

MECHANICAL BEHAVIOUR OF FILLERS IN NYLON 11

Dr. S.A. Pande

Laxminarayan Institute of Technology, Nagpur (India)

ABSTRACT

This study was undertaken to evaluate the effect of Zinc (Zn) and Polyaniline (PANI) fillers on the physical and mechanical properties of Nylon 11. The Nylon 11 was modified using (Zn) & conducting (PANI) filler with filler addition 1% and 5% (w/w). The samples were prepared using hot press molding. Present investigation was subjected to the comparative study of modulus of

elasticity, tensile strength and % elongation of the pure Nylon 11 and filled samples. The results of the comparative study reveals that the tensile strength, % elongation, and Young's modulus of Nylon 11 decreases with increasing % of filler content, which can be attributed to the introduction of discontinuity in the structure.

KEYWORDS: Nylon 11, Metal filler, Conducting Filler, Mechanical Properties

1. Introduction

The incorporation of metallic fillers into polymers is an extremely active area of research. Many studies exhibited the change in physical properties of polymers by addition of various metal fillers [1-4]. Further several studies reported variation in mechanical, electrical and thermal properties due to addition of metal fillers in insulating polymer matrix.

The effect of the addition of fillers on the structural, mechanical and dielectric properties for different fillers and filler concentrations has been reported by Haralompos Zois et.al. [5]. They observed that the filler spatial distribution was random in (PE-Fe, PA-Fe and POM-Fe) composites. It has been reported that in PE/POM-Fe composites, the polymer matrix is two phases and the filler particles are localized only in the POM phase, resulting in an ordered distribution of the dispersed filler particles within the blend.

The characterization of composite materials containing a mixture of aluminum flakes and Nylon 6 powder was studied by G. Pinto et.al. [6], wherein they observed that for certain sizes of particle fillers, the hardness decreased initially with the increase of metal concentration, possibly because of poor surface contact with the nylon matrix, but, starting from a certain value, there is increase in hardness. They further reported that the hardness of samples is not influenced by the presence of the smallest particle filler.

Numerous studies have been carried out on metal filled Nylons [7-10], but not many on metal filled Nylon 11. S. Bahadur & A. Kapoor [11] studied the tribological behaviour of Nylon 11 reinforced with particulate inorganic fillers proportions, wherein the influence of the fillers (ZnS, PbS and ZnF_2) on transparent film

formation & chemical changes during the wear process were studied. They observed that in case of PbS – Nylon composites, the filler dissociate during the wear process, thus provide strong adherent transfer film which led to increase the wear resistance of the composite, whereas when ZnS and ZnF₂ fillers were used in nylon, the wear rate of nylon increased.

Some work has been reported on effect of filler type, non-uniformity of filler concentration, role of metal and metal deactivators in polymer degradation [12-15].

In recent years, lot of emphasis has been given to the replacement of metals by conducting polymers, as these polymers offer low cost, they are rust free, and therefore become commercially important than metals. Polymers can be made to conduct electricity relatively much easier by compounding them with high loadings of conductive metals such as copper, silver and gold, or, where cost considerations are important by carbon. The use of conducting

polymer as a filler in insulating polymer is not much been reported.

Jan-Chan Huang [16] studied the use of carbon black as conductive filler in polymer and polymer blends. He observed that several percolation models are applicable to CB/Polymer blend. In his work he studied the polymer structure of the filled polymers, molecular weight, surface tension, physical properties etc. W. Jia et. al. [17] reported that almost all properties of low density polyethylene (LDPE) have been improved by addition of polyaniline in LDPE matrix.

Therefore it was thought interesting to investigate the effect of both metal and conductive polymer fillers on Nylon 11. In the present work, an attempt has been made to understand the crystal structure of melt cast pure and modified Nylon 11 at room temperature. The modification in pure Nylon 11 has been carried out by addition of fillers (1% and 5% w/w). The effects on structural, morphological, and mechanical behaviour of Nylon 11 after using fillers have been reported.

