Polyamide 66/ ricinoleic acid- ethylene ethyl acrylate (PA 66/ EEA-R.Acid) MWNT blend Nanocomposites

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Abstract : Polyamide 6,6/ Ricinoleic acid (R.Acid)- Ethylene ethyl acrylates (PA 6,6/EEA-R.Acid) blends and their nanocomposites were prepared by melt compounding using a twin screw extruder and also were prepared by melt compounding PA 6,6/EEA-Ricinoleic acid with Multi wall carbon nanotubes (MWNT), To investigate tensile test and impact test of Mechanical Properties, The analysis PA 6, 6 is increases with incorporation of the EEA-Ricinoleic acid 15 Wt (%) present in the PA 6,6 matrix and the various parts of the MWNTs.
Keywords : EEA-R.Acid; PA66, Mechanical Properties.

1. Introduction

The use of polymer blends as composites matrices to produce conductive materials at low conductive filler content has been studied for more than two decades. In 1987, Geuskens et al. [1] studied the electrical conductivity of polymer blends containing carbon blacks. They showed that the conductivity of rubber/polyethylene blends filled with carbon black is much higher than the conductivity of the polymer filled with carbon black at the same loading level. Such a result was explained by the selective localization of the carbon black particles in the multiphase polymeric system. This concept is known as double percolation. The carbon black-filled blend phase percolates (first percolation) and the carbon black forms a network within the percolated blend phase (second percolation). More recent studies [2,3] have also exploited the concept of double percolation for different blend systems and different conductive fillers. Among them, carbon nanotubes have attracted tremendous attention since their discovery in 1991 by Sumio Iijima [4]. They present unique atomic structure and properties such as very high aspect ratio (1000–10,000), high strength to weight ratio, high mechanical properties, and high thermal and electrical conductivities [5–11]. The concept of double percolation using carbon nanotubes has been studied to improve the electrical conductivity of polymer blends. Potschke et al. [12,13] have worked with composites of polycarbonate (PC) filled with multiwall carbon nanotubes

(MWNTs). These composites were then mixed with polyethylene (PE) in order to get co-continuous structures exhibiting double percolation. The MWNTs were found to stay in the PC phase. The authors have also studied blends of PC containing MWNTs with PP containing nanoclay [14]. The MWNTs stay well dispersed in the PC while the nanoclay migrates from PP towards the interface. Wu and Shaw [15,16] have studied composites of poly(ethylene terephtalate) (PET) filled with MWNTs. These formulations were then mixed with poly(vinylidene fluoride) (PVDF), polypropylene (PP), high density polyethylene (HDPE) or polyamide 6,6 (PA6,6). In the case of PP and HDPE, wetting coefficient evaluation predicts that the MWNTs should locate at the interface but the fraction of MWNTs which migrates from PET is only 7%. In the case of PVDF and PA6,6, the wetting coefficients predict that the MWNTs should stay in PET and the experimental results confirm this prediction. Li and Shimizu [17] have studied conductive co-continuous blends of PVDF/polyamide 6 (PA6) filled with carbon nanotubes. The MWNTs were exclusively located in PA6 phase. Meincke et al. [18] have studied the properties of MWNTs filled PA6 and its blends with acrylonitrile/butadiene/styrene (ABS). The MWNTs were found to stay in the PA6 phase also creating a triple-continuous structure. Zou et al. [19] have studied the morphology of poly (phenylene sulfide)/polyamide 6,6 blends with various amounts of acid treated MWNTs. It was observed that the MWNTs are preferentially located in the PA6,6 phase. In all these studies, the filler was found to concentrate in the more polar phase. As the filler was first added in the more favourable phase, it was not possible to determine if high aspect ratio nanoparticles are able to transport from one phase to the other one or to the interface. More recently, Potschke et al. [20] have presented migration of MWNTs from HDPE concentrates to PC and PA. The MWNTs were well dispersed in the PC and PA matrix and electrical percolation was achieved at lower MWNTs contents as compared to

2. Experimental work

2.1 Materials

The Polyamide 66 (PA 66) used in this study was obtained from DuPont India Pvt Ltd., under the trade name of Zytel 101L^{TM} and PA 66 has a melt flow index value of 11 g/10 min (275°C@ 0.325 kg) and melt temperature range from 260°C to 270°C. EEA-Ricinoleic acid with density 0.87g/cm^3 and melt flow index value of 23g/10 min (280^{0}C/2.16 kg) was commercially obtained from Dupont India Ltd., under the trade name Elvaloy 2715. Sun Nano Pvt Ltd, China, provided the multi wall carbon nanotube under the trade name of SN 300, with tube diameter 10-30nm with purity of 90%.

2.2 Preparation of blends

Prior to blending, PA 66 and MWNTs were dried at 80^{0}C in an oven for 12 hrs. PA 66 composites were prepared using twin-screw extruder Bersforft, FRG (L/D= 30, L=1m) in the temperature range of 250-285^{0}C and a screw speed of 150 rpm. To study the effect of blending on PA 66, MWNT, and EEA-R.Acid upon exfoliation of the MWNT and dispersion of the EEA-R.Acid particles, three blending sequences were adopted.

