

ENHANCEMENT IN MECHANICAL PROPERTIES BY SMA-COMPATIBILIZER FOR ABS AND PA6 BLEND

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ABSTRACT

Blend of ABS and PA6 material are investigated over a range of composition using a compatibilizer (KEMZER-SMA). Different composition of ABS and PA6 in varying ratio from 80:20, 60:40, 40:60, 20:80 with incorporating 2, 4, & 6wt % of compatibilizer and without compatibilizer.

In general, incorporation of the compatibilizer can lead to high mechanical properties using different wt% ratio. Unlike the commonly used compatibilizer in ABS/PA6 blend, SMA is compatible with ABS polymer matrix core phase, polybutadiene rather than shell phase of SAN. By addition of small % of SMA can dramatically increase the MFI of the blend. This shows improved dispersion of ABS particles in the matrix that reduce the viscosity of the melt blend. The compatibility and interaction of the component in the blends were characterized by FTIR and MFI. A Blend of both polymers improves toughness, mechanical strength and dimensional stability with the help of SMA compatibilizer. The issues of compatibility and toughening of ABS/PA blend are discussed and current challenges are highlighted.

Keyword - Miscibility, ABS/PA6 blend, Compatibilization, Blending sequence, Mechanical properties

1. INTRODUCTION

The polyamide group belongs to the attractive class of engineering thermoplastics due to its strength/stiffness allied to chemical and wear resistance. However, they tend to fail in a brittle manner in the presence of notch under impact loading, process instability, high mould shrinkage, easy to be attacked by oxidizing agent, dimensional instability due to its moisture absorbance and high-water affinity. Also, PA6 requires UV stabilization, on the other hand ABS has some superiority over PA6 in high water resistance, low mould shrinkage and cost competition although it lacks in mechanical and thermal properties in comparison to PA6.

Blending of ABS with PA6 is known commercially to offset the drawbacks of each polymer and broaden the performance of blends having a balance combination of specific properties. Blend of ABS and PA are of technological interest as they display inherent superior combination of properties from their parent polymer including good impact strength, modulus, heat, chemical and abrasion resistance.

PA6 is a crystalline polymer and ABS has SAN matrix which is an amorphous polymer hence simple blends of ABS and PA6 generally exhibit poor mechanical properties due to their unfavorable molecular interaction. My interest in ABS/PA6 blends has been stimulated by the numerous options that are available for reactively coupling these two immiscible polymers. A particularly appealing strategy is the addition of a polymer that is miscible with the SAN

phase and that can react with the amine end groups of the nylon phase. By introducing this third component which acts as an interfacial agent to reduce the interfacial tension and promote adhesion at the interfaces. This third component, generally known as compatibilizer may be a block or graft copolymer. Compatibilizers, also referred as coupling agents, are additives that when added to the blend of immiscible materials during extrusion modifies their interfacial properties and stabilizes the melt blend.

A compatibilizer is usually added into immiscible polymer blends to intensify the interfacial strength because it has similar chain structures to the two components of the polymer blend or it reacts with one component via the functional groups (sometimes forming hydrogen bonds). Furthermore, the addition of a compatibilizer also reduces the diameters of the dispersed minor polymer phase by reducing the interfacial tension within the blend. Examples of such compatibilizing additives that have been used previously include Styrene-acrylonitrile-maleic anhydride (S/AN/MA) terpolymers Styrene acrylonitrile glycidyl methacrylate (SAGMA), Glycidyl methacrylate-methyl methacrylate (GMA-MMA), Imidized acrylic, Styrene-maleic anhydride (SMA) copolymer, improve the mechanical properties of the polymer blends as they effectively “stitch” themselves across the polymer/polymer interfaces thus reducing the possibility of interfacial failure. The approach of reactive compatibilization retards dispersed phase coalescence via steric stabilization. Both these effects promote a stable, fine distribution of the dispersed phase within the matrix phase.

TABLE 1 COMPOSITION AND CODING OF ABS/PA6/SMA BLENDS

ABS (wt %)	PA6 (wt %)	COMPATIBILIZER SMA (WEIGHT %)			
		0%	2%	4%	6%
80	20	A0	A1	A2	A3
60	40	B0	B1	B2	B3
40	60	C0	C1	C2	C3
20	80	D0	D1	D2	D3

2. EXPERIMENTAL

General purpose molding grades of ABS Absolac 920 by INEOS Styrolution ABS Limited; India and PA6 Grade Gujlon E-35 melt viscosity by GSFC; India were used to prepare the different blends of study. This KEMZER-SMA copolymer by Chembond chemicals private Ltd. was used as compatibilizer at a different ratio 2, 4, 6 wt % in the blends. The compositions of the blends prepared are given in Table 1. Melt blending for the preparation of the blends was performed by a APEX RXT35 conical intermeshing co-rotating twin- screw extruder, L/D = 48 and 600 rpm, with ECON underwater pelletizer screw diameter 36mm using an extruder temperature profile: Feed zone: 215⁰C; Compression zone: 225⁰C; Metering zone: 235⁰C; Die ring: 250⁰C; Die: 240⁰C employing the following sequential steps:

ABS and PA6 were followed by vacuum drying overnight at 80⁰C ABS and PA6 with different composition of SMA compatibilizer blended in a tumbler mixer for approximately 30 minutes to enable good distribution and dispersion of the compositions. The dry blends were then vacuum dried at 80⁰C overnight prior to extrusion compounding. The extruded and pelletized blend formulations were vacuum dried at 80⁰C prior to Injection Moulding by 180 tonnes EPM-180 Injection Moulding Machine at 210-250⁰C. The Injection moulded specimens for testing of various properties in accordance to ASTM were conditioned for at least 40 hours at 23±2⁰C and 50% RH prior to testing Ambient and Sub ambient notched impact resistance of notched 2.53-inch, specimen was determined accordance to ASTM 256-93 by a CEAST Impact Tester, RESIL 25. Tensile properties were characterized by measuring stress at break, yield stress and corresponding elongation as a function of blend composition in accordance to ASTM D638 using Type 1 dumbbells by an Instron Universal Testing Machine Model-4466. Flexural properties were characterized by measuring maximum force, maximum stress, Elastic modulus and flexural strength

in accordance to ASTM D690 using flexural specimen size 3.2*12.7*125mm by an Instron autograph Universal Testing Machine Model-123804 MFI @ 235°C /5kg load. FTIR characterization of sample at various spectral range. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range.

3. RESULT AND DISCUSSION

REHEOLOGICAL PROPERTIES FTIR ANALYSIS

MFI of ABS is <25 gm/10 min at 220°C and 5 kg load according to the standard ASTM D 1238. When we check the results of different blends we use 235°C at 5 kg load for 15 sec.

When we add smaller quantity of compatibilizer to the blend we get higher MFI as shown in Fig 1 but on further increase in the weight percentage of compatibilizer we get reduction in the value of MFI. This suggests that minimum amount of compatibilizer is enough to increase the flowability of blend, MFI reducing by increasing SMA content. Also, we get an idea from this graph that higher the ABS content in blend gives higher flowability and when we made blend with 40% ABS and 60% PA6 there is decrease in MFI of blend reason is nylon is less easy to flow compare to ABS.

The effect of first injection moulding cycles on the flow properties of blend is also determined as MFI value for virgin ABS/PA6 blend is 7.7 g/10 min and with recycling this value showed an important increase to 31g/10min after 1 cycle. This shows recycled material also has their own value and use.

MFI of various blend composition shows that blend is compatible and easily be injection moulded and amount of compatibilizer using should be minimum is more better.

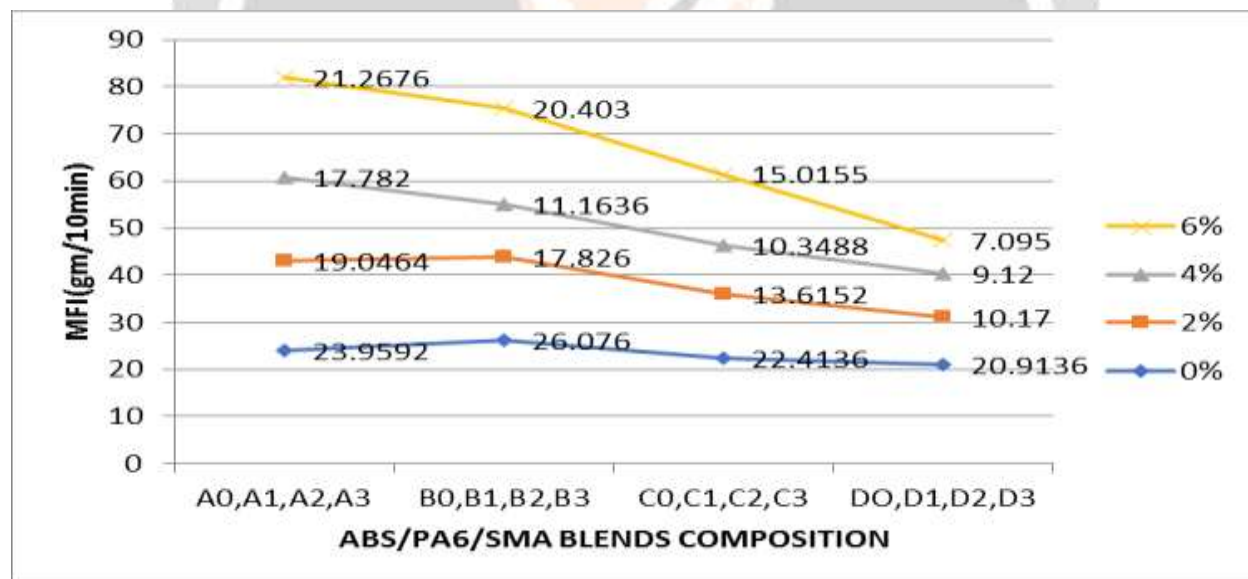


FIG -1 MFI test results in gm/10min.

FTIR ANALYSIS

In the current blend system, possible chemical reactions lead to the final morphology and therefore physical properties due to the interactions between maleic anhydride with amine end-group and epoxy group with amide and/or acid end-groups of PA6 for MAH respectively. The different FTIR spectrum shown in Figures 2,3 and 4. The imide-linkage formed as a result of interfacial grafting reaction can be identified from new peaks appeared at 1735 cm⁻¹ (imide carbonyl symmetric stretching), 1705 cm⁻¹ (imide carbonyl asymmetric stretching). The peaks appeared at 1731 cm⁻¹ (carboxylic C=O stretching) and 1710 cm⁻¹ (Amide I C=O stretching) indicate that the reaction (a) shown in seen Figure 4 also realized.

