

Structural, Thermal and Mechanical Insights of Polyphenylene oxide (PPO)/ Polystyrene (PS) polymer blends

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Abstract: The effect of addition of PPO into PS matrix on thermal behavior was studied using differential scanning calorimetry (DSC) technique; mechanical characterization by Microhardness study and polymer blend surfaces structure has been studied using atomic force microscopy (AFM). The pure polymeric samples and their blends of ratio 95:05; 90:10; 85:15; and 80:20 weight percentage has been prepared using solution casting techniques. It is found in AFM studies that due to the disruption of phenyl ring associated with polystyrene the surface topography characteristic of each constituent are destroyed upon mixing by interpenetrating poly (phenylene oxide) chains. On the basis of DSC, the glass transition temperature of the samples was determined. It is found that the glass transition temperature initially increases up to 10 wt% of PPO; however, it decreases with further increase in PPO content in the sample. Microhardness study shows that all the polymer blends have high H_v value as compared to pure PS but the H_v value for pure PPO is maximum.

Keywords: Poly (Phenylene Oxide) (PPO), Poly (Styrene) (PS), XRD, DSC, AFM, Microhardness

1. INTRODUCTION

The thermal properties (like glass transition temperature, melting point) and surface structure of polymer systems are directly related to its application in various fields (like electrical circuits, medical applications, insulation, signal transmission, shielding etc.) and needs to take into account during use of polymers. Conceivably the most explicit criterion of polymer compatibility is the detection of a single glass transition temperature whose temperature is intermediate between those corresponding to the two-component polymers. For the bulk blend systems, PPO and PS are known to be compatible in all compositions [1].

Immiscible polymer blends exhibit two glass transitions at temperatures around those of the components. Partially miscible systems are heterogeneous two-phase structure, in which only a limited amount of the other component is dissolved in both phases. Two T_g s, in these polymer pairs approach each other but do not become identical. Completely miscible blends result in homogeneous structure and exhibit a single T_g between the T_g of the individual components. Based on readily available polymers, the unusual polymer blends with a combination of properties unattainable in any single polymer component are obtainable. For instance, Completely miscible poly(2,6-dimethylphenylene oxide)/polystyrene (PPO/PS) blends having good dimensional stability, high resistance to moisture, impact resistance, low temperature impact strength, low creep, and good processability [2] are widely used in automotive instrument panels, interior finishing, business equipment chassis, electrical applications, and medical equipment. Therefore, it is significant to develop polymer blend.

Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a compressive force is applied. Some materials, such as metal, are harder than others. For elastomers and some polymers hardness is defined as the ability of the material to resist plastic deformation. It is a complex property related to various mechanical properties such as modulus, strength, elasticity, plasticity etc. Polymers are different from other material like metals and ionic solids because in polymeric material strain depends not only on the magnitude of the stress but also on the length of time during which it is applied. The chemical and morphological nature of the material is one of the very important property on which microhardness of the material is dependent and, therefore, by properly selecting the component of the material, the hardness of the material may be desirably balanced.

2. EXPERIMENTAL SECTION:

2.1 Materials

The materials used in the present investigation are Polyphenyleneoxide (PPO) and Polystyrene (PS) in powder form was supplied by M/S Fine CHEM Industries Mumbai. The solvents Acetone and Benzene of AR grade were supplied by M/S Aldrich Chemicals, Mumbai.