1. (PA 66 + MWNT) means PA 66 and MWNT with different percentages (ie. 0.15%, 0.3%, 0.45% and 0.6%), blended simultaneously.
2. (PA 66 + EEA-R.Acid) means PA 66 and different percentages of EEA-R.Acid (ie 5%, 10%, 15% and 20%) blended and optimized to get the best ratio.
3. (PA 66 + EEA-R.Acid + MWNT) different percentages of (ie. 0.15%, 0.3%, 0.45% and 0.6%) MWNT blended with the optimized PA 66 and EEA-R.Acid.

The PA 66/MWNT binary nanocomposites, PA 66 + EEA-R.Acid binary blend and PA 66/ EEA-R.Acid / MWNT ternary nanocomposites were prepared under the same compounding conditions. The extrudates were pelletized and dried. Finally these granules were injection molded as per ASTM standard using SP130 injection molding machine (Windsor, India) having a clamping force of 100T, fitted with dehumidifier in the temperature range 250 - 285°C.

2.3 Mechanical Properties

The tensile tests were performed according to ASTM D 638 using SHIMADZU AUTOGRAPH (model AG 50kN ISD MS) at room temperature. The gauge length was set at 50 mm and the crosshead speed was 50 mm/min. For the study of impact property the specimens were prepared and conditioned as per ASTM D 256

standard with testing conditions of 23±1°C and 55 ±1°C RH. The Izod impact strength was determined with ATS FAAR impact tester with 2.54 mm notch length, 45° notch angle as per ASTM D 256 A. The test results were calculated by taking the average of eight readings for each composition.

3 Results and discussion

3.1 Mechanical Properties

3.1.1 Effect of CNT loading on the tensile properties of PA 66

        The tensile properties of virgin PA 66 and nanocomposites as a function of CNT loading are shown in Fig.1, Fig.2. It is observed that with an increase in the CNT loading from 0.15 to 0.3%, there is a progressive increase in the tensile strength and modulus of the nanocomposites. An increase of 30% in tensile strength and 79% in modulus of PA 66 were obtained with the incorporation of 0.3 wt% of MWNT. The primary cause of for such improvement may be attributed to the presence of immobilized or partially mobilized polymer phases as a consequence of interaction of polymer chains with CNT. With a further increase in MWNT loading from 0.45 to 0.6 wt%, a marginal decrease in the tensile strength and modulus of the nanocomposites were observed. This behaviour may be attributed to the MWNT - MWNT interaction which results in agglomerates and induced local stress concentration in the nanocomposites.
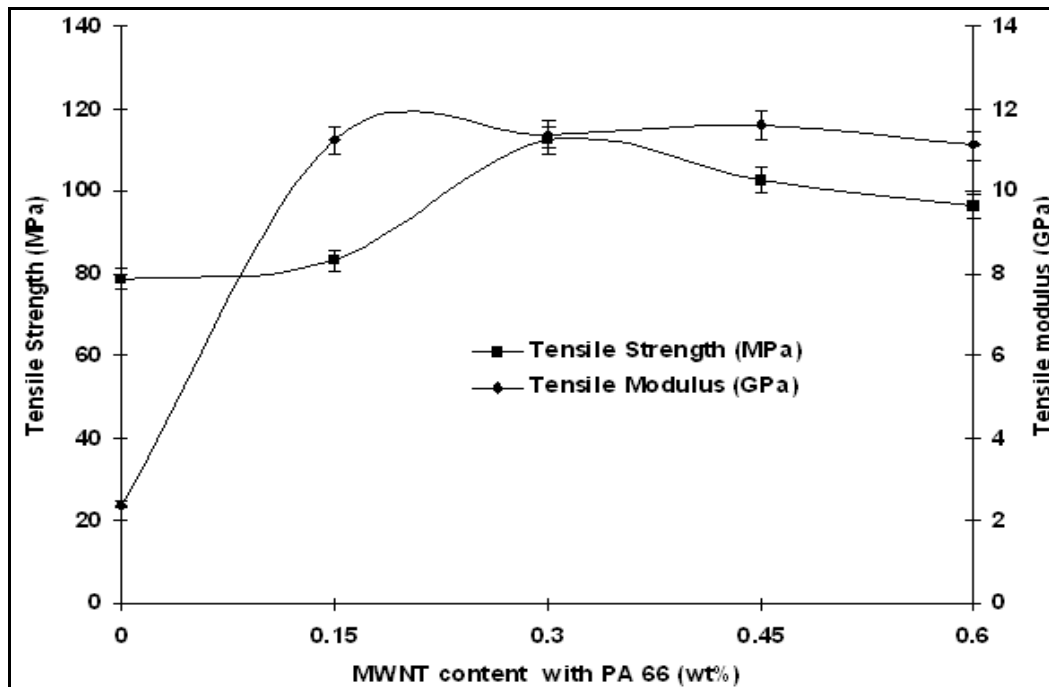

