughening of polyamide...
systems normally some interactions always remain, the rule of mixture may be modified and given as in eq 1
\[ E_b/E_m = [(E_f/E_m) - 1]q_r + 1 \] (1)

where \( E_b \) and \( E_m \) are the elastic modulus of the blend, matrix polyamide 410, and dispersed rubber phase (\(~3.2\) MPa as per technical data sheet of the supplier) and \( q_r \) is the volume fraction of POE-g-MA. The estimations based on this model showed a nearly linear trend of decrease with the increase in the volume fraction of the dispersed POE-g-MA phase. However, the experimental data remained well below the predictions from the rule of mixture in all compositions above 5 wt % elastomer, which intrinsically accommodated interaction possibility between the two phases. The inapplicability of the rule of mixture lead to explore the possibility of other theoretical models that revolve around the assumption of the absence of any interaction between the two phases, such as Isahi–Cohen’s foam model that considers the dispersed domains as essentially noninteracting as foam or void. The model may mathematically be represented as given in eq 2
\[ E_b/E_m = [1 - q_r^{2/3}] \] (2)

The estimations based on the foam model showed negative deviation in the whole composition range, indicating the absence of voids in the blend systems. This inevitably signifies the existence of chemical interaction between the terminal amide group of PA410 and the -MA moiety of POE-g-MA. The predictions based on the rule of mixture and Isahi–Cohen model are shown (Figure 6a). It is evident (Figure 6a) that the experimental data remains bounded by the predictions based on the two models. The rule of mixture thus leads to the upper bound predictions, whereas the Isahi–Cohen model leads to estimations that form the lower bound prediction. Furthermore, it is also indicated that the blends with \( \geq 10 \) wt % POE-g-MA may show a distinct biphasic morphology whereas \( \leq 5 \) wt % POE-g-MA leads to indistinct and near-uniform single-phase morphology. These observations are well in agreement with the morphological attributes obtained from SEM and AFM measurements, as discussed in the previous section. The percentage of -MA in POE-g-MA is \(~0.5\)%, which is very low for complete miscibility of the two phases in the blends, although it sufficiently ensures the reduction in the interfacial tension through the formation of a copolymer based on PA410 and POE-g-MA. Therefore, the blends may be construed as partially miscible with a biphasic architecture.

Beyond the elastic limits, the high-strain mechanical response, i.e., yield stress, may also be analyzed by using theoretical models such as (a) Nicolais–Narkis model as given in eq 3 and (b) porosity model as given in eq 8. The two models fundamentally differ in terms of their conceptual argument over the (a) presence of interphase interaction considered as an adhesion parameter as in the Nicolais–Narkis model and (b) the absence of phase interaction leading to generation of porosity as in porosity models, which are widely employed in polymer blend systems. The Nicolais–Narkis model considers the phase interaction and characterizes the extent of phase adhesion with the parameter \( K \), where a lower value of \( K \) illustrates better adhesion; i.e., for poor adhesion, the value of \( K \) may be taken as \( 1.21 \).\(^6\)

\[ \sigma_b/\sigma_m = (1 - Kq_r^{2/3}) \] (3)

\[ \sigma_b/\sigma_m = \exp(-\alpha q_r) \] (4)

