Mechanical, thermal and morphological characterization of PP/PS/HDPE ternary immiscible polymer blend for light weight automotive applications

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Abstract. Thermoplastic polymer blends investigation is significant because of the broad applications in automotive, aerospace, electrical appliances, etc. In this study ternary polymer blends of polypropylene (PP)/ polystyrene (PS)/ high-density polyethylene (HDPE) were prepared which bear superior properties appropriate for light weight automobile applications. The mechanical, thermal and morphological properties of these mixes were analyzed which promotes the application areas to which it is suitable for. PP can enhance the properties when used as a blend with other thermoplastics namely polystyrene and high-density polyethylene. The dispersed phase of minor components strengthens continuous phase by energy barring properties within the limitations. The mechanical and thermal properties of ternary blend is found to be higher than that of binary blends. The maximum value obtained for tensile strength, flexural strength and impact strength are 39.72 MPa, 49.47 MPa, 28.80 kJ/m² which are higher than binary blend and raw polymer. The results exhibit a stronger prospect for these blends even without the addition of compatibilizer.

1. Introduction
Polymer blends proved their status in all the field of engineering with their excellent mechanical and thermal properties compared with the pure polymers. The possible outcomes from these blends purely depend on the blend compositions. The continuous and dispersed phases surely recommend the mixes to the proper applications. The application areas primarily depend on properties of blends. Polypropylene is widely and commonly used commodity plastics having excellent chemical resistance, stiffness and melting point as compared to other commercial thermoplastics. The higher melt flow index of PP form continues phase with HDPE and less than 20 wt. percentage of HDPE increases the impact strength of the polymer blend. Increasing HDPE particles causes deterioration of crystallinity of PP, and these particles bridge the crack by extending the level of homogeneity within controlled process conditions. The interface created between PP and HDPE adversely affects tensile and flexural modulus[1]. Lower interfacial tension and lower viscosity ratio of dispersed to matrix surely lower the film drainage and poly dispersity increases with increase in HDPE content in PP, which leads to heterogeneity[2]. Interfacial tension between PP and HDPE decreases linearly with temperature. Thermal treatment improves the tensile properties of PP-PE blends for a range by enhancing the adhesion between them. The size of the dispersed phase is an essential factor that controls the
mechanical properties—improvement in stiffness of the blends by increasing the content of HDPE within the predicted range of compositions[3][4]. A decrease in crystallinity contribute a negative impact on mechanical properties. The favourable properties can be obtained by blending the polymers in the appropriate composition. The favourable properties that are suited for specific applications can be obtained by blending different polymers which are inherently showing their own enhanced characteristics.[5].

The addition of PS to the polymer blends beyond an optimized composition, lowers the impact strength. This can easily generate cracks in the polymer blends under an impact load. Variation in composition among phases determines the morphology of the mixes [6][7]. Elongation at break decreases with an increase of PS in HDPE. For a blend with higher concentration HDPE mix, the tensile ductility increases. Critical strain required to start crazing is effectively lower than that of inducing shear deformation[8]. HDPE has higher shrinkage compared to PS and PP. Shrinkage of phases in poly blends especially HDPE can be caused up to phase inversion[9][10]. The degradation of the polymers can be initiated by scission mechanisms inside the polymer structure. Scission include the breakage of carbon-carbon bonds in the base of the polymers to create radicals [11]. The variation of mechanical and thermal properties of ternary polymer blend of PP, HDPE and PS which is suitable for light weight automotive applications is not investigated with respect to compositional variations. Hence in this work, the properties of PP/PS/HDPE ternary immiscible polymer blends are investigated. The materials for automotive applications should be light weight, thermally stable and also offers good mechanical strength. The effect of dispersed PS and HDPE in continuous PP on the mechanical properties of ternary polymer blends is explored. The thermal and morphological characterization is also investigated to expound the thermal degradation behaviour and morphology of the fractured surface respectively. These mixes can be capable of elevating the application levels to a wide area by the addition of selective compatibilizer.