Fig – 1 Tensile strength and tensile modulus of PA 66 with different percentage of MWNT (ie 0, 0.15, 0.3, 0.45 and 0.6)
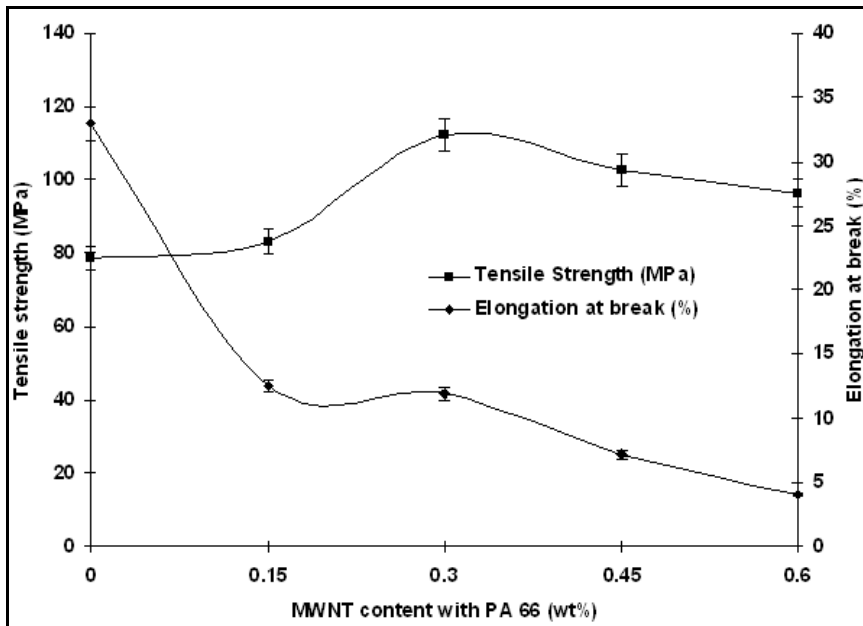
Fig – 2 Tensile strength and Elongation at break of PA 66 with different percentage of MWNT (ie 0, 0.15, 0.3, 0.45 and 0.6)

The variation of flexural strength and modulus with CNT loading are summarized in Fig. 3. The behavior similar to that of the tensile strength and modulus was observed. The flexural modulus of the nanocomposites increased progressively with the increase in the MWNT content (loading from 0.15 to 0.3wt%) as compared with the virgin PA 66 matrix. A considerable increase in the modulus of the virgin matrix was observed with the incorporation of MWNT. The flexural strength of the nanocomposites show an optimum value at 0.3 wt% MWNT loading, beyond which there is a decline in the strength. This behaviour is probably due to the presence of agglomerated CNT particles, which possibly act as stress concentration sites and cause a decrease in the flexural strength of the nanocomposites.
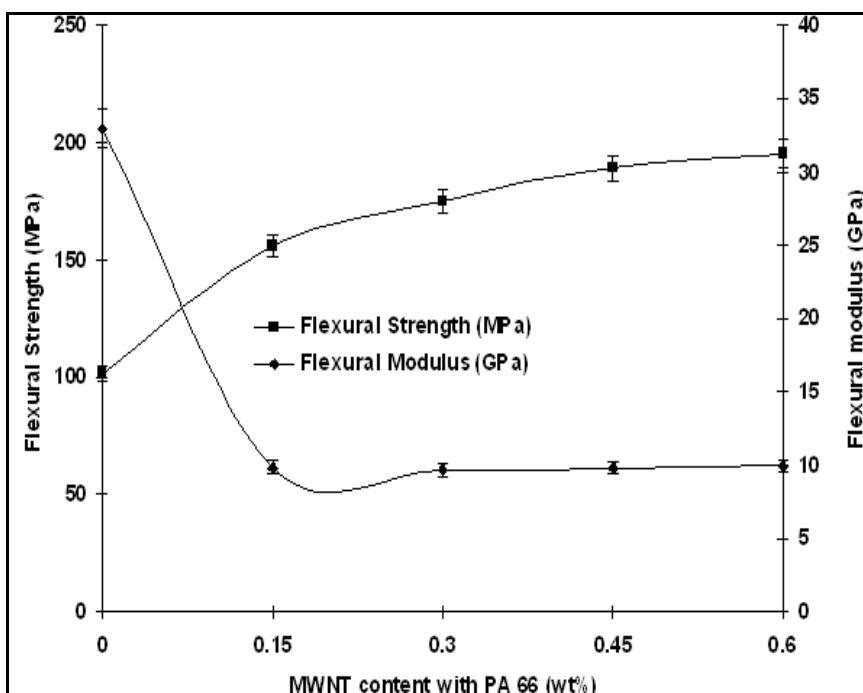

