1 Introduction
Polyamides (PAs) are among the engineering thermoplastics which have found great attractions in engineering components due to its good mechanical properties, suitable processability and low cost. However, the reinforcement of these thermoplastics is highly intended for demanding applications. For this purpose, various micro and nano particles have been examined for the reinforcement of PAs. Recently, reinforcement of these thermoplastics by carbon nanotubes (CNTs) have been the subject of some research works because of the superior multifunctional properties of CNTs such as excellent mechanical, electrical and thermal properties as well as unique geometry, i.e. tubular shape with very high aspect ratio. Most of them have focused on the solution mixing method and a few has used melt mixing method for preparing PA/CNT nanocomposites. Amongst PAs, PA6 and PA66 are the most common polyamides which can be used for producing various injection molded articles as well as textiles. These two PAs show different melting, theological and mechanical characteristics. The nanocomposites of PA6/CNT and PA66/CNT produced by melt mixing have been characterized separately [1-2]. In this investigation, the rheological and morphological characteristics of PA66/PA6 filled with multi-walled CNT (MWCNT) were explored. The rheological property is very important parameter from the view point of processing characteristics. It also reflects that dispersion state of the polymer nanocomposites. Recently, it was reported that the dispersion state of MWCNT in PA6 and PA66 depends strongly on their rheological properties [2].

2 Experimental
PA66, PA6 were purchased from Radici Group and Hyosung, respectively, and MWCNT (TNMC3, COOH content of 2 wt%) was procured from Timesnano, china. PA66/PA6 blends and PA66/PA6/CNT nanocomposites were prepared by a Brabender 350E internal melt mixer with a cavity size of 370 cm$^3$ all at chamber temperature of 280 ºC. The weight ratio of PA66/PA6 varied from 0 to 1. The ternary nanocomposites always included 1 wt% MWCNT. Injection molded specimens were used for tensile testing and dynamic mechanical-thermal experiments (DMTA, Tritec-2000). Thermal transition and crystallinities were determined by differential scanning calorimeter (DSC, Pyris 1, Perkin-Elmer) at heating rate of 10 ºC/min. The rheological properties were characterized using MCR300 with amplitude of 1 % at frequencies of 0.08-500 Hz and temperature of 280 ºC. Scanning electron microscopy (SEM, Philips XL30) was used to investigate the morphology.

3 Results and discussions
DSC thermograms of PA66/PA6 and PA66/PA6/CNT (not shown here) showed a single peak demonstrating that PA66/PA6 blends and their nanocomposites are miscible systems. The crystallization temperatures ($T_c$) and the heat of crystallizations ($\Delta H_c$) extracted from the DSC thermograms are shown in Fig. 1.
It is evident that the $T_c$ of PA66 decreases and $\Delta H_c$ of PA66 increases almost linearly by increasing the PA6 content, justifying the miscibility of PA66/PA6 system at full range of blend compositions. The same behavior, linear trend, was found to be valid for the PA66/PA6/CNT system as well. As can be inferred from Fig.1, presence of CNT (1 wt%) results in the enhancement of $\Delta H_c$ and $T_c$ of the corresponding PA66/PA6 blends. Such behavior can be attributed to the nucleating role of CNT in the polyamides which has been reported frequently by the researchers [3]. However, it is interesting to note that the extent of enhancement of $\Delta H_c$ and $T_c$ for the ternary nanocomposite compared to their corresponding binary blends depends sensibly on the PA6 content. While the amount of increment of $T_c$ in presence of CNT increases by the increase of PA6 content, the role of PA6 in the nanocomposite on the $\Delta H_c$ enhancement is found to be inverse, i.e. extent of enhancement of $\Delta H_c$ decreases by the increase of PA6 content. Such behavior will be examined further using morphological behavior in this study.

Fig. 2. Complex viscosity vs. frequency (a) PA6/PA66 blend, (b) PA6/PA66 nanocomposites.