2.2 Preparation of Blends:

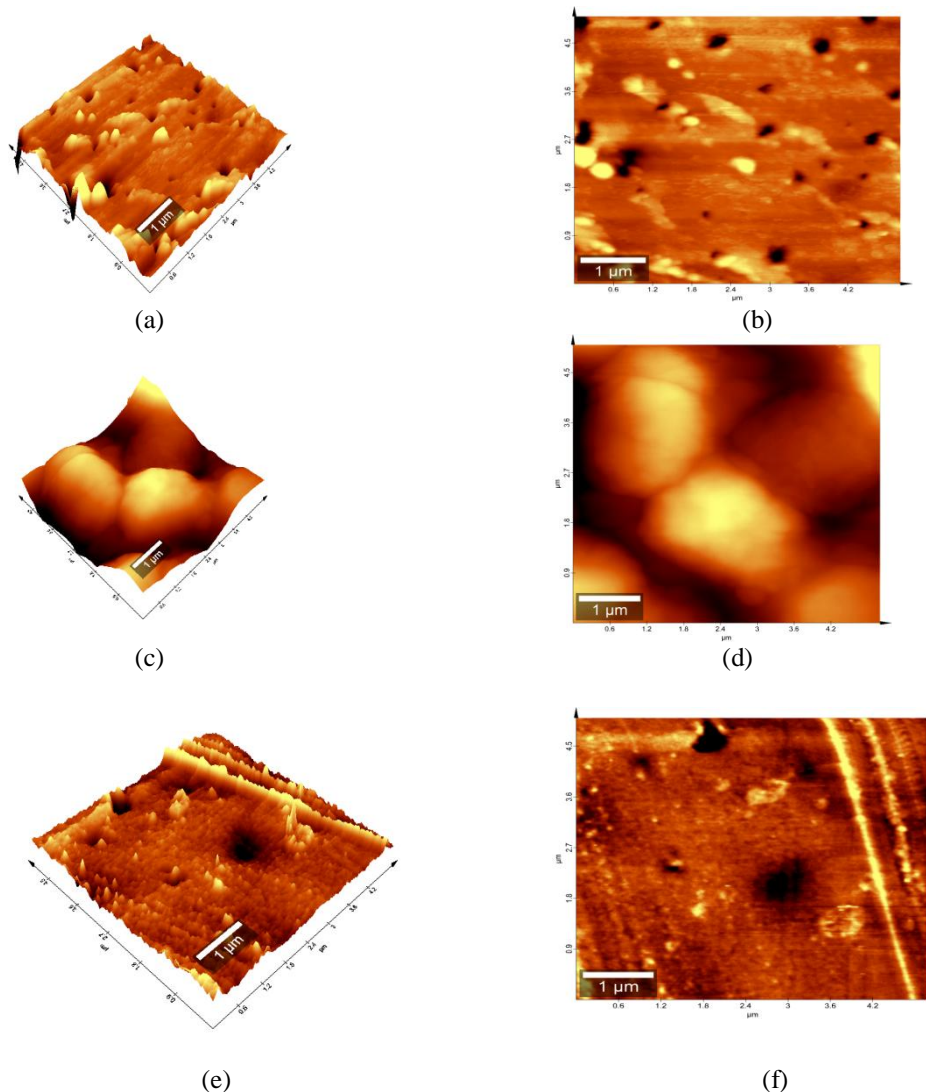
Blend films of PS and PPO in different compositions were prepared using solvent cast technique by taking PS and PPO in 95:05; 90:10; 85:15; and 80:20 weight % ratios, the sample thickness ranging from 20 to

90 micrometers for DSC, AFM analysis and 1 millimeter thickness for Microhardness measurement. The solution was constantly stirred with the help of electronic motor operating at 200 rpm for 3 h at room temperature to obtain homogeneous gel. The gel so obtained was poured on glass plate floating over mercury pool inside an oven at 50°C for 24 hrs, so as to yield films with uniform thickness. The films were then removed from the glass plate and stored in air-tight polyethylene bags for further characterization.

3. RESULT AND DISSCUSSION:

3.1 ATOMIC FORCE MICROSCOPY (AFM):

For miscible polymer system [3] the existence of spherical micro and domain structure morphology depends on the solvent and the nature of the polymer system. AFM measurement on polymer blend samples were carried out by means of Alpha 300RA AFM (SAIF, Kottayam). The surface morphology [4] of the one dimensional and three dimensional AFM images of pure PS, 5%PPO, 10%PPO, 15%PPO, 20%PPO were measured as shown in Fig. 1a- 1l respectively. Each AFM image is analyzed in terms of surface average roughness. A fine granular surface structure is exhibited by Polystyrene, while poly (phenylene oxide) appears to be coarser in texture, AFM micrographs taken for the polystyrene/ poly (phenylene oxide) blends shows no new types of morphological feature at the surface(i.e., no evidence for any phase separation). Moreover, increasing the poly(phenylene oxide) concentration in the blend mixtures led to the ongoing disintegration of the fine granular polystyrene morphology.