2. Experimental Techniques

2.1 Materials:

The Nylon 11 in the form of beads was used in the preparation of samples. Zinc powder having atomic weight 65.38 was used. The particles of Zinc were spherical in shape with 2-3 μ m size. Samples of pure and Zn filled (1% and 5%, w/w) Nylon 11 was prepared in the form of rectangular piece using hot press molding. The thickness of

the sample was 1 mm. The Zn powder was uniformly distributed in the sample.

Polyaniline (PANI) was chemically synthesized in the laboratory using potassium dichromate (K₂Cr₂O₇) as an oxidizing agent and H₂SO₄ as an acidic media [18]. Salt form of PANI was prepared in the form of powder and was used as fillers.

2.2 Mechanical Characterization

Tensile Testing

To study the mechanical properties like Ultimate Tensile Strength (UTS), % Elongation, Young’s Modulus and also the bending properties of materials of pure and filled Nylon 11, an Instron Tensile Testing Machine, Model INSTRON-4467, operated at with a 50 mm/min strain rate was used.

Following parameters were used for the present investigation:

- Cross Head Speed: 50 mm/min
- Specimen Gauge Length: 70 mm
- Sample Width: 10 mm
- Sample Thickness: 1mm
- Grip Distance: 20 mm
- Temperature: Room Temperature

Dynamic Mechanical Thermal Analysis (DMTA):

The DMTA studies were conducted by a Rheometric Scientific DMTA apparatus. Experiments were carried out on a dual cantilever arrangement in bending mode in the temperature range from - 10°C to 130°C at a heating rate of 5°C/ min. Cooling was achieved by pumping liquid Nitrogen

through the accessories provided in the instrument. Samples were scanned with an imposed frequency of 1Hz. Measurements of all samples were made in identical conditions for a valid and reliable comparison of the results.

Scanning Electron Microscopy (SEM):

It is one of the most important techniques used for the investigation of morphology of polymers. During the present work, the morphology was investigated using Leo 435 VP 501B Philips SEM.

The samples to be examined were made conductive by depositing a very thin layer of gold of thickness 800 nm on the surface. Initially large area of the samples was observed at low magnification and then the selected area was studied at higher magnification

3. Results and Discussion

The mechanical behaviour of filler added Nylon-11 with the prior system was studied

by using Instron-4467 and the values are reported in Table 1.

Sr. No.	Sample	% Elongation	UTS (MPa)	Young’s Modulus (MPa)	Glass transition temp (T _g °C)
1	Nylon 11	33.077	134.410	1278.803	73.26
2	1% PANI filled Nylon 11	21.956	69.289	1184.594	60.002

3	5% PANI filled Nylon 11	16.405	89.556	1231.820	75.802
4	1% Zn filled Nylon 11	25.693	75.644	1346.359	34.419
5	5% Zn filled Nylon 11	25.332	73.196	1188.307	58.564

Table I: The values of various parameters obtained by INSTRON-4467.

The influence of PANI contents on the tensile strength and elongation at break of PANI filled Nylon 11 is shown in Figure 1. As it can be seen that pure Nylon 11 possessed a tensile strength of about 134.410 MPa and an elongation at break of over 33.077%, the addition of conducting (PANI)

fillers has decreased both above properties of Nylon 11 filled samples. This reduction in the tensile strength and elongation at break might be attributed to the formation of complex structure due to PANI addition which was confirmed from WAXD and FTIR [19].

