

Toughness and Ductile Brittle Transition Temperature of Different Mineral Filler Reinforced TPOs Composites

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ABSTRACT

The effect of different mineral fillers (Talc, calcium carbonate, clay, mica) on the toughening behavior and ductile-brittle transition temperature (DBTT) of TPOs composites has been investigated in the paper. An attempt was made to investigate impact strength to determine the DBTT of the mineral-modified TPO composite system by employing a series of mineral fillers. Impact tests at different temperatures were carried out to detect ductile and brittle fractures. Data is then related and interpreted in terms of the basic structure-property relationship, by varying the percentage of mineral filler content in the TPO composite system. Variation of impact properties has also been correlated to the yield behavior of unmodified blends as well as mineral-modified TPO systems and DBTT of the mineral-modified blends. The data of impact & tensile tests are used to deduce model equations that are used to draw simulations for predicting the physical properties of new combined systems. Variable trends in a decrease in toughness were revealed by the results. This effect is more functional with the assimilation of talc. The viscosity of the impact modifier directly affects the crazing, shear yielding, cavitation, and dimensional stability of the composite. These factors are eventually responsible for the brittle or ductile failure of the system.

Keywords: Ductile Brittle transition, Ductility index, Toughness, Reinforcement.

INTRODUCTION

Polypropylene (PP) is one of the most widely used commodity thermoplastics, especially in automotive, electric, packaging, and consumer application (Sasimowski et al., 2019; Várdai et al., 2022). The reason for this can be found in its excellent properties, such as good processing, heat distortion temperature above 100°C, recycling ability, and favorable price/performance ratio (Makhlouf et al., 2016). PP is a semi-crystalline polymer. The performance of PP products depends on their crystalline structure, the relative amount of amorphous and crystalline phases, crystal modification, size and perfection of crystallites, dimensions of spherulites, and the number of tie molecules. While having exceptional properties, PP is frequently modified with particulate fillers and other polymers. Frequently used fillers in PP are talc, calcium carbonate, glass beads, glass fibers, mica, silica, and wollastonite (Ma et al., 2010; Ghanbari et al., 2019; Ma et al., 2007; Lee et al., 2010). Modification of PP with filler is generally done for achieving better dimensional rigidity and temperature behavior (Wu et al., 2015; Ajorloo et al., 2021). Even though PP offers many advantages, it suffers from brittle failure, especially at low temperatures, making it inadequate for applications where good impact properties are essential and thus need modification of impact resistance by other elastomers/TPOs (Saravari et al., 2014; Li et al., 2017; Ying et al., 2018). Thermoplastic olefins (TPOs) are mainly immiscible blends containing a dispersed phase of polyolefin elastomer. Thermoplastic polyolefins (TPOs), consisting of a PP matrix with a

dispersed rubbery phase, display improved properties over their virgin components (Mohite et al., 2022). The rubber particles that are dispersed in the polyolefin matrix serve to concentrate stresses and initiate local yielding in the matrix. Polyolefin elastomers have been used extensively in the plastics industry as impact modifiers for brittle polymers such as PP. When PP is modified with an impact modifier, the factors which affect its micromorphological structure are somewhat complex. Under notched impact conditions, PP shows a clear ductile-brittle transition (DBT) with a rise in temperature (Van der Wal et al., 1998). It was found that with increasing crystallinity of PP this DBTT shifts to a higher temperature (Jia et al., 2019). Plastic deformation mechanisms of PP-rubber blends are the test rate and temperature dependent, with high rates and low temperatures generally favoring crazing while high temperatures and low strain rates favor shear yielding (Jang et al., 1985; Jang et al., 1985) By varying the crystalline structure of PP, the rubber particles, in addition to promoting crazing and shear yielding, can also improve the fracture resistance of PP. When examined as a function of temperature, strain rate, or blend composition, results of rubber-modified PP show that the size and density of the damage zones increase gradually through the ductilebrittle transition. Similarly, the deformation behavior of blends of PP modified with rubber was found as a function of temperature and composition under tension (Bucknall et al., 1977; Yang et al., 1984). The fracture propagation energy is small in comparison with the fracture initiation energy for relatively brittle materials. For ductile, tough, materials, the fracture propagation energy may be larger compared to fracture initiation energy. A brittle fracture surface looks grainy, salt, and pepper appearance to the unaided eye. Ductile fracture is usually trans granular and its fracture surfaces show a plastic deformation between roughly spherical micro-voids. In short, TPO materials are long been widely used in a diverse range of structural applications. These include daily household appliances to more heavy-duty parts required for building and automotive industries. The main advantage of TPO lies in the fabricability, aesthetics, structural integrity, lightweight, and of course cost to performance ratio. To meet the ever-demanding requirements of stiffness and dimensional rigidity TPO is being reinforced by different types of mineral fillers.