2. Materials and methods
Polymers used in this work are commercial homopolymer polypropylene (H110MA) supplied by M/S Reliance Industries Ltd. Gujarat—melt flow index (MFI) 11 gm/10min (ASTM D1238, 230 °C/2.16 kg). High-Density Polyethylene (HDPE) (HD50MA180) purchased from Reliance Industries Ltd., India with an MFI 20 gm/10min (ASTM D1238, 190 °C/2.16 kg). Polystyrene (PS) for this experimentation was obtained from Supreme Petrochem Ltd.- MFI 12 gm/10min (ASTM D1238, 200 °C/5kg).

PP/PS/HDPE blends prepared in a Thermo Hake Record with twin-screw extruder using the melt-mixing process maintains at a preferred temperature, rotor speed and mixing time as per Figure 1. The melt produced from the mixing process pressed in a hydraulic pressing machine to sheet forms and then cut it into small irregular pieces. The pieces injected in to microinjection moulding machine maintaining at a temperature of 180 °C and test specimens are prepared as per ASTM standards for testing mechanical properties. The studies done with blend compositions mentioned in Table 1 and fixed higher and lower values of composition in Table 2 based on literature surveys [12,13,14].

| Sample (S) | PP (wt. %) | PS (wt. %) | HDPE (wt. %) |
|------------|------------|------------|--------------|
| S1         | 87.5       | 6.25       | 6.25         |
| S2         | 87.5       | 0          | 12.5         |
| S3         | 87.5       | 12.5       | 0            |
| S4         | 75         | 12.5       | 12.5         |
| S5         | 75         | 6.25       | 18.75        |
| S6         | 75         | 18.75      | 6.25         |
| S7         | 75         | 0          | 25           |

| Sample (S) | PP (wt. %) | PS (wt. %) | HDPE (wt. %) |
|------------|------------|------------|--------------|
| S8         | 62.5       | 25         | 12.5         |
| S9         | 100        | 0          | 0            |
| S10        | 62.5       | 18.75      | 18.75        |
| S11        | 75         | 25         | 0            |
| S12        | 50         | 25         | 25           |
| S13        | 62.5       | 12.5       | 25           |
Table 2. Range of blend composition

| Components | Lower (wt.%) | Higher (wt.%) |
|------------|-------------|--------------|
| PP         | 50          | 100          |
| PS         | 0           | 25           |
| HDPE       | 0           | 25           |

3. Method of characterization
Shimadzu Autograph AG-I series universal testing machine according to ASTM D 638 and ASTM D 790 was used to evaluate the tensile and flexural properties of the samples. RESIL Impact Tester (CEAST) according to ASTM D 1238 was used to evaluate the impact strength of the preferred samples. Maximum five samples were analyzed and their average values were recorded. Thermal stability of ternary blends was analyzed. This was done in TA-Q 600 semi instrument in nitrogen atmosphere for sample of 5-7mg and temperature of 400 °C – 1020 °C at 20°C/min. The morphology of the fractured cross-section sample from tensile was examined using Field Emission Scanning Electron Microscope (SEM, JEOL Model JEM 19 2100) in vacuum atmosphere.