Fig –3. Flexural strength and Flexural modulus of PA 66 with different percentage of MWNT (ie 0, 0.15, 0.3, 0.45 and 0.6)
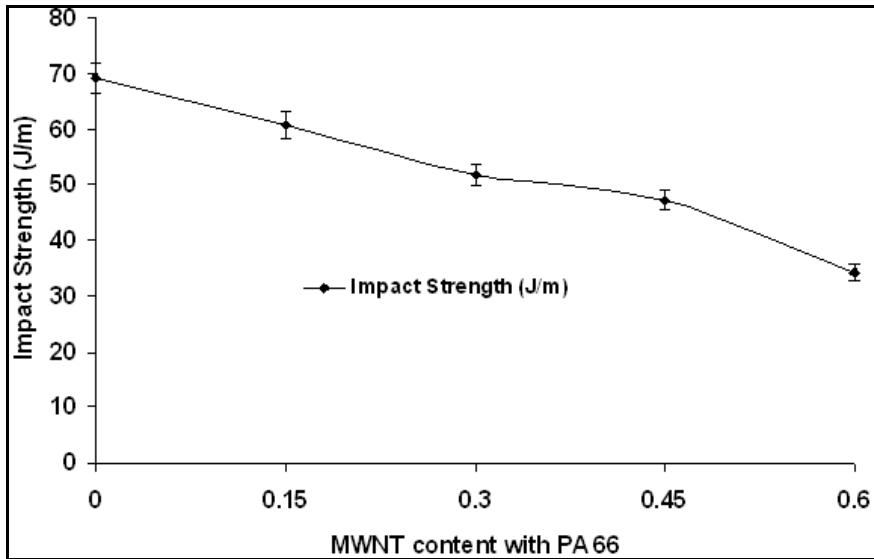
Fig –4. Impact strength of PA 66 with different percentage of MWNT (ie 0, 0.15, 0.3, 0.45 and 0.6)

The impact strength of the virgin PA 66 and the nanocomposites values are enumerated in Fig.4. It is evident that the impact strength of the virgin matrix decreases with the incorporation of MWNT. The decline in the impact strength with the addition of MWNT loading is probably due brittle nature of PA 66 with MWNT.

3.1.2 Effect of elastomer loading on mechanical properties of Polyamide 66

The tensile properties of the EEA–*g*–MA toughened PA 66 blends are reported in Fig.5,Fig.6. It is evident from the test results that with an increase in EEA–*g*–MA content, there is a decrease in tensile strength and modulus as compared with virgin PA 66. The decrease in tensile strength and tensile modulus of virgin PA 66, with the addition of 15 wt% EEA-*R.Acid* were found to be 33% and 4% respectively, which is primarily due to the presence of soft elastomeric phase which reduces the crystallinity and stress level of the virgin PA 66 to produce shear yielding.
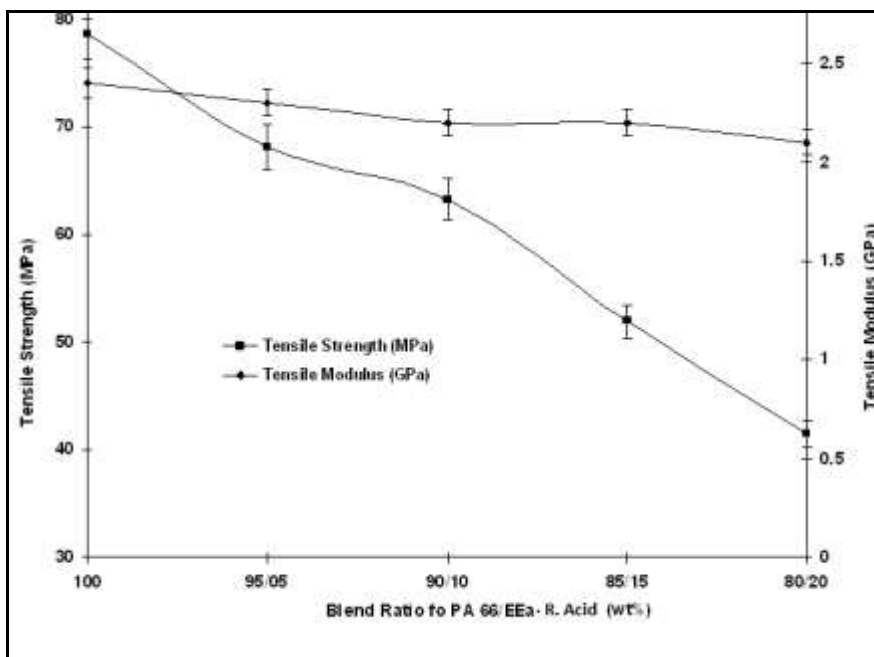

Fig – 5 Tensile strength and tensile modulus of PA 66 with different percentage of elastomer (ie EEA-R.Acid)
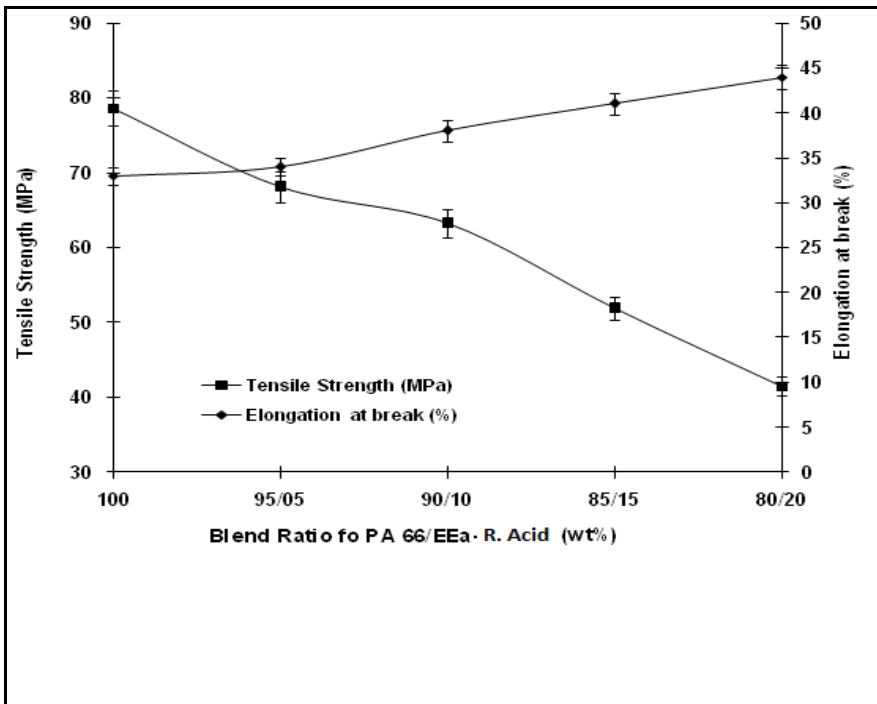
Fig –6. Tensile strength and elongation at break of PA 66 with different percentage of elastomer(ie EEA-R.Acid)