The investigated blend systems lead to a \( K \) value of 0.86, indicating intermediate adhesion. The Nicolais–Narkis model outcomes showed negative deviation at lower loadings of rubber, i.e., at \( q_r \sim 0.10 \), and a transition to positive deviation could be obtained above \( 10 \) wt % POE-g-MA content indicating the existence of phase interaction till \( 15 \) wt % POE-g-MA loading, as shown (Figure 6b). Further incorporation of rubber tends to exceed the experimentally determined values. In contrast to the Nicolais–Narkis model, the porosity model, which conceptually deals with the noninclusion of the contribution from the minor/dispersed phase on the load-bearing ability of the material and thereby assumes the presence of a minor phase in the macromorphology of blends as pores or voids, showed a near conformity to the experimental data. The parameter \( \alpha \) in the porosity model signifies poor adhesion when its magnitude is higher, indicating the presence of stress concentration in the blends. The theoretical values obtained from the porosity model have been found to be closer to experimentally determined values of yield stress (\( \sigma \)) with \( \alpha = 1.93 \) (Figure 6b). The correspondence of domain size (\( D_a \)) and interparticle distance (\( r \)) to impact energy (as the resistance to instantaneous loading) as a function of the rubber concentration (\( q_r \)) reaching a maxima at \( 15 \) wt % POE-g-MA may further be correlated to the observed deviations from the understanding of the porosity parameter (\( \alpha \)) and adhesion parameter (\( K \)) based on yield stress (\( \sigma \)) data. The remarkable enhancement in impact toughness indicated by a jump of \(~15\)-fold, upon incorporation of \( 15 \) wt % POE-g-MA, reiterated the possibility of enhanced phase adhesion that
is further supported by the parameters $\alpha$ and $K$ corresponding to the porosity model and Nicolais–Narkis model, respectively.

2.5. Dynamic Mechanical Analysis. The variation of storage moduli with temperature at a frequency of 1 Hz is shown (Figure 7a). The dynamic mechanical responses showed similar trends in storage decay irrespective of the blend compositions in the entire temperature range. The neat polyamide 410 matrix, i.e., NE-00, and the blend with 5 wt % POE-g-MA content (NE-05) showed resembling responses till 30°C and showed nearly identical responses at a temperature above 30°C. Such an observation indicates the subdued effect of elastomer in NE-05 in conditions close to the room temperature. Furthermore, such effects clearly reveal the polyamide matrix-dominated effect of the blends at temperature >30°C. Interestingly, ~50–60% decrease in the storage modulus could be seen in the temperature range of −60 to +60°C irrespective of the blend composition. However, in the proximity of room temperature, i.e., close to ~40°C, NE-00 and NE-05 have shown comparable magnitudes of storage moduli, although upon further incorporation of POE-g-MA above 5 wt %, i.e., for NE-10 and NE-15 blends, about 18% decrease in the storage moduli values was registered. A substantial extent of loss in storage moduli could be noticed when both elastomer concentration and temperature (as influencing parameters on storage behavior) were increased. The damping behavior of the blends evaluated in terms of the loss tangent ($\tan \delta$ = loss modulus/storage modulus) showed two distinct peaks at −43 and 68°C corresponding to the second-order transition ($T_g$) of POE-g-
peak could be observed in the blends with a POE-g-una. The nature and position of the tan δ peak corresponding to the polyamide phase remained grossly unaffected in all blend compositions.