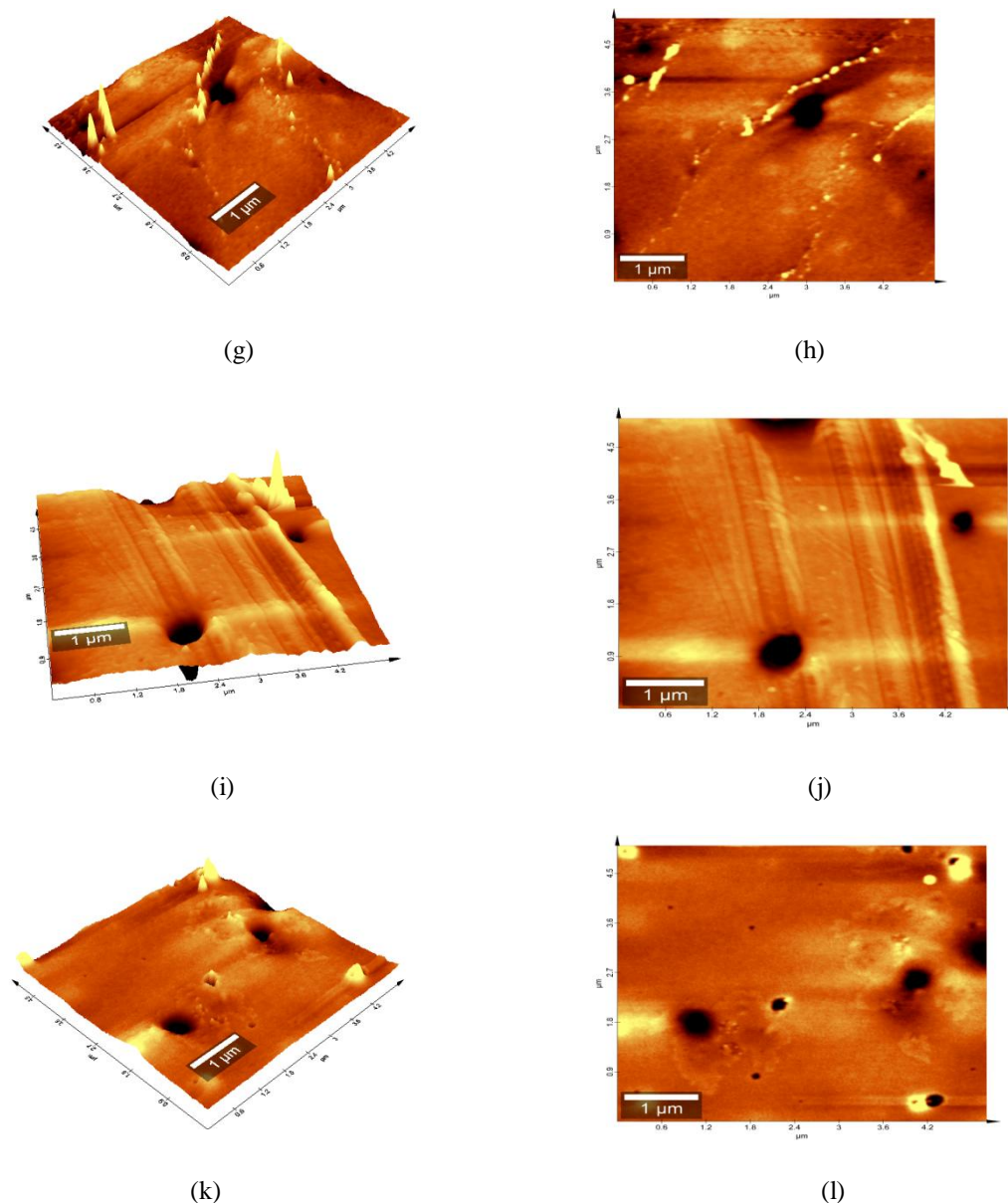


Fig 1: AFM images of (a) 3D image of pure PS (b) 2D image of pure PS (c) 3D image of pure PPO (d) 2D image of pure PPO (e) 3D image of 5% PPO + PS (f) 2D image of 5% PPO + PS (g) 3D image of 10% PPO + PS (h) 2D image of 10% PPO + PS (i) 3D image of 15% PPO + PS (j) 2D image of 15% PPO + PS (k) 3D image of 20% PPO + PS (l) 2D image of 20% PPO + PS

3.2 Differential scanning calorimetry (DSC):

DSC measurement on polymer blend film samples were carried out by means of Mettler Toledo DSC 822e (STIC cochin) The differential scanning calorimetry (DSC) curve of pure PS, pure PPO, 5%PPO+PS, 10%PPO+PS, 15%PPO+PS,20%PPO+PS are shown in fig. 2a- 2f.

From Table 1 it is very clear that glass transition temperature of pure PPO is higher in comparison to pure PS and other PPO: PS blends. As the PPO content in PPO:PS blend increases, the glass transition temperature also increases upto 10wt.% of PPO above this value, glass transition temperature starts decreasing for 15 and 20 wt.% of PPO. The appearance of single Tg for all the blend samples indicates single phase behavior of the material and also confirms the miscibility of PPO with PS.