The variation of flexural properties of PA 66/EEA–*g*–MA blends as a function of EEA–*g*–MA content is also enumerated in Fig.7. As implied from the test results, there is a sequential decrease in flexural strength and flexural modulus with the incorporation of EEA–*g*–MA into PA 66 matrix. This behavior is probably due to the formation of the rubber phase at the interface region. The presence of elastomer in the blend reduces the stiffness of the virgin polymer due to an associated reduction in the effective cross sectional area of the sample.
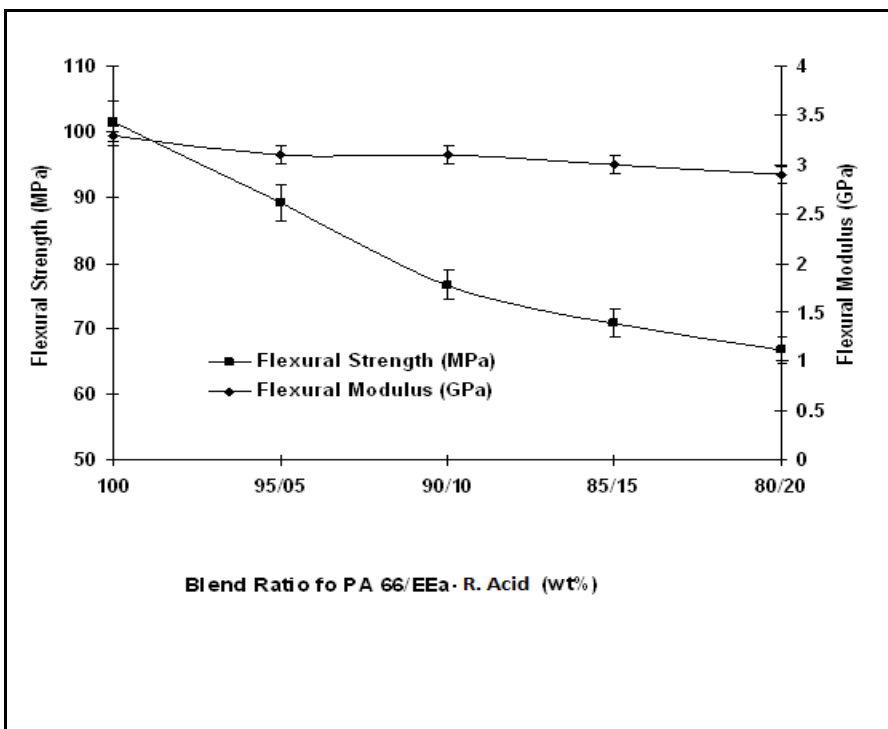

Fig – 7. Flexural strength and Flexural modulus of PA 66 with different percentage ofelastomer(ie EEA-R.Acid)