MATERIAL AND EXPERIMENTAL

Polyolefin modifiers:

The impact modifier studied is olefinic copolymers having a melt flow index of 1.2 gm/10 min at 190 °C. An ethylenebased α -olefin elastomer, produced by Mitsui Chemicals, i.e. ethylene butene elastomer TAFMERTM DF610.

Polypropylene:

The polypropylene matrix studied is a copolymer of intermediate melt flow index grade Moplen EP 540P produced by LyondellBasell used having an M.F.I of 15g/10 min at 230°C. HDPE grade HD 50MA180 produced by reliance industries of melt flow rates 20 g/10min at 190°C is also used to enhance the impact property of blends.

Fillers:

Talc, Calcium carbonate, micronized calcined clay, and mica were selected to reinforce these TPOs composites system. Impact modifiers were blended with polypropylene with 20% of loading.

Blend Formation:

Various blends are formed by varying the percentage ratio of polypropylene matrix and different fillers from 0 - 40% while keeping the impact modifier and HDPE constant. The various compositions of the blend to be formed are shown in the table below table.

Table - 1 Blend formation with Different Mineral Fillers

Filler	Filler %	PP 540T	50MA180	Tafmer DF 610
Talc/	0	75	5	20
calcite	10	65	5	20
/ Mica / Clav	20	55	5	20
	30	45	5	20
	40	35	5	20

Blending and specimen preparation:

Thermoplastic polyolefin compounds featuring olefinic co-polymer were compounded in co rotating omega 20, twin screw extruder with a screw diameter of 19.7 mm. Typical PP extrusion condition maintained, with extrusion melt temperature set at 190 - 220 deg c. Finally, compounds were palletized and injection molded into test specimens sample pellets were injection molded into test specimens using a 100-ton Kaptiva injection molding machine using standard PP molding conditions.

Conditioning:

Injection-molded samples were conditioned for 48 hours in a humidity chamber before testing. 23 ^oC ambient temperature and 65% relative humidity were maintained.

Mechanical testing:

Mechanical properties such as the notched izod Impact test was carried out according to ASTM 256 J.J impact tester, XJDU- 5.5 series. Notched impact strength at low temperatures for ductile-brittle transition temperature was measured by cooling test samples in a deep freezer at different sub-ambient temperatures for 3 hours and testing at room temperature before any warming happens to the molded samples. The polymer ash or resin burn-off test was performed according to ASTM D 5630 to determine filler weight fraction (W_f) in the composites after the compounding process.

Tensile elongation at yield and elongation at break are determined as per ASTM D 638 by using LLOYD, LR 10 PLUS series Universal testing machine (UTM).

RESULT AND DISCUSSION

Impact Strength

As shown in fig-1, the impact resistance decreases as a function of an increase in filler level. When PP is blended with elastomer, the latter gets first dispersed as small domains in a matrix of the amorphous phases of PP. These elastomer domains, in turn, impose regions of discrete zones of occlusions which due to their inherent elasticity and backbone flexibility absorb the energy associated to impact and impose restriction of crack growth through the matrix to the crystallite boundaries and restrict catastrophic failure.

The additions of the filler significantly reduce the impact strength of the blend due to the increasing stiffness of the matrix by restricting the chain mobility in the amorphous phases. As a result of this, flexibility and rate of stress transfer decrease.



Fig: 1 Impact Strength vs Filler Content

As shown in Fig 1 there is a gradual fall in impact strength. The trend varies from filler to filler guided by nature as well as coating criteria. The better impact retention of the coated talc is because of the better wettability of the polymer matrix and improved polymer filler interaction with interfacial adhesion due to coating. But the Mica-filled grades show much inferior impact retention which is the lowest. The difference in impact behavior for talc and mica-reinforced composites can be explained based on their basic structural features. Both are layered silicate minerals, in which mica forms planar thin platelets with a very high aspect ratio, with biaxially oriented plates having a high surface area compared to thickness. Thus, mica results in stronger reinforcement of the matrix making it more rigid and stiff, thereby causing more restriction on the effective stress transfer during impact.

Although no reference data was available relating polymer-filler interaction to impact strength, we have tried to deduce an equation for the same which can guide as a route to predict the impact of filled materials.

Fig 1.1 is shown the plot of relative changes in impact strength with filler content for different fillers.



Fig: 1.1 Relative changes in impact strength vs filler content for different fillers.