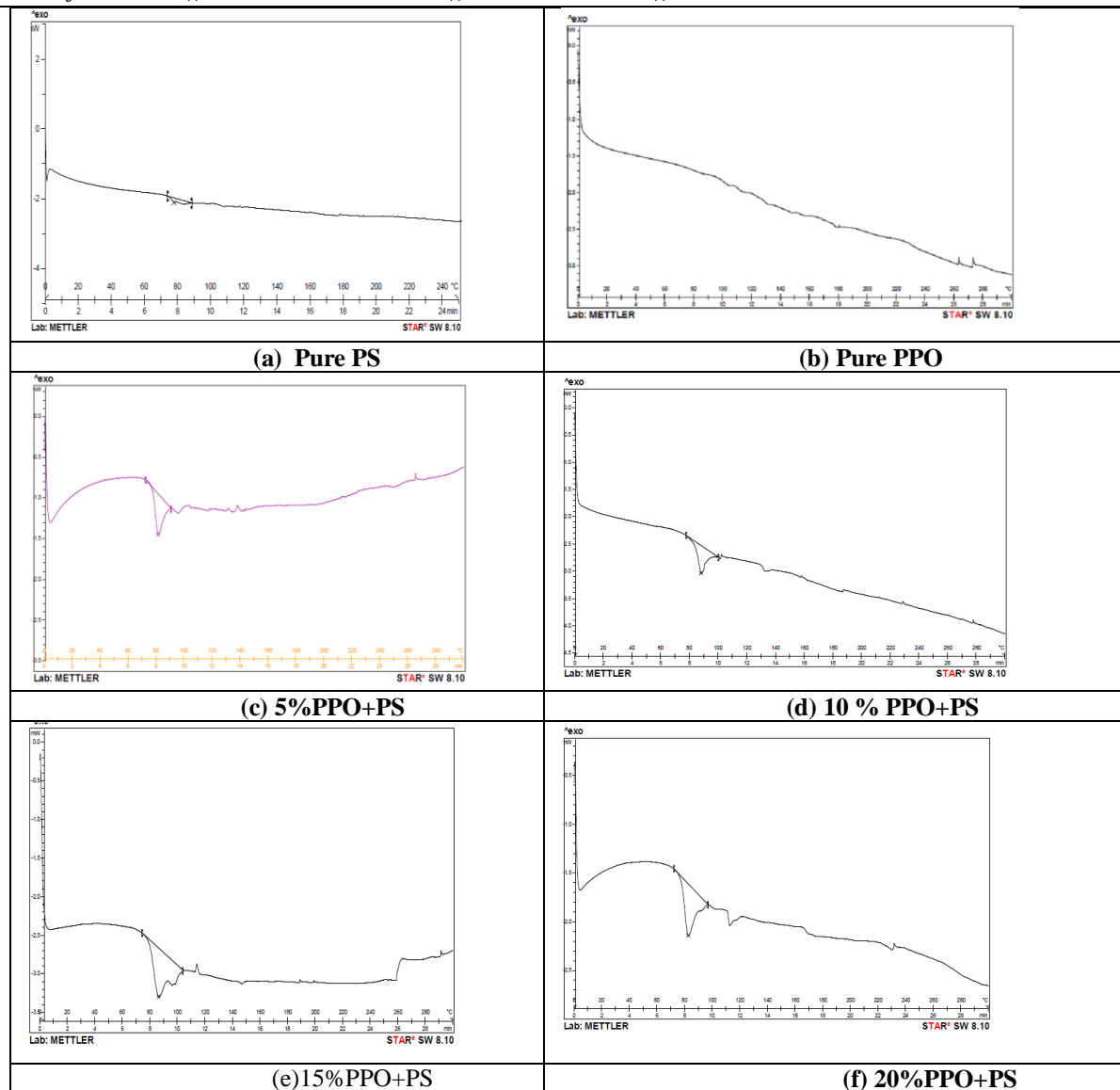


Fig 2: DSC thermogram of (a) pure PS (b) pure PPO (c) 5% PPO + PS (d) 10 % PPO + PS (e) 15 % PPO +PS (f) 20 % PPO + PS.

Table 1: Glass transition Temperature T_g (°C)

S. No	Weight % of PS	Weight % of PPO	Glass transition Temperature (°C)
1	100	0	77.94
2	95	5	81.63
3	90	10	88.24
4	85	15	86.40
5	80	20	82.61
6	0	100	182.23

3.3 Measurement of Microhardness

The micro indentation hardness technique has in recent years found to have widespread application in polymer research [5]. A very attractive feature of this technique is its ability for the micro-mechanical characterization of polymeric materials [6]. This technique on one hand is relatively simple and on the other hand very sensitive to the phase behaviour of the heterogeneous system, it may serve as an important tool in gaining a straightforward and deeper insight into the microstructure morphology correlation [7]. Microhardness measurement on polymer blends film samples (1mm thickness) were carried out by means of mhp-160 microhardness tester. Indentation was made with a Vickers's diamond pyramidal indenter having a square base and pyramidal angle of 136° between the opposite faces attached to Carl-Ziess NU-2 microscope. Samples of dimension 0.25 cm² was cut and fixed firmly with non reactive adhesive on an optically plane glass plate in such a way that surface to be indented was perfectly horizontal. The plate along with the sample was then mounted on the stage of the microscope, so as to avoid any displacement of sample during indentation. The load ranging from 10 to 80 g was applied gently at a steady rate; care was taken to avoid any jerk and vibration during indentation. The time of application of load was kept 30 sec in each case. The length of the diagonal made by the indenter was measured by a micrometer eyepiece with an objective of sufficient magnification.

Fig 3 illustrates the variation of H_v with load of indentation for pure PS, pure PPO, and PPO/PS polymer blends. In all the curves, the microhardness increases at a faster rate up to a load of 30g, and thereafter, up to 60g this rate of increase slows down, however, beyond 60g, H_v tends to saturate as no appreciable change in the value of H_v are observed with further increase in load. The increase in H_v with increasing load can be explained on the basis of strain hardening phenomenon [8].