4. Results and Discussion
4.1. Mechanical Properties
4.1.1. Analysis of Tensile Strength. The tensile strength was analyzed at three different constant compositions and compared with pure polypropylene. Here (Figure.2) PP shows a tensile strength of 37.48 MPa. Blending PP with PS and HDPE with a composition varying from 6.25 to 25 wt.%, we can observe that a gradual change of strength in between 32.55 to 39.72 MPa. PP/PS/HDPE blend are incompatible due to the lack of interaction at the interphase which reflected in the deterioration of mechanical properties. Here 62.5PP/18.75PS/18.75HDPE, 87.5PP/6.25PS/6.25HDPE and 75PP/18.75PS/6.25HDPE shows better strength of 38.64 MPa, 39.68 MPa and 39.72 MPa respectively. This clearly indicates that increase of PS in the composition affects the whole structure.
due to the increase in the particle size which creates difficulty for the dispersed phase to protrude through the continuous phase. These forms molecular irregularity in the phase structure. In this case, the variation of PP affects the strength, but the optimized concentration of PS and HDPE provides a balanced strength for un-compatibilized ternary polymer blend. In other compositions the strength varies due to the irregular phase interphase structure provided by HDPE and PS on PP. The lowest strength recorded was 32.55 MPa for 50PP/25PS/25HDPE. 90PP/10PS shows a tensile strength of 36 MPa and for 80PP/20PS as 30 MPa [13]. It was reported that for 80PP/20HDPE has the tensile strength of 32.95 MPa [12] and 29.5 MPa [15]. Compared to all above binary blends, ternary blend of PP/PS/HDPE exhibits enhanced tensile strength. The deterioration of crystalline behaviour was not affected due to the small addition of PS. The shrinkage of PS was lower inside the matrix as compared to PP and HDPE[1][7][16][17].

4.1.2. Analysis of Tensile Modulus. 75PP/18.75PS/6.25HDPE blend (Figure.3) shows a maximum tensile modulus of 1614.64 MPa. According to Xie Zhimi et al. [18], reported that the modulus of PS is very high as compared to PP and HDPE. So, for that reason addition of PS to the blends increases the modulus of polymer blend. In another paper of Fatemeh Abbasi et al. [19], 80PP/20PS shows a two-phase morphology and the particle size of dispersed phase PS are larger in size and have broad size distribution over the whole structure. In this study, properties of the blends increased by the addition of PS while concentration of HDPE does not impart any influential increment. The viscosity of PS is low as compared to PP and HDPE. Hence the energy required for PS particles to come out from the HDPE and PP matrix is high. In some cases, this will not be achieved. Also this creates a decline in the value of tensile modulus. The lowest value reported as 648.00 MPa for 62.5PP/25PS/12.5HDPE. J. Lin et al. [1] reported a decrease in tensile modulus of blends with increase in HDPE content. The explanation is phase partition of HDPE, which offers ascend to HDPE particles that act as a nucleating agent for PP. The spherulite size of PP diminished, which unfavourably influences the crystalline nature of PP/HDPE mixes.

4.1.3. Analysis of Elongation at break. Figure 4. shows the results of elongation at break of various compositions of blends. The incorporation of PS dispersed phase on the PP/PS/HDPE blends shows a decrease in elongation. According to R. O. Ebemele et al.[20], the nature of PS microstructure, the presence of phenylene ring on each other carbon particle of the primary chain of polystyrene delivers an unbending configuration with sufficient steric obstacle to make the polymer mixes more resolute. The blend 87.5PP/0PS/12.5HDPE shows a maximum elongation of 6.73%. The decrease of HDPE in ternary blends shows a region on transition from ductile to brittle. The blends shows a matrix droplet morphology with large domain no uniformity distributed in the PP matrix[21]. Elongation at break is higher for PP and PP matrix blends and at the same time higher elongation causes lower in the brittleness[7].

4.1.4. Analysis of Impact Strength. Impact strength of various compositions of PP/PS/HDPE ternary polymer blends were analyzed (Figure 5.). The impact strength obtained maximum for 75 PP/6.25 PS/18.75 HDPE was 28.80 kJ/m². Here the effect of ductile material contributes more on the continuous and dispersed phase. Brittle PS polymer with ductile material did not result in increase in impact strength[15]. Increase of composition of PS causes an increase in the size of PS particle in the continuous phase leads to poor adhesion[22]. This leads to unequal distribution of stress between the layers. In the case of 87.5PP/6.25PS/6.25HDPE shows an impact strength of 28.21 kJ/m². The brittle material transverse the stress locally and this will not provide a clear travel path through the interphase. Hence the cracks occurs easily at the interphase with an increase in the PS content[23].