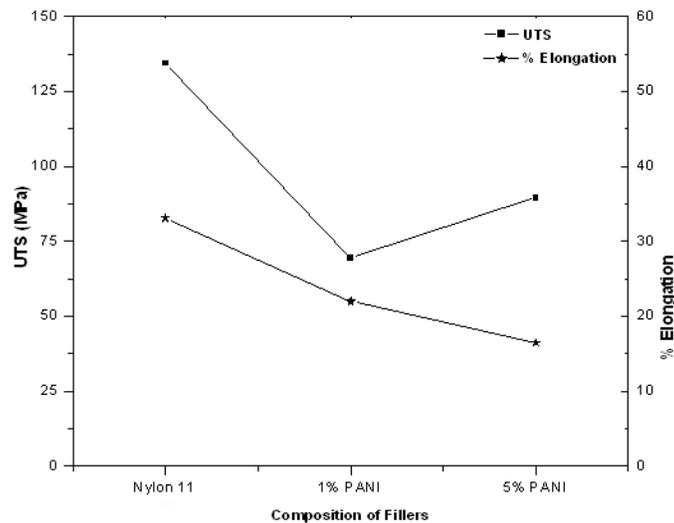


Figure 1: Variation in UTS and % Elongation of PANI filler

The same behaviour of reduction in the mechanical properties with respect to the filler addition was observed by S Bose, H Raghu and co-workers [20] in the mica filled Nylon 6. The same observations were also conformed by B Moustafa, A Faizalla and co-workers for filler in PMMA [21], Ali Gungor for polymer composites filled with Fe powder [22], by S N Maiti and P K Mahapatro [23] for Ni-powder filled polypropylene composites, M J Zaini, M Y A Faud and others for PP-oil palm wood

filler composites [24], S Bose and P A Mahanwar [25] for coupling agent addition in Nylon 6. All these researchers have seen that the reduction in the mechanical properties is due to the discontinuities in structure, the type of additions and formation of complex structure. These researchers also emphasized the need of coupling agent for the improvement in mechanical properties.

The morphology of PANI filled Nylon 11 has been already studied and reported [19]. It has been observed that the complex between the Nylon 11 and the PANI has been probably formed by the PANI coordination with the amide group. This has been confirmed from FTIR of PANI filled Nylon 11.

The X-ray scan also reveals that there is a partial shift from α to γ structure and an increase in intensity of γ peaks. The same behaviour is seen in SEM micrographs of the filled samples, which indicates more disturbed structure due to increase in % of PANI as shown in figure 2.

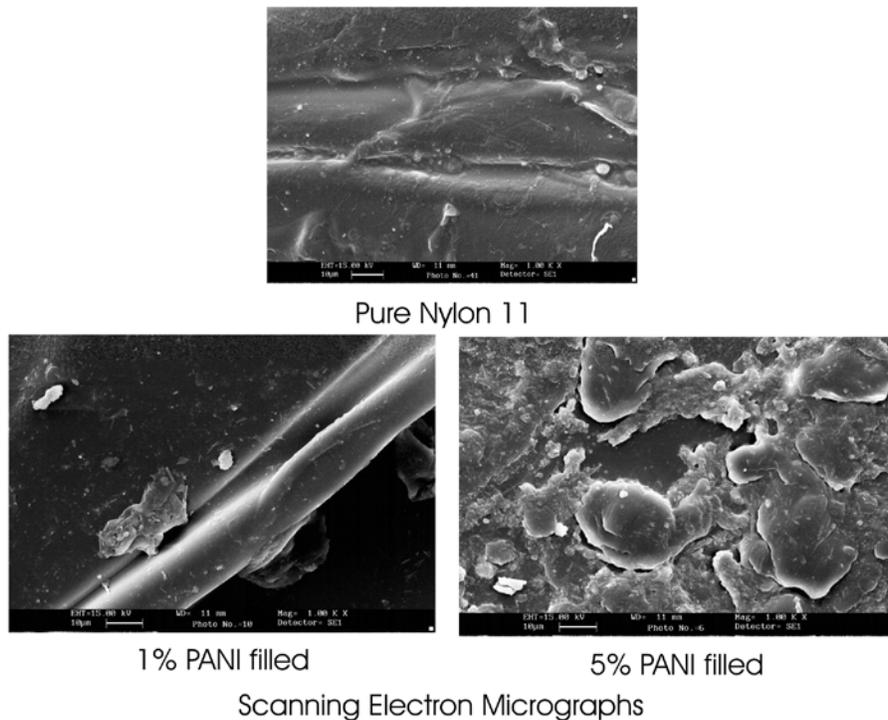


Figure 2: SEM of Pure and PANI filled Nylon 11

The mechanical behavior of the polymeric materials is expressed by two stage process i.e. initially chain sliding or chain mobility at low load condition and then chain breaking after the elongation or intermolecular bridging of complex chain structures at high load situations. The same behavior has been seen by T. Kawaguchi [26] during the study of mechanical behavior of nylon systems.