The trend of the impact variation follows one exponential relationship with filler content. That can be expressed by Arrhenius' type of equation 1 as below:

$\mathbf{I}f/\mathbf{I}p = \mathbf{A}_{1} \mathbf{x} \mathbf{E}\mathbf{X}\mathbf{P} \wedge [(\mathbf{1}-n) \mathbf{x} \mathbf{F}]$ (1)

Here If is for the impact strength of the filled system, Ip is related to the unfilled system, F is for the filler content, A is the Arrhenius' constant, and n is the polymer-filler interaction parameter. The data obtained from Fig 1.1 and equation 1 is tabulated in table 1 for different fillers. The implication of the same will be referred to later to explain the extent and mechanism of reinforcement.

 Table 1 Arrhenius's constant and interaction parameter for different fillers

Filler	Arrhenius Constant A	Interaction Parameter n
Talc	1.07	1.0232
Calcite	1.005	1.0098
Clay	1.07	1.0264
Mica	1.022	1.0276

DUCTILE BRITTLE TRANSITION TEMPERATURE

To investigate the impact behavior in more depth and relate this with the change in ductility of the composite caused by the stiffing we have studied the Ductile-Brittle Transition Temperature (DBTT). The DBTT is the transition temperature where failure mode transition from ductile (no or partial break with definite ductile behavior) to brittle (complete –break with sharp fracture) occurs. The result shows that DBT shifted towards higher temperature as the filler content increased and it is maximum in the 40% filled composition. This observation indicates TPO composites with higher filler level reduces the flexibility and increase the brittleness transition temperature to higher values. This again fairly well substantiates the graph presented in Fig 2. Based on experimentally observed DBTT of the different systems and calculated DBTT of the basic compositions by log additive rule, we can further proceed to investigate the appearance of a higher degree of brittleness in the reinforced composites. For the same first we have taken a plot of DBTT against the filler level applied as shown in Fig 2



Fig: 2 Variation of DBTT with filler content

The change in pattern for different fillers shows the same trend as we have observed for impact strength variation. To quantify the variation and to relate the same with polymer filler interaction we have taken relative changes in DBTT with filler level as shown in Fig 3



Fig: 3 Relative changes in DBTT with filler level

Since DBTT changes from subzero to room temperature, we have taken the relative changes by converting temperature to absolute scale Deg. K. This way all the values will be on a positive scale. The plot in Fig 3 indicates all the systems follow the same exponential relationship with filler level as expressed by Equation 1.1. The coefficient values are shown in Table 2.

$$dT_{f} / dT_{p} = A \times EXP(1-n_{3})f \qquad (1.1)$$

 Table 2 Coefficients of Polymer Filler Interaction Effecting

 DBTT

Filler	Α	n
Talc	1.0225	1.0027
Calcite	1.0006	1.0013
Clay	0.995	1.0029
Mica	0.999	1.0033

A close comparison of Arrhenius' constants and interaction parameters as presented in tables 1 and 2, clearly indicate their proximity and similar trend and thus signifies the importance of DBTT on room temperature and flexibility criteria of material as is often judged by impact resistance.

Judgment of overall flexibility and hence the suitability of the material under service, when subjected to a shock, is better expressed by elongation behavior and is mainly guided by the ductility index of the material. The ductility index can be determined by using DBTT data relating to Elongation at yield and calculated ductility index of the composites.

This can be further explained by plotting a graph between elongation at yield and DBTT. It is evident from this graph 3.1 that elongation at yield decrease as the DBTT increases. This is because as the filler content increases it restricts the polymer chain mobility and increases the brittleness. Therefore, DBTT increases, and elongation as yield decreases.



Fig 3.1 Variation of DBTT with Elongation at Yield

Another critical fact is coming from Fig 3.1 that except for calcite all the clay, mica, and talc shows a similar superimposing trend with DBTT, and yield point are concerned, whereas calcite shows a completely different trend. This can be explained by considering of respective reinforcement mechanisms and structural features of the different fillers.

RELATIONSHIP OF DUCTILITY INDEX WITH IMPACT RESISTANCE

The importance of the ductility index to investigate fracture behavior and reinforcement has been presented in the literature. Since fracture energy is the energy associated with the material under the fracture and is calculated as the area under the stress-strain curve, the same can be approximated by taking elongation at break. Since the material that is ductile at room temperature has got good elongation at break and this is the guiding factor for the energy at fracture. Same way elongation at yield can be approximated for the yield energy.

Therefore, in this article, we take the ductility index as follows-

$$DUCTILITY INDEX = \frac{(E Brk- Eyld)}{(Eyld)}$$

The plot of the so calculated Di is plotted against the filler level as shown in fig- 4, which indicates that Di falls off with increasing filler level.

A careful examination reflects the trend in variation can be expressed by the "Arrhenius" equation:

 $Di = A_2 x EXP^{n} [(1-n2) x f]$ (2)

Here Di is the ductility index, A is the Arrhenius constant for the system, n is the Arrhenius exponent, expressing polymer filler interaction, and f is the employed filler level. The values obtained from equation 2 are presented in Table 3. If we compare the values of the interaction coefficient as obtained from all the trend lines and presented in tables 1 through 3, we have fined a similar trend and strikingly close values of interaction parameters obtained for different studies.