The effect of maleic anhydride grafted EEA content on notched izod impact strength of various PA 66/ EEA–*g*–MA blends is displayed in Fig.8. and the values are indicated from the experimental values it is evident that incorporation of EEA-*R.Acid* results in a considerable increase in the izod impact strength of PA 66 matrix. Experimental findings reveal brittle characteristics of the virgin matrix with impact strength of about 69.3J/m, and the incorporation of elastomeric phase leads to an increase in the impact strength of the polymer matrix. The blend prepared by incorporating 15 wt% EEA–*g*–MA shows optimum performance with an increase of about 102% in impact strength as compared with virgin PA 66. This phenomenal transition from brittle to ductile behaviour is probably due to the presence of smaller elastomeric domains, which are effectively dispersed within the PA 66 matrix, thereby leading to dissipation of more impact energy. The blend prepared with 85:15 ratio of PA 66/EEA–*g*–MA exhibit optimum impact strength, and has been taken for further investigation.
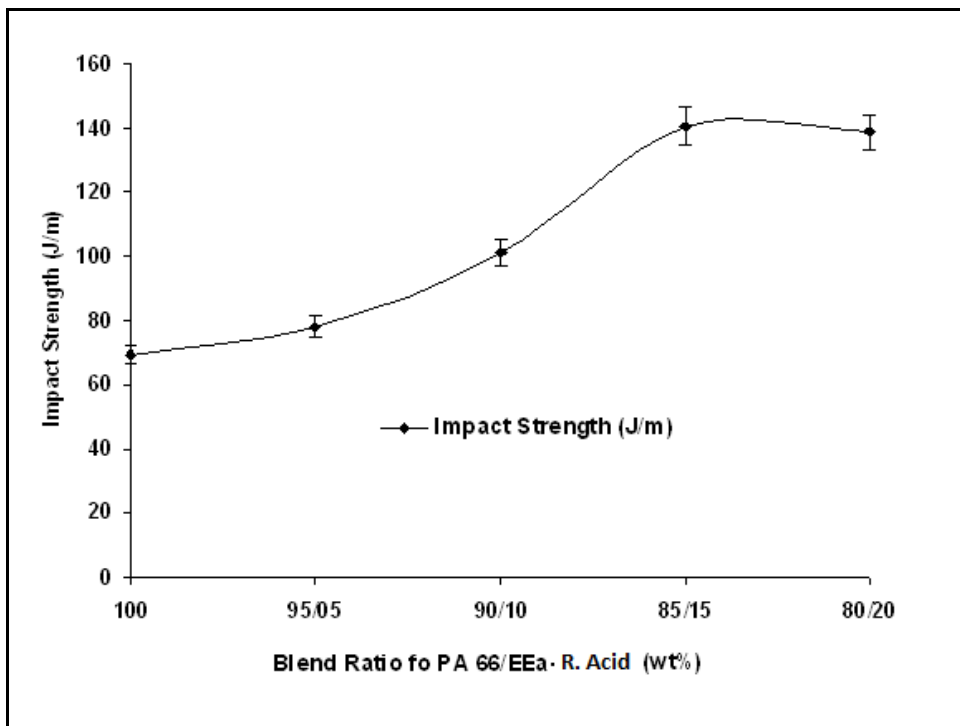

Fig – 8. Impact strength of PA 66 with different percentage of elastomer(ie EE-R.Acid)

3.1.3 Effect of MWNT loading on the mechanical properties of PA 66/EEA-*R.Acid* blends

The mechanical properties of PA 66/EEA–*g*–MA blend with various wt % of MWNT are depicted in Fig.9. It is evident that the tensile property of the blend increases with addition of 0.3wt % of MWNT. The tensile strength of blend matrix increases from 51MPa to 100 MPa in PA 66/EEA-*R.Acid*/MWNT, which indicates the stiffening effect of MWNT. A similar increase in tensile modulus to the tune of 40% by the addition of 0.3wt% MWNT. The primary reason for such an improvement is probably due to the presence of immobilized or partially mobilized polymer phases as a consequence of interaction of polymer chains with the PA 66 matrix.
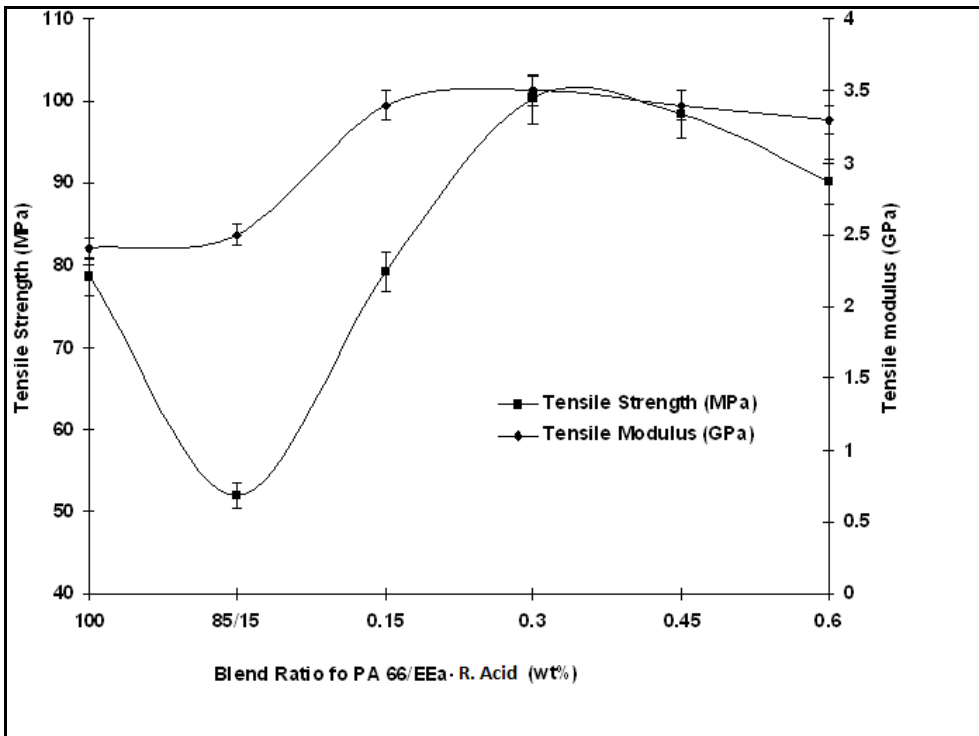
Fig –9 Tensile strength and tensile modulus of PA 66/EEA-R.Acid/MWNT