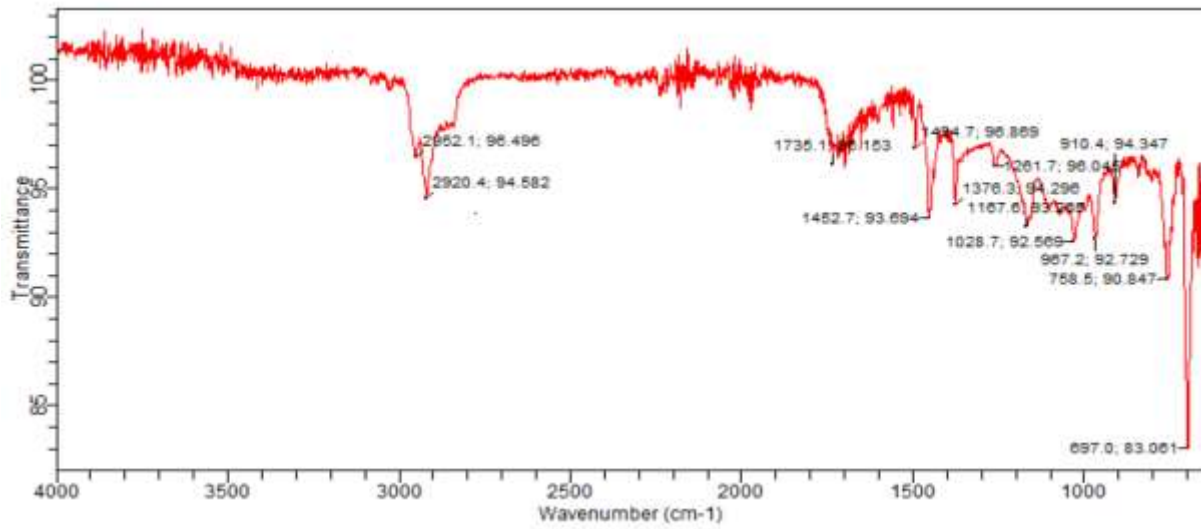


FIG 2 FTIR Spectrum For ABS

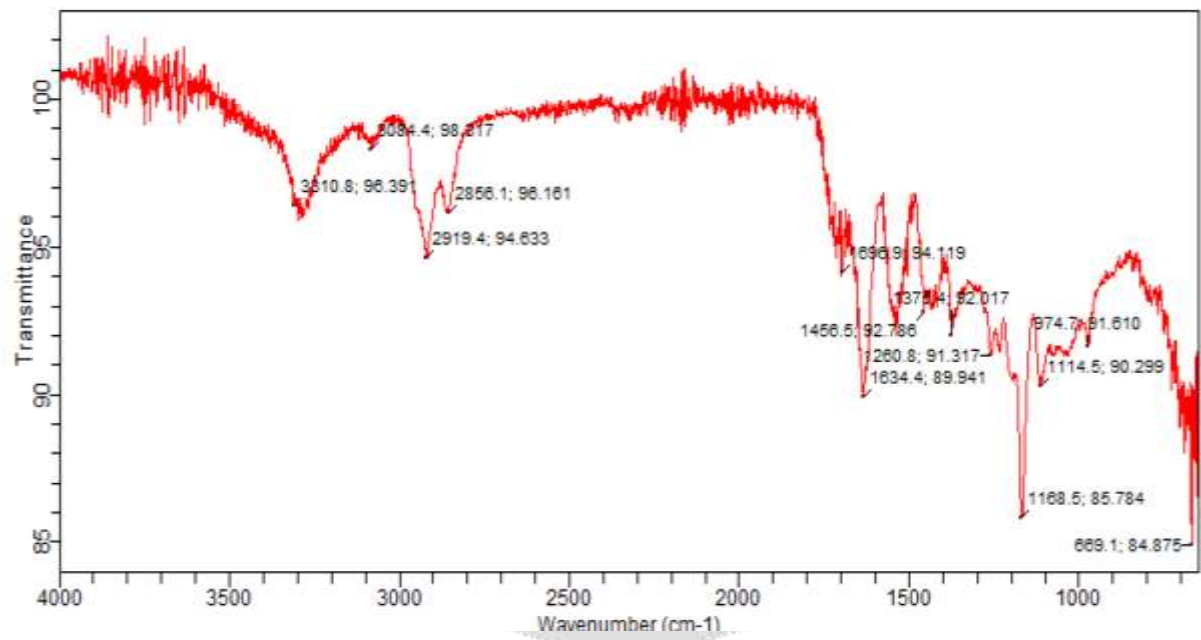


FIG 3 FTIR spectrum for PA6

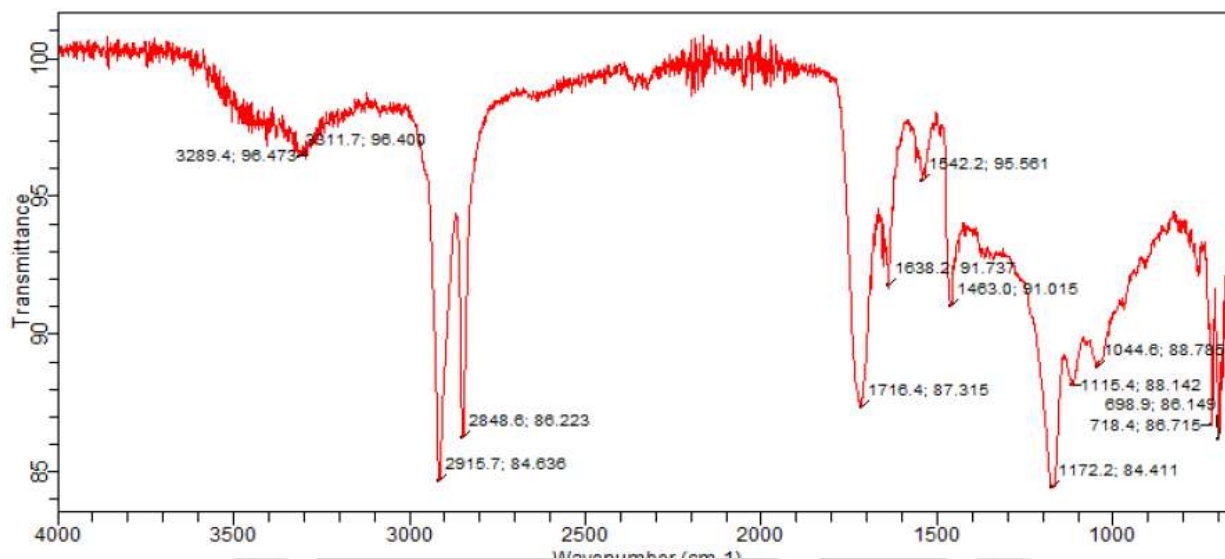


FIG 4 FTIR spectrum for compatibilized blend

TENSILE TEST RESULTS

Tensile properties were characterized by measuring stress at break, yield stress and corresponding elongation as a function of blend composition. The results are shown in Figures 5,6,7 & 8 where tensile stress at yield, tensile modulus and elongation at break are plotted as function of blend composition. The data points represent the mean value of several experimented samples tested.

TENSILE STRESS AT YIELD

From Figure 5 it is observed that the tensile yield stress of control ABS is 446.2kgf/cm². The yield stress values for the blends gradually increase over control ABS with incorporation of PA6 from 601.9kgf/cm² at PA6 20 wt% through to 615.9kgf/cm² at PA6 80 wt% respectively, representing an increase by a factor of 1.15. It is also observed that while the tensile yield stress increases gradually with incorporation of PA6, the values taper from PA6 40 wt% to 60 wt%. The observations indicate the stemming of adhesive forces arising from the graft reaction of the compatibilizer with PA6. Modification of PA6 with epoxide may be accompanied by partial cross-linking which ultimately increases the tensile yield stress of the blends [6]. Also, chain lengthening can be a dominating positive effect of this partial cross-linking.

Further decrease in crystallinity of PA6 resulted by blending might play a role as well. Qualitatively, increase of tensile yield stress indicates increasing positive synergism that results from good interphase adhesion of discrete PA6 particles at lower weight percentages through to the evolution of co-continuity of the ABS and PA6 phases at higher PA6 weight percentages as supported by the SEM analysis of the blends. The results are also indicative that optimal yield stress values are obtained once a co-continuous phase is evolved as seen for the blends incorporating PA6 60 wt% and 80 wt%.