From Figure 1, as the percentage of PANI increases from 1% to 5% it has been seen that the UTS increases while % elongation

decreases. The higher value of % elongation in 1% PANI, is might be due to the plasticizing action of filler, while decrease in % elongation at higher PANI content is due to antiplasticizing effect. This has been observed during the measurement of Tg using DMTA. The Tg values are given in tabulated form in Table I.

From Table 1, it has been observed that at 1% PANI filler the Tg decreases. The reduction in Tg is associated with the plasticizing action of filler. The plasticizing and antiplasticizing effect of dopant has

been extensively studied by many researchers [27-29]. At 5% PANI, the Tg increases. It is an example of an antiplasticizer. Such increase in Tg values can be explained on the basis of decrease in the free volume of the mixture. Such volume

contraction can be caused by strong interaction between the amide group of Nylon 11 and the powder. This leads to the stiffening of the Nylon chains. The stiffening of chains is one of the effects of antiplasticizing action of the powder [30].

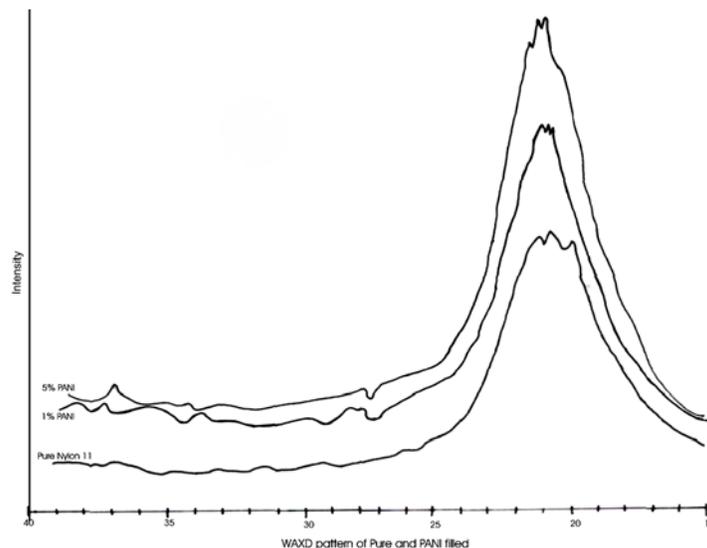


Figure 3 : WAXD Analysis of Pure and PANI filled Nylon 11

In current work, the added 1% PANI particles may have entered into the crystalline region as is observed from WAXD (Figure 3). The WAXD studies reveal the phase change from $\alpha \rightarrow \gamma$ have taken place, thereby reducing its order of crystallinity. All the outcome indicates that the addition of 1% PANI filled Nylon 11 enters into the crystalline region of Nylon 11. And the amide group has been pushed out of the plane of polymer chain causing volume contraction, leaving a slightly deformed or pleated structure. Thus the hydrogen bonds must have appreciably weakened, which might have resulted in reduction of glass transition temperature.

The FTIR of PANI filled Nylon 11 has been studied, it confirms that, PANI forms a complex with Nylon 11 chains just like dopant. Therefore on the basis of FTIR results, it can be suggested that, the complex

between the Nylon 11 and the PANI must have formed by the PANI co-ordination with the oxygen of the amide group.

As the concentration of PANI is increased (5% PANI), the complex is formed between the Nylon 11 and PANI which further pushes the chains of Nylon 11 so that the Amide group goes out of plane as to form a tightly bound hydrogen bonds. This can be observed by shifting the peak position during WAXD analysis.