Nevertheless, with further increase in MWNT loading from 0.45 to 0.6wt %, there is a marginal decrease in the tensile strength and modulus of the blend matrix. This behaviour is probably due to carbon-carbon interactions, which result in agglomerates and induces stress concentration in the nanocomposites that leads to reduction in contact surface between the carbon nanotube and the polymer matrix.
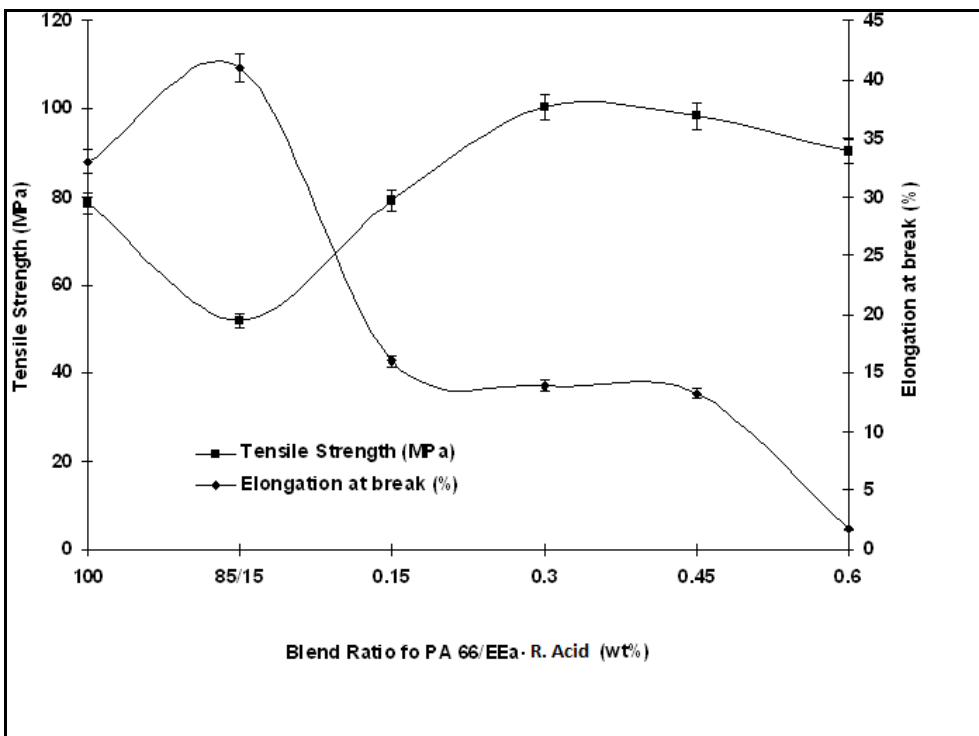

Fig –10 Tensile strength and elongation at break of PA 66/EEA-R.Acid/MWNT

The flexural properties of the virgin matrix of PA 66/EEA-*R.Acid* blend and its nanocomposites are also shown in Fig.10. The flexural strength and modulus of the blend matrix increases progressively with an increase in the MWNT content from 0.15 to 0.3 wt %. Addition of MWNT content to the tune of 0.15 to 0.3 wt %, results in a marginal enhancement in the flexural properties of the blend. PA 66/EEA-R.Acid/MWNT blend nanocomposites exhibit optimum improvement in flexural strength to the tune of 70% compared to nylon 66/EPDM-R.Acid blends which reveals improved dispersion of the delaminated MWNTs within the blend matrix thus confirming the fact that MWNT acts as a compatibilizer at the interfacial region between the blend matrix and the MWNTs.
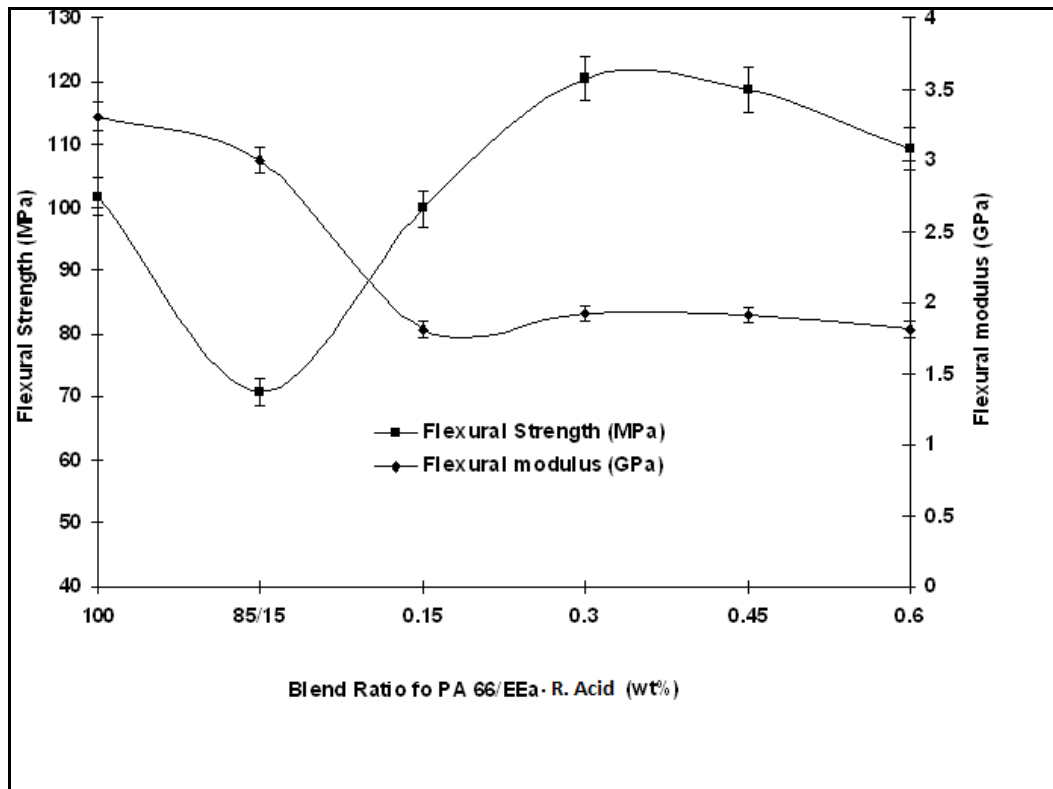