Every composition of ABS/PA6 blends gives best result like A80:20 gives tensile stress at yield 601.9kgf/cm², B60:40 gives 583.1 kgf/cm², C40:60 gives 402.9kgf/cm², D20:80 gives 615.9kgf/cm² with further addition of shows tremendous increase in tensile stress at yield in Batch C3 with highest 6%compatibilizer weight % ratio 671.4 kgf/cm². Also, Batch D2 gives higher result compare to without compatibilizer blend composition.

When we add 2 wt % of compatibilizer in 80:20 ratio we get lower tensile stress at yield compare to without compatibilizer batch. Those blends which are already giving higher test results does not require to incorporate

compatibilizer in higher wt% because it reducing the best properties of the blend that blend already possess without compatibilizer. On the other hand, compatibilizer did wonder for that blend ratio which are giving less tensile stress at yield without any compatibilizer that is BatchC1, BatchC2, BatchC3. It is also observed that while the tensile yield stress increases gradually with incorporation of PA6, the values taper from PA6 40wt% to 60wt%. The observations indicate the stemming of adhesive forces arising from the graft reaction of the compatibilizer with PA6. Modification of PA6 with epoxide may be accompanied by partial cross-linking which ultimately increases the tensile yield stress of the blends [4].

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ELONGATION AT BREAK

Fig7 shows that the elongation at break of control ABS is 14%. Incorporation of PA6 results in significant change in values of elongation even at PA6 20 wt%. The first significant change in elongation at break, twice that of control ABS at 40%, occurs for the blend A incorporating PA6 80 wt%. Increasing the PA6 ratio to 80wt% blend D0 without compatibilizer results in a sharp increase in elongation at break to 89.2% nearly 8 times that of control ABS. For blend incorporating PA6 40 and 60 wt%, the elongation at break begins to taper to decrease without compatibilizer but with compatibilizer batch C3 and batch D2 shows sharp increase in elongation at break 69.5% and 52.5%.