Fig: 4 Relationship in ductility index with filler level

 Table - 3 Arrhenius Constant and Interaction parameter affecting ductility index

Filler	Α	n
Talc	19.8	1.017
Calcite	19.8	1.006
Clay	21.1	1.023
Mica	21	1.023

The analysis of the ductility index and filler level further enables us for analyzing the relationship between impact resistance and ductility index. Such a relationship is not available in the literature to date. However, it is well established that the material which has higher impact resistance are having a good ductility index. Also, the relationship of DBTT with Di has been qualitatively investigated. But unfortunately, no models were proposed to quantify the relationship. We have seen that impact strength is related to filler content by an exponential relation

$$\begin{pmatrix} \frac{\text{If}}{(lp)} \end{pmatrix} = A_1 \times e^{(1-n_1)f} \qquad \dots 3$$

$$\ln \left(\frac{lf}{lp}\right) - \ln A_1 = (1-n_1) f$$

$$f = \frac{\ln \left(\frac{lf}{lp}\right) - \ln A_1}{1-n_1} \qquad \dots 3.1$$

The relationship of Di with filler level as shown in equation 2 enables us to draw the following,

ln Di - ln A₂ = (1 - n₂) f
f =
$$\frac{\ln \text{Di} - \ln A_2}{(1 - n_2)}$$
 ...3.2

Now by equating equations 3.1 and 3.2 we get

$$\frac{\ln\left(\frac{lf}{lp}\right) - \ln A_1}{1 - n_1} = \frac{\ln \text{Di} - \ln A_2}{(1 - n_2)}$$
$$\ln \text{Di} - \ln A_2 = \frac{\ln\left(\frac{lf}{lp}\right) - \ln A_1}{1 - n_1} \times \left[(1 - n_2)\right]$$
$$\ln \text{Di} = \left[(1 - n_2)\right] \times \frac{\ln\left(\frac{lf}{lp}\right) - \ln A_1}{1 - n_1} + \ln A_2$$
$$\ln \text{Di} = B \times \ln\left(\frac{lf}{lp}\right) - \ln A_1 + \ln A_2 \quad \dots 3.3$$
Where B is the ratio of interaction parameters $\frac{1 - n_1}{1 - n_2}$

$$\ln \text{Di} = \text{B} \ln \left(\frac{lf}{lp}\right) - (\text{B} \ln \text{A}_1 + \ln \text{A}_2)$$

Taking the constant terms on one side and replacing with a third constant C we get

$$\ln \text{Di} = B \ln \left(\frac{If}{Ip}\right) + \ln C$$
Where $\ln C = (\ln A_2 - B \ln A_1)$
Thus $\text{Di} = \left(\frac{If}{Ip}\right)^B * C$
3.4

This indicates a relative impact resistance is related to the ductility index by the power-law equation where the value of B is guided by polymer filler interaction and the power exponent C is related to the Arrhenius constant. Now a plot of Di is shown against If /Ip in fig 5. The trend line indicates that Di is related by the power-law model with relative impact resistance.





 Table - 4 Arrhenius Constant and Interaction parameter for

 different fillers Studied

Filler	С	В
Talc	1.3552	0.6517
Calcite	1.5226	1.1551
Clay	1.0558	2.6581
Mica	1.1317	1.953

CONCLUSION

Mineral fillers reduce the toughness of the TPO composite system. The level of reduction is different for different fillers. The same happens as a result of differences in brittleness temperatures of all these four different minerals-modified TPO blends and the ductile-brittle transition temperature set by the same. It shows the lower toughness with higher filler content and it's also applicable to brittleness which becomes higher. The drop in impact strength or brittleness can be associated with the disappearance of the plastic deformation of the polymer matrix.

It is also showing that calcite-filled TPO composites have lower brittleness temperatures compared to other fillers, while mica and clay-reinforced TPO composites have higher brittleness temperatures. This might be due to the high aspect ratios, which increase the wettability of the fillers by the matrix. A good balance of impact and stiffness was observed in the Talc-modified TPO composite. The analysis of the ductility index and filler level establishes the relationship between impact resistance and with ductility index. The result shows that materials that have higher impact resistance are having good ductility index. As an outcome of this study, an important prophecy is made that relative impact resistance is related to the ductility index by the power-law equation, such a relationship is not available in the literature to date. All these evaluations indicate that varying ratio of filler with TPOs affects the ductility index, toughness, and DBTT. It has significant use in automotive industries to establish low-temperature toughness.

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