4.1.5. Analysis of Flexural Strength. As per the Figure 6., flexural strength of blends was discussed. The maximum flexural strength obtained is 49.47 MPa for 75PP/12.5PS/12.5HDPE. The variation of flexural strength shown above figure is from 34.65 MPa to 49.47 MPa. According to H. Sutar et al.[24], in PP added poly blends bear more flexural properties when compared to HDPE. The study of R. Anjana et al. [12], discussed about PP/PE blends and PP/PE nanocomposites, it was explained that 80PP/20PE blends recorded a flexural strength of 39.61 MPa. In our study, the flexural strength obtained for 87.5PP/0PS/12.5HDPE was 40.59 MPa. The little effect of HDPE causes a slight change
in the flexural value. In 87.5PP/12.5PS/0HDPE the strength recorded as 41.71 MPa. According to Asha K Krishnan et al. [13] 80PP/20PS reported a flexural strength of 37.8 MPa. In our case PP and PS are high flexural strength polymers, that may be the reason for the synergistic effect in the properties. In the case of 75PP/12.5PS/12.5HDPE, recorded value of 49.47 MPa is the highest, the value gained by the increase in the contribution of PS phase which crosses the behaviour of HDPE in that matrix. The lowest recorded value of 34.47 MPa is due to lower concentration of inherent high strength polymers.

4.1.6. Analysis of Flexural Modulus. Figure 7. represents the flexural modulus of various compositions of ternary blends were investigated. The maximum flexural modulus was recorded as 2048 MPa and the range was in between 1018 to 2048 MPa. The highest value obtained for 75PP/12.5PS/12.5HDPE and minimum for62.5PP/12.5PS/25HDPE. For binary blends the flexural modulus was recorded in between 1202 to 1505 MPa. It is clearly showing that ternary polymer blends exhibit an 86% increase in the value of modulus as compared to pure polypropylene. According A. Krishnan et al. [13] the addition of PS to the matrix makes the composite rigid and less flexible. HDPE inherently shows lower flexural modulus as compared to PP and PS. The addition of HDPE also decreases the crystallinity order of PP and this in turn shows a decrease in the values. But in some cases the effect HDPE is nullified by the addition of PS to the polymer matrix[1].

Figure 2. Tensile Strength of PP/PS/HDPE blend

Figure 3. Tensile Modulus of PP/PS/HDPE blend

Figure 4. Elongation at break of PP/PS/HDPE blend

Figure 5. Impact Strength of PP/PS/HDPE blend
Mechanical properties like tensile strength and modulus, elongation at break, impact strength, flexural strength and modulus are very significant for automotive applications. The PP rich blends were more preferred in roof lines, inner coverings of doors, door handle parts etc, in order to reduce the weight to some extent. While incorporating new materials, an intensive information about the maximum stress that the material withstand before it breaks, its elastic regions, ductility of materials, resistance of materials under dynamic load, highest stress experienced within the material at its moment of yield etc. should be known. In this study of ternary polymer blends, the maximum tensile strength and modulus was obtained for the composition of 75PP/18.75PS/6.25HDPE and elongation at break for 87.5PP/0PS/12.5HDPE. The impact strength that means the maximum resistance of materials when it undergoes dynamic load is for 75PP/6.25PS/18.75HDPE. 75PP/12.5PS/12.5HDPE shows the maximum flexural strength and modulus. The above outcomes clearly satisfies the level of applicability in light weight automotive parts to some extent.