The results strongly suggest that co-continuous morphology achieved via compatibilization is responsible for the significant enhancement in the elongation at break values [6]. In other words, the compatibilizer constitutes bridges between the two phases and makes the links stronger. T1 and T4 composition of blend gives higher elongation at break as well as with compatibilizer batch 3C46, batch 4B28 gives higher elongation at break compare to other various composition of blends with compatibilizer.

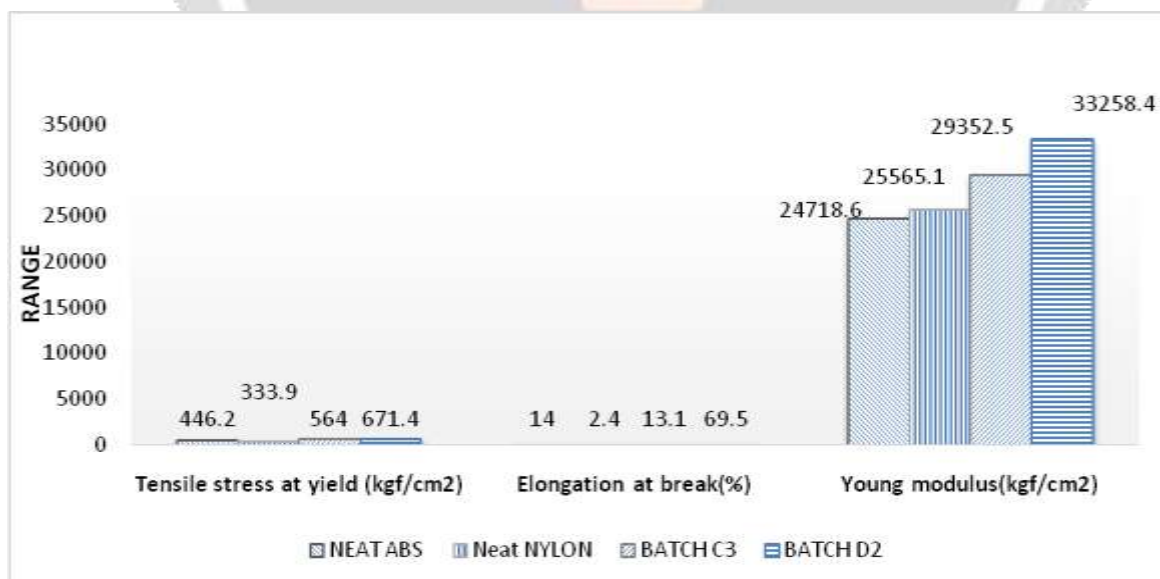


FIG 5 Tensile Test Data Of Best Composition

TENSILE MODULUS

With increase in percentage of compatibilizer there is tremendous increase in tensile modulus of every batch exclude batch B2 in which we used ABS/PA6 60:40 ratio 2% compatibilizer used blend gives higher tensile modulus than other two batches of batch B2. Without compatibilizer reference blends gives lesser tensile modulus compare to with compatibilizer. Tensile strength of various batches found to increase with the increase of PA6%, ABS which is having the rubbery main chain of polybutadiene so it is having lower tensile strength but with increase of percent of PA6 the tensile strength increases.

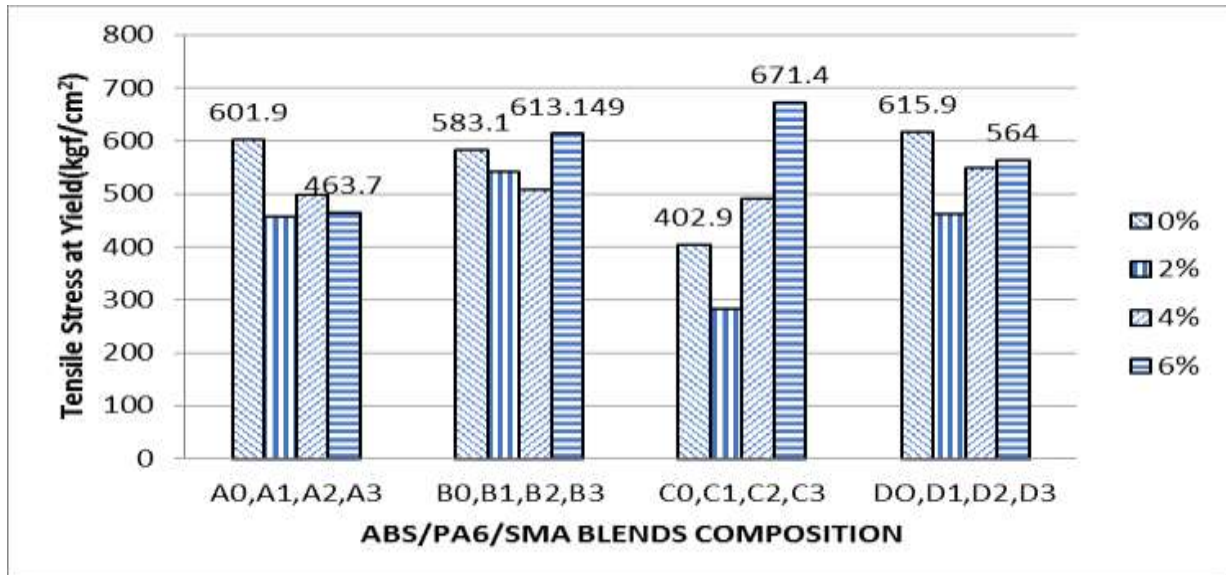


FIG 6 Tensile stress of yield result of ABS/PA6/SMA with T1(80:20),T2(60:40),T3(40:60),T4(20:80)