In the polymer chains, there is spectrum of micromodes of deformation. Every micromode is achieved by its characteristic temperature and stress condition. When sufficient number of micromodes becomes active, large scale plastic deformation begins. As the load increases, the specimen is subjected to greater and greater strain hardening and consequently, the increase in the value of H_v is observed. The phenomenon has also been explained with the help of theory given by Amontons [9]. According to this theory, the microhardness may be correlated to the frictional force. The coefficient of friction decreases with increasing load and the frictional force is found to increase linearly with increasing load. Thus the variation of H_v with load is curvilinear and microhardness initially increases with increasing load. On applying load polymer blends are subjected to some strain hardening. Finally, when H_v value tends to saturate, the polymer blends are fully strain hardened.

3.3.1 EFFECT OF PPO

The effect of PPO content in the PPO/PS blends, microhardness has been investigated by varying the concentration of PPO from 5 wt. % to 20 wt. %. The results are shown in fig.3 which reveals that the value of H_v is maximum for pure PPO and minimum for pure PS, thus pure PS is soft in comparison to pure PPO and PPO/PS blends. The result also reveals that the value of H_v increases with increasing load up to 60g and tends to saturate beyond this load on the sample.

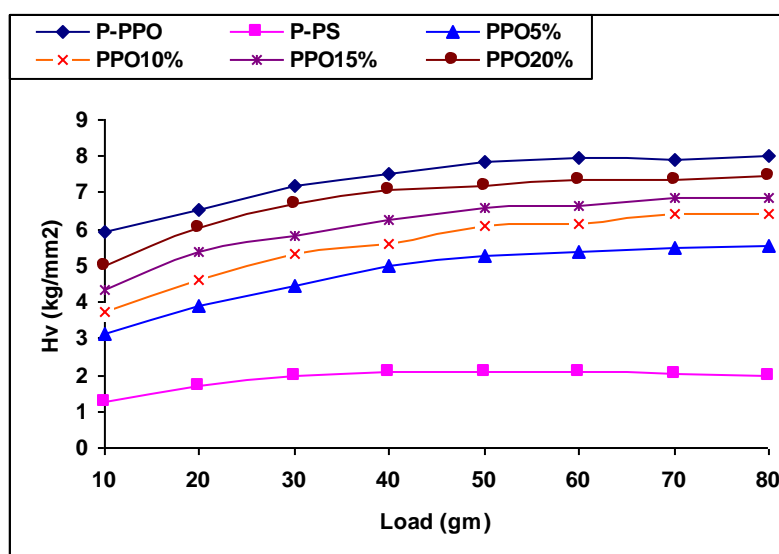


Figure 3. Variation in Microhardness with load.

The dependent nature of microhardness of materials can be determined by strain hardening index of Mayer's law [10]. This gives the relation between load L and length of diagonal d.

$$L = a \cdot d^n$$

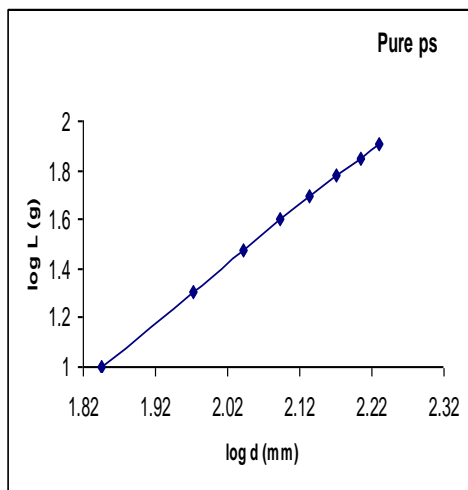
Taking logarithm on both side of the equation, we have

$$\text{Log } L = \log a + n \log d$$

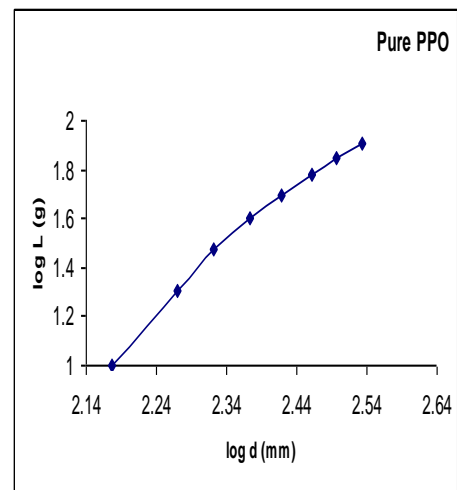
Where a is constant i.e. load for unit dimension and n is logarithmic index number which is measure of strain hardening