As the percentage of PANI increases, there is an improvement in UTS, which might be due to more complex and rigid structure. The FTIR study⁸ has also indicated the existence of 5 additional new peaks in 5% PANI along with the shifting of peaks observed in 1% PANI. This has resulted due to linking of two polymers, viz. Nylon 11 and PANI probably at the amide group and

thus forming a more complex structure. The same behaviour is seen in SEM micrographs of the samples, which indicated more disturbed structure due to increased percentage of PANI as shown in **Figure 2**.

X-ray study also reveals that there is a partial shift from α to γ structure and also increase in intensity of γ peaks. FTIR results indicate formation of new bonds due to complex formation between PANI and Nylon 11. This complex formation might have resulted in bringing about the change in

crystalline structure of Nylon 11. The increase in UTS values for PANI filled Nylon 11 indicates that the complex formed between the additive and Nylon 11 must be very strong and can sustain a higher load. From these measurements, it was concluded that plasticizing action of PANI is the result of breaking of bonds between PANI and Nylon 11 chains while antiplasticizing action of PANI has resulted in stiffening of Nylon chains due to strong interaction and volume contraction [19].

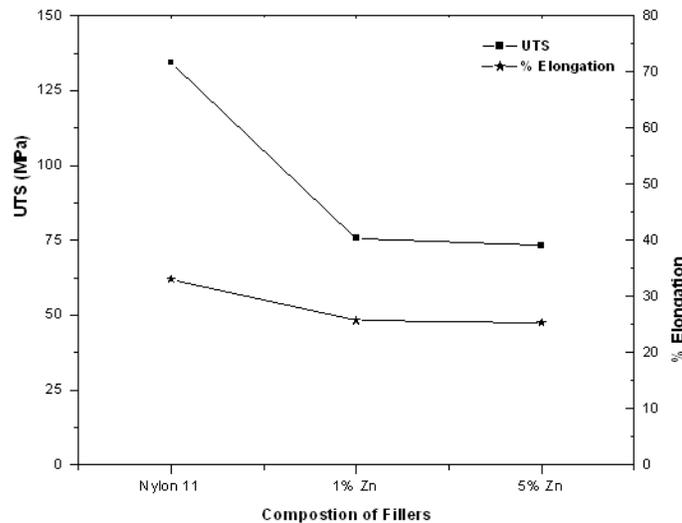


Figure 4: Variation of UTS and % Elongation of Zn filled Nylon 11

Similarly in case of Zn addition in Nylon systems, it is observed from the figure 4 that UTS and % elongation more or less remains constant for both concentrations of Zn. The % elongation is slightly better due to plasticizing effect which has been conformed from decrease in Tg in both the cases [9]. The measurement of DMTA is used for measuring the glass transition temperature of the polymers.

From Table I it can be observed that glass transition temperature of Nylon 11 generally reduces after filling Zn particles. The reduction in glass transition temperature

(Tg) has been associated with the plasticization effect of plasticizer.

It is known that when a polar plasticizer is introduced into a polar polymer, the polar groups of polymer strongly bind with one or two plasticizer molecules. Shielded by the plasticizer molecules, the polar groups of the neighbouring polymer chains cannot interact with each other and also the number of polar groups on the polymer chains becomes smaller and hence the polymer passes into the glassy state i.e. hardens at lower temperature.

True plasticizing action of the plasticizer, is the weakening of second order (Van der Waal's) attraction forces between the polymer chains because of the interposition of the plasticizer molecules. The screening of the polar groups takes place up to a certain extent. It is necessary that the plasticizer should form a complex.

In the present work, added Zn powder does not form any complex with Nylon 11 and remains as dispersed particles in Nylon 11 matrix. Chemical bonds are not formed between the polymer chain and metal particles.

The addition of Zn powder remains a physical mixture in Nylon 11. However, the effect of addition of Zn powder on Nylon 11 is similar to that of plasticizer.

In the present work, in case of 1% Zn filled Nylon 11, the added Zn particles enter into the crystalline phase of Nylon 11 as is evident from WAXD analysis which has already been reported elsewhere [31]. WAXD studies have revealed that the phase transformation from $\alpha \rightarrow \gamma$ has taken

place. The interposition of Zn particles in between the Nylon 11 chains therefore can have the effect of weakening of second order (Van der Waal's) attractive forces between the polymer chains. Hence the glass transition temperature reduces.

