

Study of Mechanical Properties of Multiwall Carbon Nanotubes (CNT) Based Polyamide6/Hytrel Polymer Nano Composites

M. Sawant¹, B. F. Jogi¹, P. K. Brahmankar¹, D. Ratna²

¹(Department of Mechanical Engineering, Dr. Babasaheb Ambedkar Technological University, Raigad)

²(Naval Materials Research Laboratory (DRDO), Ambernath, Mumbai, India)

ABSTRACT : It was planned to develop polymer matrix composite through polyamide 6 (PA6)/Hytrel blends and multiwall carbon nanotubes (MWNT) by melt-mixing technique with improved mechanical properties which can be utilized for several potential applications. The specific objective of this work is to study the effect of MWNT as nano filler in the presence of polymer matrix on the mechanical properties of the polymer based nano composite materials. It is envisaged that a polymer layer adsorbed on the MWNT surface may improve mechanical properties due to good adhesion between the filler and the matrix material. Few characterization techniques are utilized to study the advanced nano material. Crystallization and phase change behavior of PA6/Hytrel blends and MWNT studies through differential scanning calorimetry (DSC). Mechanical properties are studied with the help of dynamic mechanical thermal analysis (DMTA) and tensile testing methods.

Keywords – Multiwall carbon nanotubes (MWNT), Mechanical properties, Crystallization

I. INTRODUCTION

To achieve the desirable properties of polymeric materials, blending of polymers is an important tool which often gives rise to the possibility of enhancing the overall properties of the material. The ultimate properties of the blends are strongly influenced by the constituent of blends components. In recent decade, the concept of utilizing nano fillers (carbon black, clay, carbon nano tubes, graphite, etc) to stabilize the blends has received a great deal of interest both from scientific and industrial point of view. In recent times, carbon nanotubes (CNT) have emerged as potential filler in view of its mechanical properties replacing the conventional fillers like carbon black or fibers or clay [1]. The introduction of nano fillers in polymer matrices creates a class of novel materials (nanocomposites) exhibiting superior mechanical, thermal, electrical and barrier properties which is suitable to replace many existing materials for engineering applications. In this context, use of CNT (singlewall carbon nanotubes and multiwall carbon nanotubes) in polymer matrices have gained considerable attention in the scientific and industrial community due to the possibility to utilize the unique mechanical, thermal and electrical properties of CNT [1-4]. CNT based polymer nanocomposites possess high stiffness, high strength and good electrical conductivity at relatively low concentrations of CNT [5-6]. These enhancements in properties are due to the distinct properties of CNT. Several research groups have reported the useful results regarding the possibility of introducing CNT for mechanical enhancement in polymer/CNT composites. Much effort has been focused on designing approaches for dispersions of individual CNT in the polymer matrix composite and improving the interface between the matrix and the CNT. Polyamide/Hytrel blends will have been useful as commercially important because of relatively low cost of Hytrel and its contribution towards the dimensional stability, ease of fabrication, surface quality of the moldings and good toughness. PA6 has good strength and good chemical resistance but low elongation and low processibility due to moisture absorptive nature, where as Hytrel has high impact strength, high elongation and low moisture absorptive. Blending of these two polymers can impart synergistic effect leading to blends with good chemical properties as well as impact strength [6-7]. Furthermore, MWNT have the excellent mechanical properties are considered as nano filler materials for this study along with the polymer blends as matrix.

II. EXPERIMENTAL

The polyamide 6 (PA6, relative viscosity 2.8, Mv = 38642 in 85% formic acid) used in this work was supplied by GSFC, Gujarat, India under the trade name Gujlon M28RC. Hytrel (4056) was supplied by Dupont USA. Multiwall carbon nanotubes (MWNT) (p-MWNT, average length: 1.5 μ m, average diameter: 9.5 nm, Carbon purity > 95 %) were supplied by Iijin Nanotech, South Korea. PA6/Hytrel blends and MWNT was planned to prepare by melt-mixing in a twin-screw extruder at 230 °C to 260 °C with a rotational speed of 50 rpm. All