Fig. 2 displays the variation of complex viscosity versus angular frequency. It is evidenced that PA66/PA6 blend show shear thinning behavior over the whole frequencies investigated in this study. This behavior is also observed for the ternary nanocomposites but at low frequencies, i.e. less than 10 Hz. Shear thinning exponents, which can be obtained from the power law relationship, i.e. $\eta=A\omega^n$, were found to be $n=\sim-0.025\sim-0.07$ for PA66/PA6
blends and $n=-0.03$ to $0.09$ for PA66/PA6/CNT nanocomposites. At higher frequencies, the ternary nanocomposites show almost Newtonian behavior which may be attributed to the alignment of CNT at higher shear rates.

The effect of PA6 content on the complex viscosity of PA66/PA6 blends and their nanocomposites at selected angular frequencies are demonstrated in Fig. 3. It is revealed that the viscosity of blends varies from 205 Pa.s for pure PA66 to 85.4 Pa.s for PA6, i.e. almost 60% reduction in viscosity of PA66 by increasing the PA6 content. Much lower viscosity of the PA6 compared to PA66 is possibly due to the higher temperature of rheological tests compared to the melting temperature of PA6, i.e. $T_m = 217$ °C. It is to be noted that the variation of complex viscosity with PA6 content obeys the rule of mixture with good precision at least at low frequencies, i.e. linear trend, which is a unique characteristic of miscible system. This result is in accordance with DSC data presented in Fig. 1.

As shown in Fig. 3, it is found that the incorporation of CNT leads to the enhancement of complex viscosity of the samples due to the formation of polymer-CNT interactions restricting the molecular mobility. From Fig. 3, it appears that the extent of enhancement in the viscosity build up by incorporation of CNT is restricted by increasing the PA6 content. Wang et al. [4] reported that the incorporation of CNT at low contents, less than 0.5 wt% in their study, in PA6 leads to the reduction/minor increase in complex viscosity possibly due to the enhancement of free volume caused by the formation of viscous surface layers around the CNT leading to easier flow. The restricted increase in the complex viscosity of PA66/PA6/CNT at higher PA6 content can be attributed to the promotion of the formation of viscous surface layer around the CNT. As the mixing temperature for all the samples were set to be 280 °C where the viscosity of the PA6 is very small, as shown in Fig.3, the extent of enhancement of viscosity of PA6-rich system is restricted even at 1 wt% loading possibly due to the easier formation of viscous surface layer.

The rheological data presented above can be used to explain the dispersion of CNT in the PA66/PA6 systems via melt mixing method. Kasaliwal et al. [5] showed the CNT bundles may be dispersed via two competing
mechanisms including rupture and erosion mechanisms. In PA66/PA6/CNT systems investigated here, due to the lower viscosity of PA6-rich system, the infiltration of melt into the CNT bundle is encouraged for the PA6-rich systems due to their lower viscosity leading to domination of erosion dispersion mechanism [5]. On the other hand, for PA66-rich system, the rupture mechanism, in which higher shear stress destroys the agglomeration, is supposed to be dominant mechanism.

Fig. 4. SEM microphotographs of (a) PA66/CNT and PA6/CNT.
Actually, the erosion mechanism occurs slowly but the breakage of CNT is very limited and the CNT is well infiltrated. The rupture mechanism often leads to fine dispersion but with a high risk of fiber breakage leading to lower aspect ratio of CNT. Fig. 4 depicts the SEM images of CNT filled compounds at two extremes of PA66-rich and PA6-rich systems, i.e. PA66/CNT and PA6/CNT. As can be seen for PA66-rich system, a uniform dispersion of CNT is observed, whereas the presence of bunch of dispersed CNTs emphasizes the domination of erosion mechanisms for PA6-rich systems during which polymer melt is infiltrated first into the CNT agglomerates.

Thermal transition behavior and evolution of crystalline structure in existence of CNT presented in Fig. 1 can be explained based on the dispersion mechanisms defined above. The infiltration of CNT bundles by the polymeric melt for PA6-rich nanocomposite makes possible higher polymer-CNT interfacial area signifying the nucleating role of CNT. Such behavior makes possible the nucleation of crystallites at higher temperature during the cooling of melt resulting in higher T_c in presence of CNT. However, the limited increase of ΔH_c for PA6-rich nanocomposites can be attributed to the confinement of polymers within the CNT bundles which is caused by the melt infiltration. Such confined polymer melt restricts the growth of crystalline structure leading to lower increase in the ΔH_c for PA6-rich nanocomposites.

4 References