5. Thermogravimetric analysis
To study the material’s thermal stability and also weight change that occurs as a sample is heated at constant rate can be analyzed by using thermogravimetric analysis. Weight reduction of a polymer because of thermal degradation is an irreversible cycle. This thermal degradation is generally identified with oxidation whereby the molecular bonds of a polymer are attacked by oxygen molecules [25]. Figure.8 shows the effect of blend composition on the thermal stability. Onset of thermal degradation is represented as the loss of 5 wt.% of the sample. In the analysis of ternary polymer blend mentioned in Table 3, that is 87.5PP/6.25PS/6.25HDPE and 75PP/18.75PS/18.75HDPE possess the onset of degradation as 246.67 °C and 268.38 °C respectively. Binary blend with the composition of 87.5PP/12.5HDPE reports onset degradation temperature of 287.06 °C. Reported value for onset degradation of pure PP and HDPE are 286.3 °C, 361.01 °C and 50PP/50HDPE has 300 °C. It is clear that addition of PP decreases the thermal stability of the blend. Thermal degradation causes chain scission and thereby reduces the chain length which in turn reduces the molecular weight. When HDPE is exposed to thermal environment, it results in chain branching and ends in cross linking. In PS diffusion of free radicals fasten the degradation [26].
6. Scanning Electron Microscopy

SEM images of the polymer samples are shown in Figure 9. SEM image shows that the polymer samples possess droplet matrix morphology near the interphase. SEM images show that there is a clear interaction between HDPE/PP phase and PS droplets are surrounded in continuous phase. Morphology of PP/PS blends exhibits a morphology in which spherical domain of PS phase is surrounded by the continuous PP phase[13]. In our analysis too it is observed that spherical domain of PS phase protrude through the continuous phases of PP and HDPE. N. Virgilio et al.[23]clarified the morphology of PS droplet situated at the HDPE/PP intephase where the PP/PS interfacial strain is lower than HDPE/PS. The viscoelastic force following up on the PS droplet during the mixing cycle are potentially sufficiently able to drive them from the HDPE/PP interphase into PP phase.

| PP (wt.%)| PS (wt.%)| HDPE (wt.%)| T_d (5%) °C | T_d (50%) °C | T_d (100%) °C |
|---------|---------|------------|-------------|-------------|--------------|
| 87.5 | 6.25 | 6.25 | 246.67 | 350.15 | 404.05 |
| 87.5 | 0 | 12.5 | 287.06 | 377.83 | 413.04 |
| 75 | 18.75 | 18.75 | 268.38 | 371.89 | 407.62 |

| PP (wt.%)| PS (wt.%)| HDPE (wt.%)| T_d (5%) °C | T_d (50%) °C | T_d (100%) °C |
|---------|---------|------------|-------------|-------------|--------------|
| 87.5 | 6.25 | 6.25 | 246.67 | 350.15 | 404.05 |
| 87.5 | 0 | 12.5 | 287.06 | 377.83 | 413.04 |
| 75 | 18.75 | 18.75 | 268.38 | 371.89 | 407.62 |

**Figure 8.** TGA curves of polymer blends

**Figure 9.** SEM images of ternary blend. a) 75PP/18.75PS/6.25HDPE with scale at 20µm (b) 75PP/6.25PS/18.75HDPE with scale at 10µm (c) 75PP/12.5PS/12.5HDPE with the scale at 5µm (d) 75PP/18.75PS/6.25HDPE with the scale at 50µm
7. Conclusions
The ternary polymer blend PP/PS/HDPE were prepared in different compositions. Their mechanical, thermal and morphological characteristics were studied. It was observed that tensile strength of ternary blend (PP/PS/HDPE) is found to be higher than other reported common polymer binary blends. Impact strength shows a decrease in behaviour as compared to PP/HDPE binary blends and there is an improvement of 6.9% in tensile modulus reported for 75PP/18.75PS/6.25HDPE. The flexural strength and modulus of 75PP/12.5PS/12.5HDPE has the maximum value of 49.47 MPa and 2048 MPa respectively. The morphological characteristics supports the enhanced mechanical properties of the ternary polymer blend. From our studies it is observed that ternary polymer blend exhibits tailored mechanical properties compared to binary blends.

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