blend components were pre-dry in vacuum oven at 115 °C for 4 h. In blends with PA6/Hytrel and MWNT will melt-mixed in twin screw extruder then blends passed through water for cooling and it palletize by palletizing machine. The specifications of the twin screw extruder DSE 25 are as follows: maximum operating temperature: 400 °C, maximum torque: 2*90 Nm, screw speed: 550 per min , maximum melting pressure 300 bar, supply voltage: 208-240 V AC. Injection-molded samples (according to ASTM D 638, Type IV, thickness: 5 mm; length 50 mm, parallel length: 13 mm) were prepared using mini injection-molding machine from EGLE. The specifications of the DSM mini injection molding machine are as follows: maximum shot volume: 100%, maximum operating temperature: 400 °C, maximum injection force: 1-12000 N, Supply voltage: 208-240 V AC. The injection-molding parameters maintained for all the compositions were injection pressure 3 bar, shot volume: 95% melt temperature 240 °C, mold temperature 60 °C, holding time 60 sec and cooling time 2-3 min. Izod impact strength testing (Tinius Olsen 892) is an ASTM standard method of determining impact strength (toughness). Impact tests are used in studying 'toughness' of material, that is the ability of material to absorb energy during plastic deformation because of high toughness the material have strength and at the same time large durability. A notched sample is generally used to determine impact strength. Test specimen dimensions and tolerances as per standard ASTM D256 are 64 x 12.7 x 8 mm. Various tensile properties such as yield strength (σ_y), stress at break (σ_b), Young's modulus (E_t) and elongation at break (ϵ_b) determined by using universal testing machine (UTM). UTM (Hounsfield Tinius Olsen) gives the result of stress-strain curve. Toughness can be calculated from area under the stress-strain curve. Test specimen dimensions and tolerances as per standard ASTM D638 Gauge length 50 mm, width 13 mm, thickness 5 mm. All samples for the DMTA measurements had prepared by injection molding. DMTA had carried out using Gabo in the bending mode and the furnace will heat at 2 K/min from -100 to 150 °C, with a frequency of 1Hz. The furnace had flushed with liquid nitrogen throughout the measurements to prevent oxidative degradation of the samples.

III. RESULTS AND DISCUSSIONS

The MWNT filled blends show superior mechanical properties in the tensile tests and in IZOD notched impact tests. It is also concluded that the elongation at break, as an indicator for the toughness of the materials, decreases dramatically when adding carbon nanotubes to polyamide 6. In case of the PA6/Hytrel blends maximum toughness is also observable in 85/15 percentage content as shown in Table 1, further increase in percentage of hytrel in blends decreases the toughness. In case of the MWNT filled blends increase in stiffness is also observed in the high filler content region, due to it may be decrease in toughness compared to 85/15 PA6/Hytrel blend. However toughness is much higher than neat PA6 as shows in Table 1.

Table 1 IZOD notched impact tests of PA6/Hytrel blends

Samples	Sample Codes	B. E. (J)	Impact Energy (J/m)
Polyamide 6	PA6	1.86	199
90/10 wt % of PA6/Hytrel blends	N90H10	2.8	220
85/15 wt % of PA6/Hytrel blends	N85H15	2.20	240
80/20 wt % of PA6/Hytrel blends	N80H20	2.10	234
75/25 wt % of PA6/Hytrel blends	N75H25	2.9	230
85/15 wt % of PA6/Hytrel blends with 1 wt % of MWNT	N85H15U1	1.85	190

The mechanical behavior of blends is strongly decided by the contribution of each component and the interfacial adhesion between the phases. It is well realized that elongation at break and toughness are the important tools to monitor the adhesion between phases whereas the tensile strength is related to the morphology, domain size and size homogeneity. Moreover, it can be seen that the PA6/Hytrel blends has a much lower yield strength than neat PA6, but the % elongation at break is higher as compared to neat PA6. The stress-strain curves for PA6, PA6/Hytrel blends, 85/15 wt% of PA6/Hytrel blends and 1 wt % of MWNT with 85/15 wt% of PA6/Hytrel blends are shows in the Fig. 1. The stress-strain curve in the yield region provides an appearance of a broad

