



Super-toughening polyamide-612 by controlling dispersed phase domain size: Essential work of fracture assessment



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ABSTRACT

A new pathway to super-toughen polyamide-612 (PA-612) by incorporating domains of soft poly(octene-co-ethylene)-g-maleic anhydride (POE-g-MA) via melt blending leading to more than ~1100% increase in notched Izod impact strength vis-à-vis fracture toughness enhancement is demonstrated. Fourier transform infra red (FTIR) studies showed effective phase interactions between PA-612 and POE-g-MA whereas dynamic mechanical analysis (DMA) revealed a reduction in loss-peak intensity at ~45 °C with increase in the soft phase fraction. The optimal dependence of fracture-toughness (*in plane-stress*) on domain-size (D_n) of dispersed-phase in the form of a reduction in resistance to crack initiation indicated by essential work of fracture (w_e) and linear increase in resistance to crack propagation indicated by non-essential work of fracture (βw_p) of the blends ≥ 10 wt% of POE-g-MA content is correlated to an increase in domain-size $\geq \sim 0.3 \mu\text{m}$. Fracture surface morphology indicated crazing to be responsible for the transition in fracture behavior, i.e. remarkable toughening of PA-612 at the critical rubber phase domain size range of ~ 0.2 – $0.3 \mu\text{m}$.

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1. Introduction

Engineering plastic materials that are dimensionally stable and fracture resistant may be attractive to automotive and structural sectors when the toughness criteria at room temperature are ensured. In this regard, polyamide-612 being a matrix with comparably higher dimensional stability and low moisture sensitivity than the other polyamide analogs, the aspects pertaining to toughening may need viable attention both technologically and economically. In this regard melt blending of elastomeric/rubbery soft-phase with the matrix polyamide may lead to many advantages including modifying the morphological requirements at the micron-scale causing an enhancement in resistance to crack initiation and propagation apart from increasing the overall impact strength. Theoretically, the key factors controlling the toughening mechanism of blends are: (a) type and amount of rubbers, (b) size of the micro-domains of dispersed phase, (c) inter-particle distance and (d) interaction/adhesion between matrix and rubber [1]. Reportedly, the optimum soft-phase (rubber) particle diameter of ~ 0.2 – $0.4 \mu\text{m}$ leads to maximum toughening of rubber-toughened polymer blends [2]. However, most extensive literature survey though arrives at a general consensus on rubber phase induced

toughening of polymers, it does not necessarily conform to any critical or fixed range of rubber/soft-phase/impact modifier loading that may lead to maximum toughness enhancements. The methods of measurement of toughness of polymers, blends and composites were reported to be widely variable, ranging from notched and un-notched Charpy and Izod tests to area under the uni-axial tensile stress–strain curves. These methods though are practicable their relevance in leading to deeper insights into the aspects responsible for toughening remains debatable because toughness as a material property is testing-geometry dependent and most of the ductile polymer based systems in reality do not undergo complete fracture. Therefore, energy based toughness evaluation methods such as essential work of fracture (EWF) approach was found widely acceptable in characterizing intrinsic toughness of polymeric materials, including that of toughened binary and ternary blends, micro- and nano-structured polymeric systems. The method enables the partitioning of the two energy components that are responsible for fracture initiation and fracture propagation.

For example, Yin et al. [3] reported on the largely improved impact toughness due to the formation of melt processed induced core cell particles that effectively act as particles bridges and thereby enabling the absorption of fracture energy via penetration of micro-crack propagation in case of PA-6/EPDM-g-MA/HDPE blends. Su et al. [4] studied PET/POE/POE-g-MA (PET:POE = 80:20) blend systems and found that an optimization of toughening could be attained at 3 wt% of POE-g-MA, where the notched impact

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strength enhanced 15-fold relative to neat PET. The observed toughening behavior was attributed to a combination of good dispersion of elastomer phase (particles) and optimally appropriate interfacial adhesion. Ma et al. [5] have investigated on tough PA-6/EPDM-g-MA (80:20) blends which can further be potentially toughened with β -nucleated thermoplastic vulcanizates (TPVs). Another similar attempt led to a significantly enhanced level of toughness, i.e. 10-fold increase due to addition of TPV into elastomer modified PP matrix such as PP/EPDM-g-MA [6]. Ozkoc et al. [7] have reported on fracture toughness of olefins based compatibilized PA-6/ABS blends where significant increase in w_e by >15-fold and in βw_p by >18-fold were reported by EWF method using SENT specimens. Similarly the fracture toughness of K-g-MA compatibilized PC/K-resin blend was reported where an increment in w_e up to ~33% could be observed without substantially affecting βw_p [8]. Fung and Li [9] investigated fracture characteristics of PET/SEBS-g-MA binary blends under quasi static and impact loading conditions, where an increase in fracture toughness from ~7 kJ/m² to ~17 kJ/m² with 10 wt% of EPDM-g-MA incorporation was reported. Furthermore, such an increase was found to have a correspondence to >60-fold increase in Charpy impact strengths of the blends at identical levels of elastomer loading. Such remarkable increment was attributed to the development of prominent outer plastic deformation zone (OPDZ), which was microscopically characterized as a consequence of de-bonding of rubber particles and subsequent cavitations of PET matrix. Wang et al. have put forth a comparative evaluation of POE-g-MA based blends of semi-crystalline nylon 6 vis-à-vis an amorphous polyamide (a-PA) [10]. The increases in fracture toughness in these systems are characterized by an arrested crack tip which led to the propagation of a critical upper limit and inter particle distance (IPD) with respect to the soft-phase domain size i.e., of elastomeric phase. The increase in fracture energy by >5-fold and by >3.5-fold for a-PA and nylon-6 respectively was attributed to resistance of rubber particles followed by crazing and massive shear yielding of matrix. In an effort to investigate the effect of reactive compatibilization of PA-6/EBA blends Balamurugan and Maiti [11] have reported more than 3-fold increase in w_e along with more than 20% reduction in βw_p for the uncompatibilized binary and compatibilized ternary blend systems at identical levels of EBA-contents (EBA or EBA + EBA-g-MA = 10 wt%). Similarly Pegoretti and Ricco [12] have reported on EWF of neat PA-66 and PA-66/rubber blends, where an increase in w_e and decrease in βw_p in 7 wt% rubber filled blend have been attributed to a threshold average particle diameter (d_n) of 139 ± 27 nm, above which w_e and βw_p were reported to remain unaffected or follow a decreasing trend. In a unique effort to understand the matrix softening effect, Tang et al. [13] have systematically evaluated the effect of β -phase PP on the fracture behavior of dynamically vulcanized PP/EPDM blends. It was reported that above 0.3 wt% β -nucleating agent incorporation the β -crystallinity of the PP phase appreciably increased to ~15–35% which has a correspondence to an increase in w_e by more than 15% without significantly affecting the βw_p . The study thus reiterates the fact that β -modification of PP matrix in binary PP/EPDM elastomer blend may effectively lead to increase in resistance to stable crack initiation.