Fig –11 Flexural strength and flexural modulus of PA 66/EEA-R.Acid/MWNT
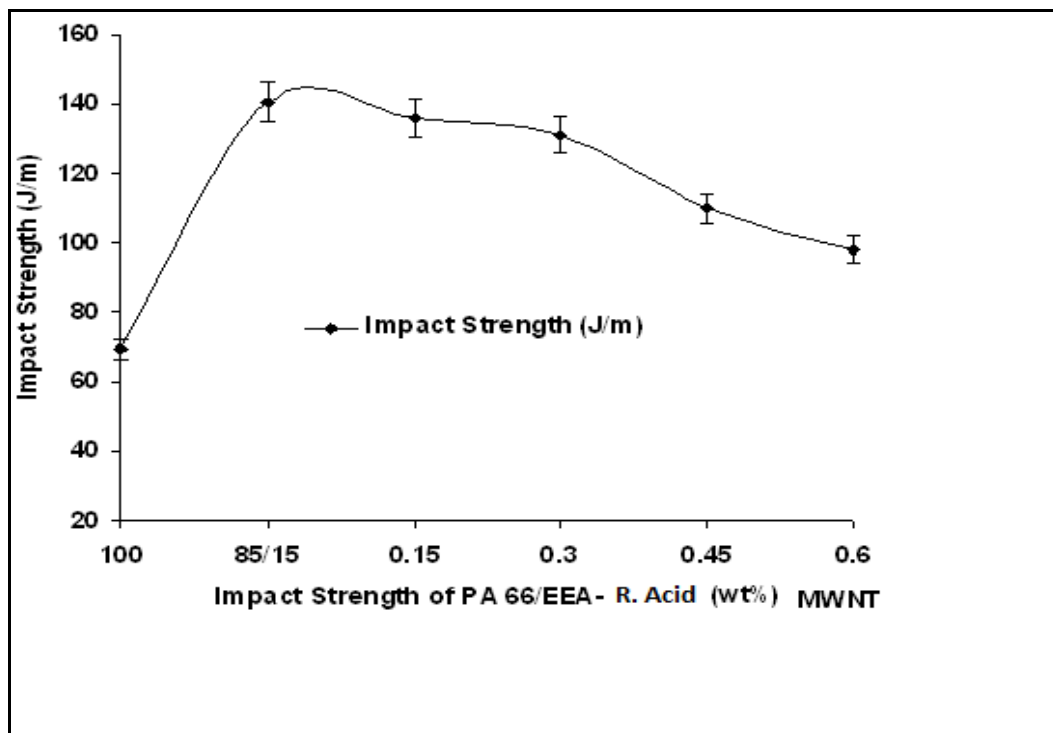
Fig –12 Impact Strength of PA 66/EEA-R.Acid/MWNT

From the Fig.11.It could be observed that the impact strength increases shows a 89% increment with the incorporation of 0.3wt% MWNT with PA 66/EEA-R.Acid (85/15). This further confirms the increased affinity of MWNT within the blend matrix that results in uniform dispersion of the delaminated nanotubes in both the polymers and increased ability to absorb the impact load.

4. Conclusion

PA66/MWNT, PA 66/EEA-R.Acid and PA66/EEA-R.Acid/MWNT nanocomposites were prepared by melt compounding using an intermeshing counter-rotating twin screw extruder. The reduced modulus and strength of alloys with functional rubber addition was counteracted by incorporation of MWNT without significant negative effects on the impact strength. EEA-R.Acid has a viscosity close to Polyamide 66 melt at 275^{0}C and so produce submicron particle size or even fine co-continues phase in Polyamide 66. Comparison of mechanical properties of this rubber toughened polyamides with virgin polyamides shows significant increase in impact strength and elongation at break, which is a very interesting results and show excellent toughening of Polyamide 66 with EEA-g- MA rubber. The EEA-R.Acid phase was finely dispersed at a scale smaller than 0.5 nm at all concentrations. In the other hand, by incorporation of MWNT, tensile modulus and strength significantly increased even relative to other reports. Now, we have a product with improvement all mechanical properties relative to virgin Polyamide 66.

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