2.6. Domain Size—Ductility—Toughness Interdependence. The substantially remarkable enhancement in impact toughness in the case of semiductile or brittle plastics is technically referred as “super toughness”. The influencing parameters bringing out such effects based on Wu’s percolation model are elastomer concentration, domain size (\(D_n\)) and interparticle distance (\(\tau\)) of the dispersed phase. For example, the super toughness in the case of polyamide 6 was reported when the Izod impact energy exceeded 800 J/m for 20 wt % EOR-g-MA loading with a dispersed phase domain size of <0.4 \(\mu\)m. In contrast, the use of a maleated elastomer with polyamide 6 has reportedly lead to super toughness at an elastomeric impact modifier loading of 10 wt %, especially when the matrix is an amorphous polyamide. Therefore, the super toughness may be construed as a qualitative term that only signifies the extent of improvement in impact toughness. Contextually, in the case of polyamide 410/POE-g-MA blends, the blend composition NE-15 with 15 wt % POE-g-MA dissipated the maximum impact energy (\(~\sim 290\) J/m), which is well above \(~\sim 1500\)% compared to that of the neat polyamide 410 (\(~\sim 18\) J/m). Such a remarkable improvement is not known for any toughened polyamide system. Since the impact energy, fundamentally, has a correlation with the dispersed phase domain size, interparticle distance, ductility ratio, yield stress, and interfacial area, a comprehensive mechanistic discussion on the possibility of intrinsically correlating such material parameters/properties has been attempted and is shown (Figure 8). The impact energy dissipation increases with the domain size (\(D_n\)) and ductility ratio (\(d_\mu\)) in the vicinity of the composition range with POE-g-MA of 10–15 wt %, as indicated in Figure 8. It is well reported by that domain size (\(D_n\)) of the dispersed phase in the range \(~\sim 0.2–0.4\) \(\mu\)m effectively enhances the toughening via cavitation or shear yielding processes, while the relatively larger elastomer particles (\(~\sim 2–3\) \(\mu\)m) facilitate the multiple crazing phenomena, leading to brittle fracture. In the investigated blends, the domain size remained broadly in the range of \(~\sim 0.24–0.38\) \(\mu\)m in the entire composition range. Such an observation evidently emphasizes on cavitation-dominated toughening as the primary mechanism behind enhanced impact energy dissipation of PA410/POE-g-MA blends. The SEM micrographs of xylene-etched impact failed specimen lending further support to such a theoretical remark pertaining to the mechanistic pathway behind a toughening process is displayed (Figure 9). The absence of plastic deformation characteristics such as elongated fibrils or strips or stretched domains clearly indicates a polyamide matrix-dominated failure behavior of the blends with 5–10 wt % POE-g-MA content. The debonding at the interface is attributed to mismatch in the phase moduli of PA410 and POE-g-MA phases. This caused the creation of new debonded surface like that in cavitation-assisted failures, when the blend specimens were subjected to impact loading, and hence effective impact energy dissipation is limited in NE-5 and NE-10. However, in NE-15 and NE-20 blends, the extensive plastic deformation with shear yielding could be observed clearly and is discussed in the subsequent section. The effective energy dissipation in such blends is related to significant reduction in interparticle distance (\(\tau\)) vis-à-vis a proportionate increase in domain size (\(D_n\)). Such a scenario of increased \(D_n\) and reduced \(\tau\) effectively facilitates the stable crack propagation under instant high strain loading and thereby dissipates more impact energy with stretched domains of the relatively lower modulus elastomeric phase. The elongated domains were reported to be critically responsible for absorbing high-impact energy, and due to strong phase adhesion, matrix-shear yielding may take place, an aspect discussed in the subsequent section dealing with failure surface morphology. Reportedly, the synergy effect of both cavitation and matrix yielding sufficiently enhancing toughness manifold is illustrated in several polyamides and other condensation polymers. In the present context, the enhancement in impact toughness by more than 15-fold compared with neat polyamide 410 matrix reaffirms the possible role of similar mechanistic attributes.

2.7. Failure Surface Morphology. The scanning electron microscopy (SEM) images of the xylene-etched impact
fracture surfaces of the blends clearly indicate elastomeric (POE-g-MA) phase inclusions in the PA410 matrix for the blends with 5−10 wt % POE-g-MA content (Figure 9). On the other hand, the blend compositions with ≥15 wt % POE-g-MA content showed continuous channels of POE phase (xylene-etched), indicating the possibility of coalescence of elastomeric domains during high-impact failure of the blends. It could also be observed from the micrographs that the blends with 5−10 wt % POE-g-MA showed relatively smoother topography than the blends with 15−20 wt % POE-g-MA where the surfaces appeared topographically more corrugated and uneven. The smooth topographic features indicate lesser extent of energy absorption by the material prior to failure compared with the materials leading to more uneven and corrugated surfaces post fracture, as the net surface area created due to fracture is higher in the uneven surface morphology. These indicated that in blends with 15−20 wt % POE-g-MA the extent of energy dissipation is more intensive than in the blends with lower extent of POE-g-MA. The surface micrographs distinctly reveal the transition in the underlying deformation mechanism from a cavitation-dominated toughening mechanism in the blends with 5−10 wt % POE-g-MA to shear yielding/shear banding in blends with 15−20 wt % POE-g-MA content. Isolated droplets under high-impact deformation leading to deadhesion of the dispersed phase from the PA410 matrix facilitates the creation of a state of distribution of voidlike structures, which intrinsically absorb impact energy through the debonding/d-adhesion phenomenon that involves the balancing of surface energy through creation of new surfaces. On the other hand, blends with ≥15 wt % POE-g-MA content undergo shear-yielding type of failure, as evident from the stretched-strip type marks on the surface of the wide ridges-type interspersed PA410 matrix. The phase-composition-dependent mechanistic attributes of these investigated blends are further illustrated in the schematic detailing the dispersed phase cavitation and deformation-assisted shear-yielding phenomena (Figure 10).