yield peak, which is nearly absent with progressive addition of MWNT in the 85/15 PA6/Hytrel blends. Further, a drastic reduction in elongation at break with increasing MWNT content is apparent in these set of blends indicating a brittle failure. The blends with MWNT exhibit an increase in the Young's modulus with increasing filler content as shows in Figure 1 however, the tensile strength at yield is found to increase only marginally in the PA6/Hytrel blends with neat MWNT. The tensile strength of PA6/Hytrel blends with MWNT increase with increasing filler content. The 85/15 PA6/Hytrel blends show tensile strength of 40 MPa, while the blends 1 wt% unmodified MWNT exhibit a modulus of 44 MPa. The 85/15 PA6/Hytrel blends show Young's modulus of 298 MPa. The 85/15 PA6/Hytrel blends with 1 wt% unmodified MWNT exhibit a modulus of 310 MPa. In addition, this particular composition exhibits the highest stress at break.

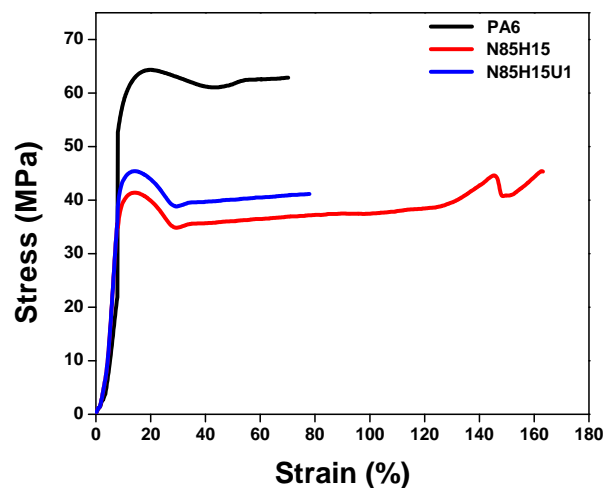


Fig. 1 Stress-strain curve of PA6/Hytrel blends with MWNT

It has been reported that DMTA measurements can be employed to get further insight into the miscibility and phase transition behaviour of the blends. Figure 2 shows the temperature dependent storage modulus (E') of the PA6/Hytrel blends with MWNT. It can be found that the E' is higher especially at lower temperature in case of PA6 as compared to the PA6/Hytrel blend components. Further, the incorporation of MWNT increases the E' of the blends significantly, especially below the glass transition temperature (T_g), which is due to the stiffening effect of the MWNT. In presence of MWNT, T_g increases as compared to PA6/Hytrel blends indicating the restriction to chain mobility due to the presence of MWNT. It has been reported in the literature, that CNT act as heterogeneous nucleating agent and influence the rate of crystallization and the crystallization temperature of the semi-crystalline polymer matrix by acting as a hetero-nucleating agent [1]. Table 2 exhibits the crystallization exotherms for 85/15 (wt/wt) PA6/Hytrel blends with MWNT. Blending of PA6 with Hytrel results in marginal increase in crystallization temperature (T_c) of PA6 phase. Further, it is observed that onset and peak crystallization temperature gradually shifts to the higher values with progressive increase in the MWNT content. Such increase in peak crystallization temperature clearly shows heterogeneous nucleating action of MWNT. PA6 exhibits bulk crystallization exothermic peak at 185 °C. Both neat PA6 and 85/15 blends of PA6/Hytrel exhibit melting endotherms in the second heating run in the DSC. It is observed that PA6 shows melting temperature at 222.21°C. Single melting endotherm has been observed in the blends with both unmodified MWNT and modified MWNT. Moreover, the melting temperature in the blends with unmodified MWNT or modified MWNT has been found to remain almost unchanged with PA6/Hytrel blend melting temperature. The degree of crystallinity (X_c) calculated from the normalized heat of fusion from the second heating cycle of DSC is listed in Table 2. The X_c is found to decrease slightly in 85/15 PA6/Hytrel blends as compared to neat PA6 manifesting the fact that hytrel influences the crystallization behaviour of PA6.