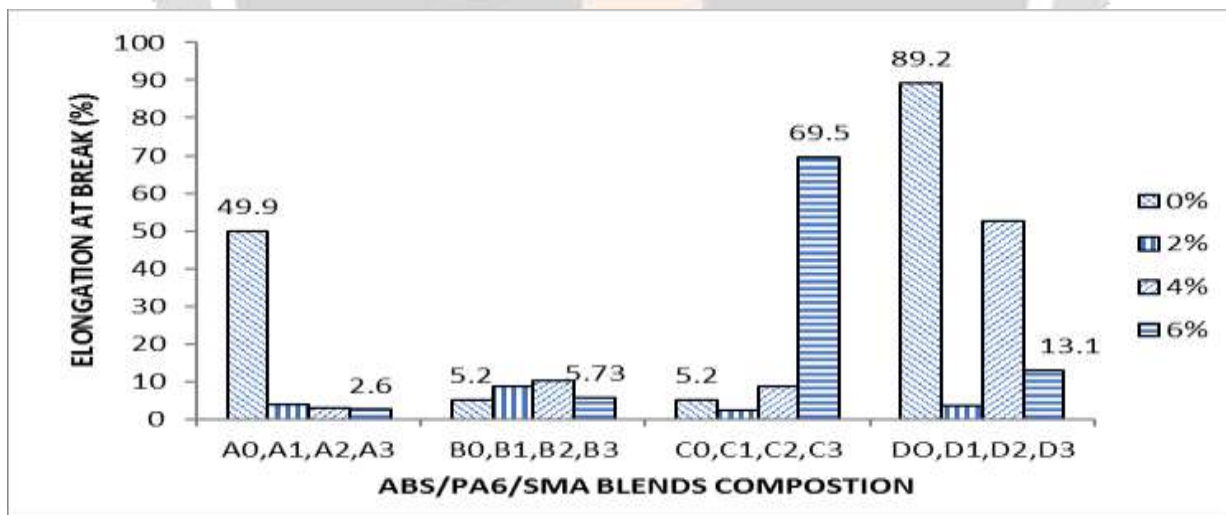


FIG 7 Elongation at Break result of ABS/PA6/SMA with T1(80:20),T2(60:40),T3(40:60),T4(20:80)

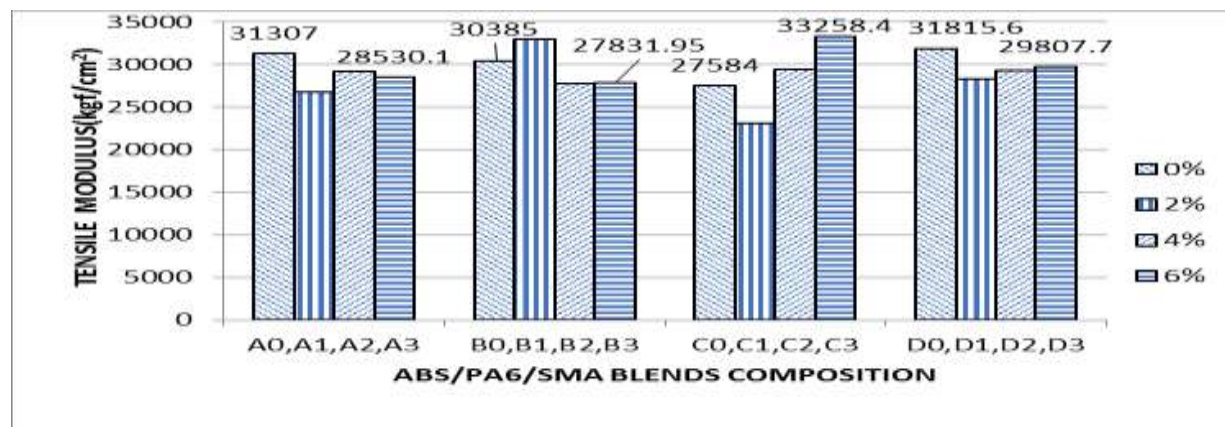


FIG 8 Tensile modulus result of ABS/PA6/SMA with T1(80:20),T2(60:40),T3(40:60),T4(20:80)