The schematic narrates the morphological alterations in the preimpact (stage-I) and the postimpact (stage-II, and stage-III) scenarios that were confirmed by the etched surface micrographs (stage-IV). The mechanistic sequence of the large-strain (impact) deformation-induced transformation in the bulk morphology has been schematically differentiated. In stage-II of postimpact, the blends with 5−10 wt % POE-g-MA undergo cavitation as a consequence of stretching, leading to phase interface failure where rubber droplets remain confined and distributed in the three-dimensional space of matrix. This is in striking contrast to the blends with 15−20 wt % POE-g-MA where the stage-II of the postimpact scenario may be a simplified two-step process involving (a) stretching/elongation of the POE-rich domains followed by (b) stretching-induced domain coalescence, giving rise to a state of quasicontinuous POE phase distributed in the matrix. These coalesced quasicontinuous POE phases when etched appear as darker channels that are POE free. Such POE-free channels are distinctly visible in the SEM images, as reproduced in the schematic shown in stage-IV (Figure 10).

3. CONCLUSIONS

The following salient conclusions were drawn from the study.

1. Toughening of biobased polyamide 410 could be remarkably increased by conventional melt-blendings with polyolefin-based copolymer grafted with a nominal amount (0.5%) of maleic anhydride.

2. More than ~15-fold enhancement in notched impact strength of PA410/POE-g-MA (85:15 by wt %) could be achieved, a phenomenal increase indicating feasibility of ultratoughening of biobased polyamides.

3. The noninterference of a polyolefin-based elastomer, i.e., POE-g-MA, with the crystalline regime of polyamide 410 intrinsically favors the retention of the attributes originating from the polyamide matrix, such as yield strength (reduced ~30%) and temperature for the onset to degradation of the blends, thereby ensuring the engineering property profile of the biobased polyamide remaining minimally compromised, when the extent of increase in failure strain (~34%) is considered simultaneously. The relaxation behavior of the two components remained unaffected on a gross level, as indicated by the two distinct loss tangent peaks obtained from dynamic mechanical analysis.

4. Estimation of theoretical micromechanical modeling of the elastic modulus and yield strength data has revealed closer proximity with experimental findings.

5. The critical domain size for ultratoughening has been found to be in the range of 0.29−0.33 μm of polyolefin copolymer domains, i.e., POE-g-MA, in the context of this study.

6. Mechanistic attributes to ultratoughening have been found to be originating from a synergistic role of cavitation-assisted domain coalescence and shear yielding of the coalesced elastomeric domains.