The strain hardening index (n) helps in calculation and understanding the stress strain behaviour. One may use it to characterize the elastic and non elastic deformation occurring in a specimen as a result of increased stress [11]. The dependence of microhardness on load can be studied with the help of Mayer's relation as stated earlier.

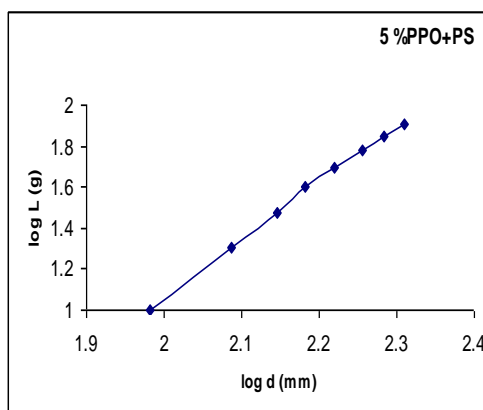
The plot of log d vs. log L, for pure PS, pure PPO and PPO/PS blend samples are shown in the fig. 4a-4f . It can be observed from these plots that there are two clearly recognizable straight lines for all the specimens. The first part of the straight line corresponds to the observation taken at low (10 to 40 g) loads and has slope n₁ of higher value, whereas the second part of the straight line corresponds to higher loads (from 40 to 80 g) having slope n₂. The values of n for pure PS, pure PPO, and polyblends having different wt % ratio of 95:5, 90:10, 85:15, and 80:20 are listed in table 2. Meyer's law indicates that the values of H_v increases continuously with load, when n is greater than 2, and H_v becomes independent of load in the saturation load region where the value of n approaches to 2. The different values of n for different specimen shows the varying degree of strain hardening which shows the changing morphology and crosslinking in the pure polymer.



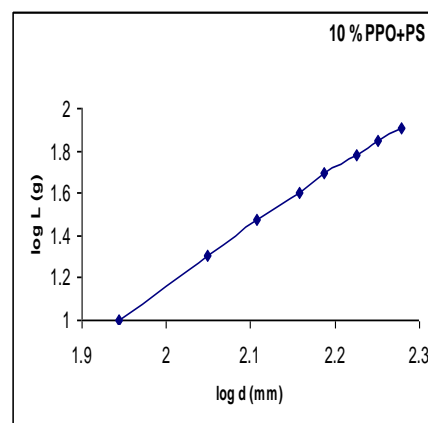
(a)



(b)



(c)



(d)