FLEXURAL PROPERTIES

Flexural property expresses the stiffness and bending strength of the material in terms of its ability to withstand under load. Data for flexural strength and moduli of control ABS and the blends A0 to D0 are given in Figures 9 and 10 respectively. The flexural strength of control ABS is 43.45 N/mm^2 . Incorporation of PA6 20 wt% shows a very minor increase in the value of flexural strength to 63.6609 N/mm^2 and is considered comparable to control ABS. On incorporation of PA6 40 wt% in the blends, a gradual increase in flexural strength to 115.90 N/mm^2 for blend batch B3 incorporating PA6 80 wt% is decrease in result is obtained. The improvement in rigidity over control ABS is slight by 1.12 times over control ABS. The regular minor increases in values of flexural strength show a positive deviation from the additivity. The positive deviation is mainly caused by rich interfacial adhesion between the blend components. This enhancement in the interfacial adhesion is due to better compatibilization effect of the added SMA copolymers [4], which deeply protrudes into the two interfaces and plays major role for this synergistic effect. Thus, strong interaction between ABS and PA6 phases leads to the improved flexural strength though minor. Incorporation of increasing PA6 wt% 20 and 40 in the blends shows a gradual minor increase in moduli from 2619.14 N/mm^2 for blend batch B3 incorporating PA6 40 wt% through to 2933.04 N/mm^2 for the blend and 80 wt % of PA6 which is an insignificant result shows decrease in modulus with compatibilizer. The results again show that the evolving blends morphologies attributed to the increase in domain dispersion due to greater extent of intermolecular interaction between the blend components effected by the synergistic effect of the compatibilizer does not influence the flexural characteristics of the blends

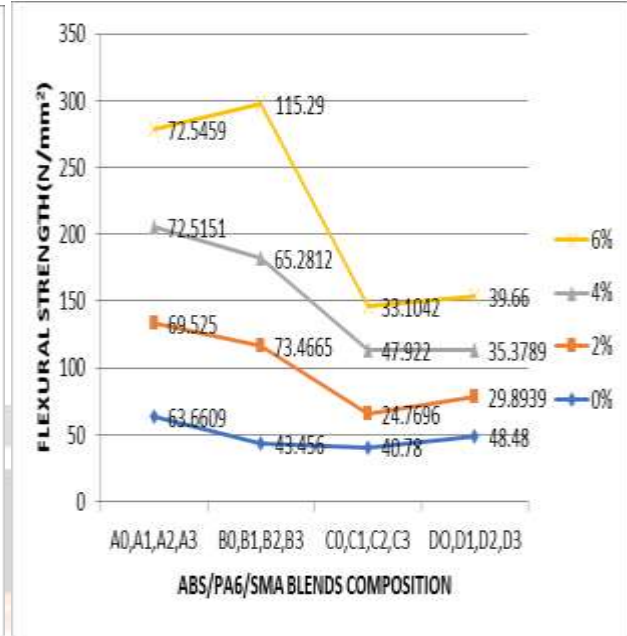
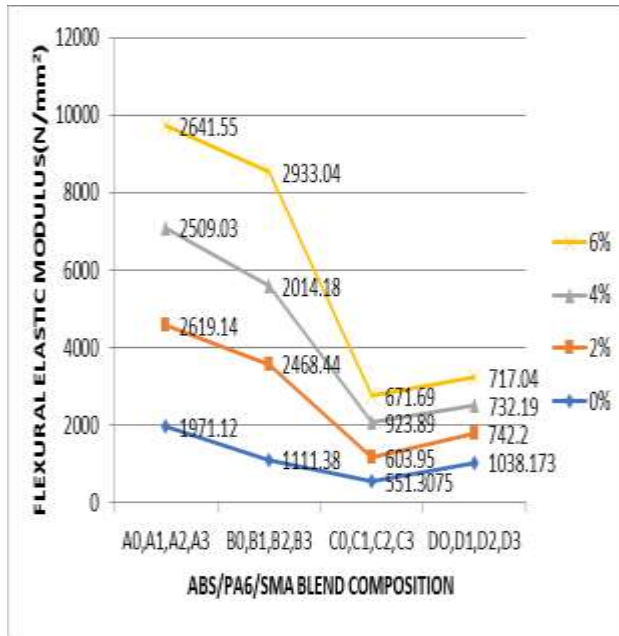


Fig.9 Flexural elastic modulus results of ABS/PA6/SMA with A(80:20),B(60:40),C(40:60),D(20:80)

Fig 10 Flexural strength results of ABS/PA6/SMA with A(80:20),B(60:40),C(40:60),D(20:80)

IZOD and CHARPY NOTCHD IMPACT STRENGTH

The notched 2.54-inch Izod impact strength of different batch determined at room temperature. It is observed that at room temperature the 2.54-inch notches Izod impact strength of virgin ABS is 93.28J/m. Incremental incorporation of PA6 20 wt% in the blends results in gradual increase in impact strength to 119.2 J/m that is without compatibilizer.

From the above data inference is drawn that toughened ABS/PA6 blends can be achieved over a broad range of compositions thus establishing the efficiency of the compatibilizer incorporated. Any possible reduction in impact strength caused by crosslinking reactions involving the SAG epoxide groups, induced by acidic impurities in the emulsion –made ABS, is essentially eliminated when PA6 and SMA copolymers are blended together prior to adding ABS in a second pass extrusion.