4. EXPERIMENTAL SECTION AND METHODS

4.1. Preparation of Blends. The raw material description with specification and the sample designation based on POE-g-MA proportion in wt % are given in Tables 4 and 5. The blends were prepared by counter-rotating a twin screw extruder (EuroLab 16- Thermo Fisher Scientific) at a screw speed of 100 rpm with varying POE-g-MA content (wt %). The blended strands were then chopped and dried at 80 °C in a vacuum oven for 24 h to remove moisture prior to injection molding. The tensile, flexural, and impact samples (as per ASTM D 638, 790, and 256) were obtained from injection

Table 4. Raw Material Details

| raw material | grade          | manufacturer    | technical data                              |
|--------------|----------------|-----------------|---------------------------------------------|
| PA410        | EcoPaxx Q530E  | DSM, Netherlands| density = 1.09 g/cc, T<sub>in</sub> = 250 °C |
| POE-g-MA     | Fusabond N493  | Dupont, India   | density = 0.87 g/cc, T = 55 °C, MAH content (%) = 0.5, MFI = 1.6 g/10 min |

Table 5. Composition of PA410/POE-g-MA Blends

| designation | PA410 (wt %) | POE-g-MA (wt %) |
|-------------|--------------|-----------------|
| NE-0        | 100          | 0               |
| NE-5        | 95           | 5               |
| NE-10       | 90           | 10              |
| NE-15       | 85           | 15              |
| NE-20       | 80           | 20              |
The cryofractured samples were then subjected to hot xylene liquid nitrogen chamber (cryoconditioned) for brittle fracture. Section of extruded strands was kept for 30 min in a closed scanning electron microscope (Zeiss EVO-50). A random morphology of POE-Electron Microscopy (SEM) of the Blends. The dispersion in injection molding. Blends in border aspects and indispensable for processing in microscopy. An average of 100 dispersed particle diameters were coated with gold to make them conductive for possible interaction with the electron gun of the scanning electron microscope. An average of 100 dispersed particle diameters was taken into account (from the image processed in Image J software) for the estimation of number average diameter, \( D_n \) (eq 6) and interfacial area, \( A_i \) (eq 7). The critical interparticle distance \( r \) was calculated using Wu’s percolation equation (eq 8) \[ D_n = \frac{\sum N_i D_i}{\sum N_i} \] \[ A_i = \frac{6\phi_r}{D_n} \] \[ \tau = D_n \left[ \left( \frac{\pi}{6\phi_r} \right)^{1/3} \right] - 1 \] \[ (6) \]
\[ (7) \]
\[ (8) \] \( N_i \) is the number of particles, and \( D_i \) is the diameter of the particles.

4.2. Thermal Characterization. The crystalline and melting behaviors of neat PA410 and blends were analyzed by a Perkins Elmer (Model Pyris 6) differential scanning calorimeter (DSC) at a constant heating and cooling rate of 10 °C/min from 20 to 270 °C in a nitrogen atmosphere. To remove thermal history, blends were heated first, (cycle 1) then cooled to obtain a crystalline peak temperature (cycle 2). In the same temperature range, the cooled samples (free with thermal stresses) were heated again (cycle 3) for the melting peak. The crystallinity of the blends was calculated from the heat of fusion of the crystalline peak of blends (\( \Delta H_m \)), heat of fusion of 100% crystalline PA410 (\( \Delta H_{m0} \)) taken as 269 J/g, \( \phi \) is the weight fraction of matrix PA410 in the blends using the equation

\[ X_C(\%) = \frac{\Delta H_m}{\Delta H_{m0} \times \phi} \times 100 \] \[ (5) \]

4.3. Rheological Behavior of the Blend. Parallel plate mode rheological response of the blends was conducted in a Malvern rotational rheometer (Bohlin Instruments) at 270 °C. The frequency sweep test was administrated for a 0.01 to 100 rad/s frequency range with a constant strain amplitude rate to ensure a linear viscoelastic response of the rheological behavior of the blend. Characterization of the melt flow index (MFI) of the neat form and blends was executed as per ASTM D1238 standard at 270 °C with a constant load of 2.16 kg in the Dynisco MFI apparatus. The MFI shows the melt flow of blends in border aspects and indispensable for processing in injection molding.