As the concentration of Zn in Nylon 11 is increased to 5%, it has been reported [31] from WAXD analysis (Figure 5); this sample contains the presence of both α and γ phase. The crystallinity has also increased slightly as compared to 1% Zn filled sample. In this case therefore, one can say that the interposition of Zn particles in between the Nylon 11 chains must have taken place so as to form the α phase of Nylon 11 along with the γ phase of Nylon 11. The Van der Waal's force between the polymer chains as far as α phase is concerned becomes stronger as compared to 1% filled Nylon 11, where only γ phase is present. Thus with further addition of Zn powder there is Zn/Zn interaction and reduced Zn/Nylon interaction. Therefore the glass transition temperature (Tg) for 5% Zn filled Nylon 11 is more than that of 1% Zn filled sample

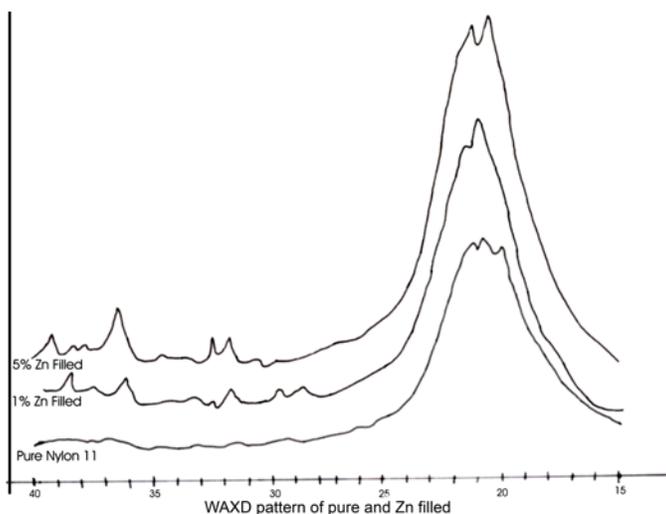


Figure 5: WAXD Analysis of Pure & Zn filled Nylon 11

This is due to weakening of second order Vander-Waal's attractive forces. This makes them possible for resulting in chain sliding, due to pushing of chains apart by Zn particles. It is evident from WAXD that the addition of Zn powder transforms the triclinic α crystalline structure of pure Nylon 11 into pseudo-hexagonal γ form, by entering into the crystalline range and slightly pushing the chain apart. During loading condition, this Zn would also help in sliding of chains, due to its inherent pseudo-hexagonal structure. It has been seen that hexagonal structure (like Massac, graphite etc) acts as antifriction material due to sliding of layers of closed packed structure. The same behaviour is seen with Zn addition

4. Conclusion

It has been observed that by addition of fillers (containing 1% and 5% (w/w)), Young's modulus, % elongation and UTS values decreases as compared to pure Nylon 11. But increase in concentration of metal particles shows a negligible effect whereas

5. Acknowledgement

The author gratefully acknowledge the support of AIIMS, New Delhi and Visvesvaraya National Institute of

in Nylon 11 which helps in sliding of chains and becomes more pronounced by the pseudo-hexagonal structure of Nylon 11 (γ form).

In case of Zn as an additive, it is confirmed using FTIR studies that it forms a physical mixture with Nylon 11 and does not form any chemical bonding with Nylon 11. However, the XRD studies indicate that there is a change in crystalline form and crystallinity of Nylon 11 due to addition of Zn [31]. Since there is no chemical bond formation between this additive and Nylon 11, the UTS show a slight decline in its value.

concentration of PANI fillers shows dependence on UTS and % elongation. Therefore a use of coupling agent between the two components might result in more homogenous structure and slight improvement in mechanical properties.

Technology, Nagpur for providing the facilities to carry out this work.