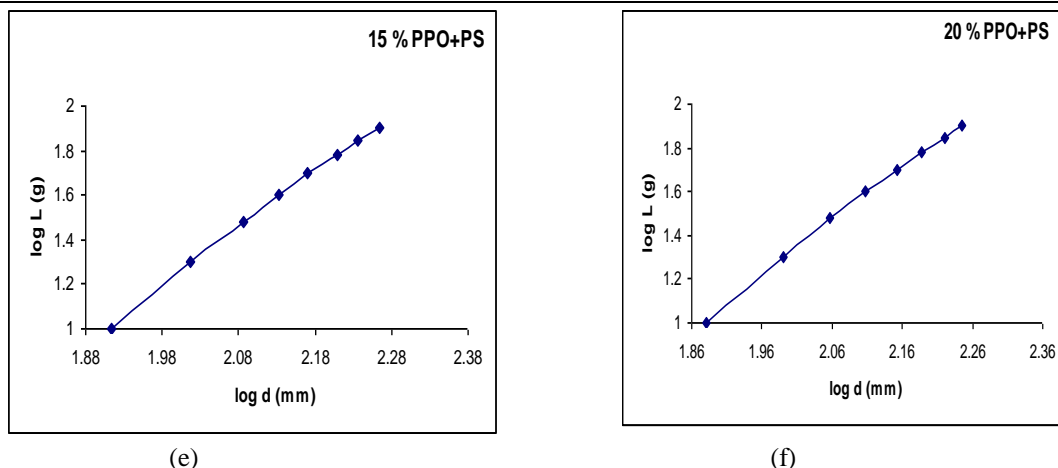


Figure 4: Log d vs log L plot for (a) pure PS (b) pure PPO (c) 5% PPO + PS (d) 10 % PPO + PS (e)15 %PPO +PS (f) 20 % PPO + PS.

Table 2 Values of slopes in low load region and high load region

S. No.	Blend sample PPO:PS in wt. % ratio	Value of Slope	
		low load region(n_1)	high load region (n_2)
1	Pure PS	2.4204	2.1746
2	Pure PPO	3.2601	1.8706
3	5 % PPO	2.9887	2.2903
4	10 % PPO	2.8431	0.9518
5	15 %PPO	2.7769	2.2839
6	20 % PPO	2.6695	2.1747

4. RESULT AND DISCUSSION

Miscibility over the entire composition range for polystyrene/poly(phenylene oxide) blends has been known for a long time and widely investigated using a variety of techniques (e.g., glass transition temperature [12], neutron scattering studies [13], etc.). Infrared [14] and ultraviolet [15] spectroscopic studies have shown that this high miscibility arises from strong interactions between the phenyl rings contained in poly(phenylene oxide) and polystyrene. Pure polystyrene or blends with a high polystyrene content tend to be brittle. However, blends with a poly (phenylene oxide) content of greater than 30% are ductile glasses [16]. The dynamics of PPO/PS become less volume dependent with increasing concentration of PS. We expect environments enriched in PS to facilitate relaxation of PPO segments because the PS has a lower T_g . This means that PS segments will tend to have relaxed when segmental relaxation of the PPO is considered [17]. These interactions can be used to account for the observed disappearance of the parent polystyrene granular surface morphology upon blending with poly (phenylene oxide). Typically for a polymer blend; one would expect surface enrichment of the component with the lowest surface energy [18]. Polystyrene and poly (phenylene oxide) have surface energies of 33 and 41 dyn cm^{-1} [19, 20]. Therefore, surface enrichment of polystyrene would be expected in the case of polystyrene/poly- (phenylene oxide) blend mixtures. Pure PS is softer than Pure PPO, when we increase the PPO content in the PPO/PS polymer blend the developed blend is harder than pure PS and as we go on increasing PPO content in the blend hardness goes on increasing. Thus hardness is minimum for pure PS, increases with PPO content up to 20 % of PPO and maximum for pure PPO.

5. CONCLUSION

The present study reveals that the polymer blends of PPO: PS can be prepared. Due to the disruption of phenyl ring stacking associated with polystyrene by interpenetrating poly(phenylene oxide) chains the surface topography characteristic of each constituent is destroyed [21]. The DSC studies support the formation of completely miscible polymer blends of PPO: PS.. The strong $\pi-\pi$ electron conjugation interaction between the aromatic rings of PS and PPO plays the key role in the miscibility of PS and PPO blends [22]. The glass transition temperature of the blend increases with PPO content in the sample up to 10 wt. %, above this value glass transition temperature starts decreasing with increasing PPO content in the sample. Pure PPO is hard polymer ($T_g = 182.23^\circ C$) when blended with comparably softer polymer PS ($T_g = 77.94$) the T_g of the blends increases. The microhardness studies indicate that the, microhardness of PPO/PS polymer blend increases with

increase in PPO content from 5- 20 wt. %, which shows the mechanical stability of PPO/PS blends. Thermal studies have been carried out to characterize the blends.

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