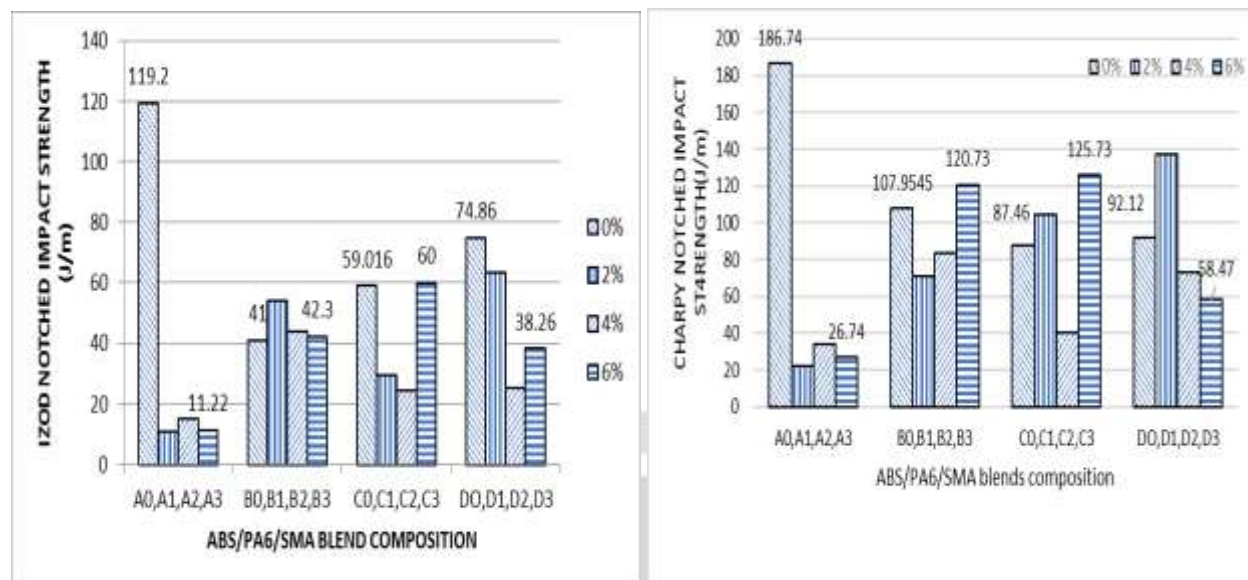


FIG 11 Izod notched impact strength result of ABS/PA6/SMA with A(80:20),B(60:40),C(40:60),D(20:80)

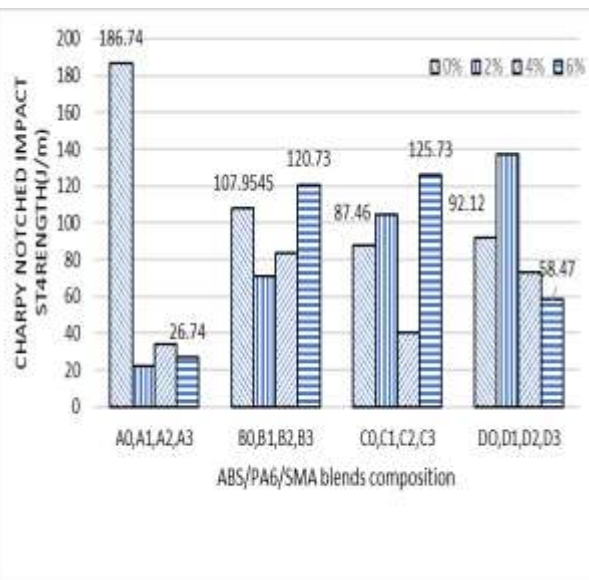


FIG 12 Charpy notched impact strength result of ABS/PA6/SMA with A(80:20),B(60:40),C(40:60),D(20:80)

4. CONCLUSIONS

Evolution of mechanical properties of different compositions of blends of ABS and PA6 in varying ratios from PA6 20 wt% to 80 wt% incorporating SMA copolymer as compatibilizer have been observed. To overcome incompatibility of the blend component, blends were prepared by extrusion compounding procedures. Of the mechanical properties studied the most significant improvements are observed for the room temperature impact strength which increases by over nearly two-fold (near super tough) at PA6 60,80 wt% over control ABS and break elongation which increases by nearly 10 times over control ABS. Significant improvements in these properties are affected in the region of phase inversion, i.e., PA6 80 wt% onto formation of a co-continuous phase. The obtained results show that optimal properties are obtained when the blend components exist as co-continuous phase. FTIR Spectrum study shows that appearing of new peak and disappearing of some peaks shows that the blend is showing compatibility having sharp peaks.

Other mechanical properties including tensile yield strength and modulus; and flexural strength and modulus are influenced by the changing PA6 wt% even though they display positive deviation from additivity and are improved over those of control ABS. Onset degradation temperatures of the blends lie between that of ABS and PA6 thus not influenced by the presence of compatibilizer. MFI reduce with the increase in SMA content (compatibilizer) Batch A0,A1,A2,A3 shows better MFI than any other batches. The tensile strength, tensile modulus and elongation at break increases with increase in compatibilizer which shows good interfacial bonding but on further increase of compatibilizer will deteriorate the properties. ABS particles in the compatibilized blend did not deboned from the matrix after the tensile test, which confirmed the enhanced interfacial adhesion. Best batches giving highest tensile modulus and tensile strength, high elongation at break with average MFI having high Charpy notched impact strength as well as flexural strength good enough is batch B1, C3, D2. flexural properties come out at its best in batch A and B all and flowability is also good of this batches.

5. REFERENCES

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