6. Reference

1. S. Goyanes, G. Rubiolo, A. Marzocca, W. Salgueiro, A. Somozo; G. Consolati, I. Mondragon, Polymer, 11, 44, 3193-3199, 2003
2. S. Cerveny, S.N. Goyanes, A.J. Marzrocca, G.H. Rubiolo, Polymer, 6, 40, pp 1495-1500, 1999
3. M.A. Berger, R.L. Mcchulloch, Composites Science and Technology, 2, 22, pp 81-106, 1985
4. R.S. Kolupayev and N.A. Bordynk, Polymer Science, 7, 23, 1652-1659, 1981
5. Haralamphos Zois, L. Apekis, Yevgen P. Mamunya, J. of Applied Polym. Science, Issue 13, Vol. 88, 3013-3020, 2003
6. Gabriel Pinto, Ana Jimenez-Martin, Polymer Composites, Volm. 22, 1, pp 65-70, 2004
7. S. Bose, H. Raghu, P.A. Mahanwar, J. Appl. Polym. Sci., 100, pp 4074-4081, 2006

8. B. Moustafa, A. Faizalla, B.M. Abd-el-Hadym *J. of Appl. Polym. Science*, 4, 67, pp 637-641, 1998
9. Gungor, J. *Appl. Polym. Science*, 5, 99, pp 2438-2442. 2006
10. S.N. Maita, P.K. Mahapatro, *Polymer Composites*, 1, 13, 47-52, 2004
11. S. Bahadur, A. Kapoor, *Wear*, 1, 155, pp 49-61, 1992
12. A.B. Monsafa, A. Faizdia, B.M. Add, E.L. Hadly, *J. Appl. Polym. Sci.*, 67, pp 637-641, 1997
13. F. Danies, B. Garnier, T. Dupuis, P. Lerendu, T. Nagugen, *Comp. Sci and Tech.* 6, 65, pp 945-951, 2005
14. Z. Osawa, *Polymer Degradation and Stability*, 20, pp 203-236, 1998
15. Gungor, J. *Appl. Polym. Science*, 5, 99, pp 2438-2442. 2006
16. Jan-Chan Huang, *Adv. in Polym. Technology*, 4, 21, pp 299-313, 2002
17. W. Jia, R. Tchoudakav, E. Segal, M. Norkis, A. Seigmann, *J. Appl. Polym. Sci.*, 2, 91, pp 1329-1334, 2003
18. A J Milton, A P Monkman, *J. Phys. D. Appl. Phys.* 1993; 26, 1468.
19. S A Pande, D S Kelkar, D R Peshwe, *Current Applied Physics*, Vol.7, Issue 5, pp 590-595, July 2007;
20. S Bose, H Ragu, P A Mahanwar, *J. Appl. Polym. Sci.*, (2006), 100, p 4074-4081;
21. B Moustafa, A Faizalla, BM Abd El Hady, *J. Appl. Polym. Sci.*, (1998), 67, p 637-641
22. Ali Gungor, *J. Appl. Polym. Sci.*, (2005), 99, 5 , p 2438-2442
23. S N Maiti and P K Mahapatro, *Polymer Composites*, (2004),13, 1, p 47-52
24. M J Zaini, M Y A Faud Z Ismail, M S Mansor, J Mustafah, *Polymer International*, (1999), 40, 1, p 51-55;
25. S Bose, P A Mahanwar, *J. Appl. Polym. Sci.*, (2006), 99, 1, p 266-272;
26. T. Kawaguchi, *J. of Appl. Polym. Sci.*, (1958), Vol. 2, Issue No. 4, p 56-61;
27. P Ghera, *Modern Plastics*, 1958; 36, pp 2-135.
28. Hyo-gun Kim and P J Harget, *J. Appl. Phys.* 1979; 50 (10), 6072.
29. M J Mehta and R D Andrews, *Polym. Prepn.* 1963; 14, 1260
30. W J Jackson, Jr. and J R Caldwell, *J. Appl. Polym. Sci.* 1967; 11, 211
31. S A Pande, D S Kelkar, D R Peshwe, *Journal of Applied Polymer Science*, Vol. 103, Issue 5, pp 3094-3098, March 2007.