In contrast to the conventional fracture parametric assessment of semi-crystalline polymer materials such as polyamides with substantial ductility/plasticity the aspects pertaining to the fracture-energy or work of fracture factors in controlling the overall failure response is less understood. Therefore the present paper fundamentally attempts to investigate on the toughening via fracture performance enhancement of polyamide-612 (PA-612; with relatively higher methylene-to-amide (–CH₂– to –NH–CO–) ratio compared to the conventional nylon 6 and nylon 66) by mixing POE-g-MA (weight fraction controlled) as an elastomer.

2. Experimental details

2.1. Preparation of PA-612/POE-g-MA blends

Commercially available polyamide-612 (PA-612) and poly (octene-co-ethylene)-g-maleic anhydride (POE-g-MA) with trade names Vestamid (DX9300) from Evonik (Germany) and Fusabond (N493) from Dupont (India) respectively, were blended in various compositional ratios. The details of PA-612 and POE-g-MA were already reported by the authors elsewhere [14]. Co-rotating type (Steer Omega-20) twin screw extruder with $L/D = 40$ has been used for the melt mixing of PA-612 and POE-g-MA at various compositional ratios to give rise to a series of [(wt/wt%: 100/0 (NE-0), 95/5 (NE-5), 90/10 (NE-10), 80/20 (NE-20), and 65/35 (NE-35)] blends. The screw speed was kept at 200 rpm, whereas the temperature profile of the extruder barrel was maintained at 220 °C in the feed zone and at 245 °C in the die zone for the preparation of the blends. The continuous strands were chopped to obtain granules which were later subjected to drying in the oven at 80 °C for ~8 h prior to being injection molded (L&T Demag make) at a pressure of 60 bars, injection time of 4 s and cooling time of 25 s to obtain plates of 80 mm × 80 mm squares of ~1 mm thickness. The injection molding temperature profile was kept at 40 °C, 222 °C, 230 °C, 245 °C, and 260 °C corresponding to the feed-zone (Z-1), meter-zone (Z-2), compression-zone (Z-3), heating-zone (Z-4) and die-zones (Z-5) respectively. Rectangular strips of dimension 80 mm × 20 mm × ~1 mm were machined from the plates for fracture mechanics investigations.

2.2. Domain size determination of dispersed phase in the blends

The cryogenically fractured and etched surfaces of PA-612/POE-g-MA blends have been investigated for their morphologies using scanning electron microscopy (SEM) on a Zeiss EVO-50 electron microscope to analyze the dispersion by measuring the domain sizes of rubbery phase in the PA-612/POE-g-MA blends. Prior to being mounted for microscopy, the samples were kept in boiling xylene for 24 h for the extraction of the rubber phase (POE). The surfaces of the specimens were made conductive by gold sputter coating. The micrographs obtained by SEM for the determination of domain sizes are shown in Fig. 1. The domain sizes of the dispersed soft phase were measured using Image J software. The morphological parameter characterized by number average diameter (D_n) was determined by the following Eq. (1), reported elsewhere [14]. The Eq. (1) may be given as below.

$$D_n = \frac{\sum N_i D_i}{\sum N_i} \quad (1)$$

where N_i is the number of particles and D_i is diameter of particles. The inter-particle (inter-domain) distances have been calculated based on percolation theory following Wu's equation [1]. The Eq. (2) may be given as below.

$$\tau = D_n \left[(\pi/6\phi)^{1/3} - 1 \right] \quad (2)$$

where D_n is the number average domain diameter of the dispersed phase (POE-g-MA) corresponding to a volume fraction ϕ . The details of the rubber modified PA-612 composition with their respective domain sizes (D_n) and inter-domain distances (τ) are given in Table 1. With the increase in rubber content τ decreased indicating the theoretical possibility of the material to readily undergo ductile failure behavior with the increase in POE-g-MA content, an observation reported earlier [14].

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