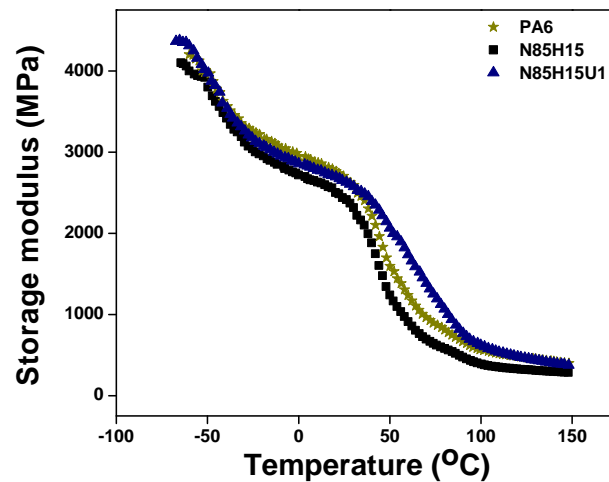


Fig. 2 Dynamic mechanical thermal analysis (DMTA) of PA6/Hytrel blend with MWNT (Storage modulus (E') versus temperature)

Table 2 DSC melting and crystallization parameters for PA6 and blends of PA6/Hytrel with and without MWNT

Sample	Crystallization Temperature (°C)	Melting Temperature (°c)	Crystallinity (%)
PA6	185.28	223.11	44.39
N90H10	188.60	222.91	27.63
N85H15	188.77	222.77	24.40
N80H20	188.91	222.37	23.20
N75H25	188.96	222.34	22.70
N85H15U1	192.90	222.70	44.19

IV. CONCLUSIONS

PA6/Hytrel blends were thoroughly investigated by mechanical and thermal characterization techniques. The mechanical properties of the blends were found to improved as compared to the blends with neat MWNT. The mechanical behavior of blend is strongly decided by the contribution of CNT and the interfacial adhesion between the phases. The strength and toughness was found to be increased in PA6/Hytrel blend with MWNT. DMTA results showed to increase storage modulus in PA6/Hytrel blends with MWNT which is due to the stiffening effect of the MWNT and also showed change in glass transition temperature in PA6/Hytrel blends with MWNT due restriction of the polymer chains in presence of MWNT. However, early crystallization was observed in the DSC curves due to the presence of MWNT which are acting as a hetero-nucleating agent. The degree of crystallinity and percentage of crystallinity was found to be increased in PA6/Hytrel blends with MWNT. But there is no change found in melting temperature in blends with MWNT. Hence 85/15 PA6/Hytrel blends with 1 wt% of MWNT exhibits improved mechanical properties and applicable for the products where higher mechanical properties are desirable compared to neat blends.

V. Acknowledgements

The authors acknowledge the Polymer Engineering Division of the NMRL, DRDO, Ambarnath for their timely help for the various testing facilities.

REFERENCES

- [1] S. Bose, A.R. Bhattacharyya, L. Häußler, P. Pötschke, Influence of multiwall carbon nanotubes on the mechanical properties and unusual crystallization behavior in melt-mixed co-continuous blends of polyamide 6 and acrylonitrile-butadienestyrene, *Polymer Engineering Science*, 49(8), 2008, 3010-3022.
- [2] S. Bose, A.R. Bhattacharyya, R.A. Khare, A.R. Kulkarni, T.U. Patro and P Sivaraman, Tuning the dispersion of multiwall CNTs in co-continuous polymer blends: a generic approach, *Nanotechnology*, 19, 2008, 3304-3312.
- [4] P.M. Ajayan and J.M. Tour, Nanotube composites, *Nature*, 447, 2007, 1066-1068.
- [5] M. Moniruzzaman and K.I. Winey, Review Polymer Nanocomposites Containing Carbon Nanotubes, *Macromolecules*, 39, 2006, 5194-5205.
- [6] P. M. Ajayan, Nanotubes from Carbon, *Chem. Rev.* 99, 1999, 1787-1799.
- [7] C.A. Harper, *Handbook of plastics elastomers and composites* (McGraw-Hill 2001), 1-90.