4.4. Morphology of the Blends. 4.4.1. Scanning Electron Microscopy (SEM) of the Blends. The dispersion morphology of POE-g-MA on PA410 matrix was analyzed by a scanning electron microscope (Zeiss EVO-50). A random section of extruded strands was kept for 30 min in a closed liquid nitrogen chamber (cryoconditioned) for brittle fracture. The cryofractured samples were then subjected to hot xylene (at \(-100^\circ C\)) for selective removal of the rubber phase for an induction period of 24 h. The etched cryofractured samples were coated with gold to make them conductive for possible interaction with the electron gun of the scanning electron microscope. An average of 100 dispersed particle diameters was taken into account (from the image processed in Image J software) for the estimation of number average diameter, \( D_n \) (eq 6) and interfacial area, \( A_i \) (eq 7). The critical interparticle distance \( r \) was calculated using Wu’s percolation equation (eq 8) \[ D_n = \frac{\sum N_i D_i}{\sum N_i} \] \[ A_i = \frac{6\phi_r}{D_n} \] \[ \tau = D_n \left[ \left( \frac{\pi}{6\phi_r} \right)^{1/3} \right] - 1 \] \[ (6) \]
\[ (7) \]
\[ (8) \] \( N_i \) is the number of particles, and \( D_i \) is the diameter of the particles.

4.4.2. Lateral Force Mode Atomic Force Microscopy (AFM) Image Analysis of Blends. To further investigate the dispersion of the soft phase in polyamide 410 matrix, the lateral force mode AFM scan of the impact specimen was conducted using Nanosurf AFM instrument. Lateral force microscopy is a static/contact mode scanning where a cantilever is subjected perpendicularly to the scanning area while restricting the scan rotation for forward and backward movement. The relative friction between the phases evolves the topology image of the specimen. The schematic of lateral force mode AFM is shown (Figure 4).

4.5. Mechanical (Quasistatic) and Thermomechanical (Dynamic) Properties. The uniaxial tensile response of the blends was studied on a universal testing machine ZWICK Z250 in room temperature (30 ± 2 °C) with a cross-head speed of 50 mm/min (following ASTM D 638). The deflection/bending strength and modulus were analyzed by the standard flexural testing procedure (ASTM D790). Impact energy (\( J/m \)) of the samples was measured by the Izod impact (ASTM D256) standard procedure with a prenotch of 45° and 2.5 mm depth. The average of five specimens of each composition was reported with standard deviation.

Dynamic mechanical analysis (DMA) of the virgin polyamide matrix (PA410) and the various blend compositions was conducted in single cantilever mode on an Q800 (TA Instruments) by using specimens of dimensions 35x13 x3 mm\(^3\) in the temperature window of −80 and 150 °C at a frequency of 1.0 rad/s and at a heating rate of 10 °C/min. The storage modulus (\( E’ \)), loss modulus (\( E” \)), and loss tangent (\( \tan \delta = E” / E’ \)) have been evaluated for qualitative assessment of the energy dissipation ability on one hand and quantitatively ascertaining shift (if any) in glass transition temperature (\( T_g \)) peaks of the two components in the blends.

| Table 6. Extrusion Temperature Profile (in °C) |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| die | zone 10 | zone 9 | zone 8 | zone 7 | zone 6 | zone 5 | zone 4 | zone 3 | zone 2 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 265 | 270 | 270 | 265 | 265 | 270 | 270 | 265 | 260 | 250 |

| Table 7. Temperature Profile (in °C) and Process Parameter Values Maintained in an Injection Molding Machine |
|-----|-----|-----|-----|-----|-----|-----|
| die | nozzle | zone 3 | zone 2 | zone 1 | feed | process parameter value |
|-----|-----|-----|-----|-----|-----|-----|
| 265 | 285 | 285 | 275 | 265 | 30 | injection pressure 61.81 MPa injection speed 127.54 m/s cooling time 25 s holding time 5 s |

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Notes
The authors declare no competing financial interest.

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