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Synthesis and Crystallization Studies of Thermo-plastic Polyster/Titania Nanocomposites

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Abstract The present work reports the non-isothermal crystallization kinetics of PET-TiO_2 nanocomposites. The average particle size of TiO_2 nanoparticles, prepared by chemical route, has been calculated 32 nm using Debay-Scherrer's formula in XRD peaks. PET-TiO_2 nanocomposites have been synthesized using solution casting method. The investigation of non-isothermal crystallization behavior has been conducted by means of Differential Scanning Calorimeter (DSC). The crystallization temperature shift to lower temperature for both PET pristine and PET-TiO_2 nanocomposites due to decrease in mobility of chain segments and heterogeneous nucleation. Also, the inclusion of TiO_2 nanoparticles may accelerate nucleation rate in nanocomposites that causes the crystallization time and absolute crystallinity fraction. The thermal conductivity of inorganic filler TiO_2 nanoparticles may affect the crystallization temperature.

Keywords: XRD, DSC, crystallization temperature, polymer nanocomposites.

1. INTRODUCTION

Nowadays Polyethylene Terephthalate (PET) is considered a high consumption polymer of important commercial interest due to its wide applications as for plastic packing (e.g., beverage bottles, cosmetic containers, food, pharmaceutical packaging) [1]. PET is a slowly crystallizing polymer that can be obtained with different degrees of crystallinity (0–50%) as a result of specific thermal and/or mechanical treatment to which it is submitted [1-2]. The thermal properties of PET are used in food-packaging, peel-able seals, lids, vacuum insulation panels etc. In the packaging industry, to improve barrier performance to ultraviolet rays, as well as adding strength, stiffness, dimensional stability and heat resistance [3]. Titanium oxide (TiO_2) is most commonly used inorganic filler in polymer nanocomposites. The use of TiO_2 is advantageous over capping agents in the chemical reduction process of metal ions, as it is free from the blocking of active sites by organic capping agents [4]. Also the inclusion of TiO_2 nanoparticles in polymer matrix, results the heterogeneous nucleation effect which provides more sites for nucleation.

Many of researches show that TiO_2 nanoparticles enhance the crystallization rate of PET, and led to a large increase in the crystallization temperature. Jeziorny and Mo's

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methods were applied to describe the kinetics of the non-isothermal crystallization process of PET matrix with incorporated surface-treated TiO_2 particles as well as pure nano-TiO_2 particles [5]. The crystallization behavior of PET based nanocomposites containing 3 wt % of different nanoparticles (MontMorilloniTe–MMT; titanium dioxide–TiO_2; and silica dioxide–SiO_2) using DSC shows all fillers behave as nucleating agents for PET except SiO_2 that acts as inhibitor in case of DIM procedure [1]. In the present study, we focus on the non-isothermal crystallization behavior of neat PET and PET-TiO_2 nanocomposites prepared by solution casting method.

2. MATERIALS AND METHODS

Firstly, TiO_2 nanoparticles have been synthesized via chemical route using $TiCl_3$ and NH_4OH solution [6]. The obtained white precipitate of TiO_2 nanopowder was dried at room temperature. These TiO_2 nanoparticles were added in PET solution with Dichloro methane (DCM) and Trifluoro acitic acid (TFA). Using solution casting method, the membranes of PET were prepared with different wt % of TiO_2 nanoparticles (1, 2, 3 wt%). Such prepared samples were used for further study of crystallization behavior with Differential Scanning Calorimeter (DSC).

3. RESULTS AND DISCUSSION

The average grain size of TiO_2 nanoparicles has been determined by X-Ray diffraction (XRD) with CuK_α radiation in the range of 20-70° (λ=0.154nm) using Scherrer equation [7]

$$D=0.89\lambda/ (\beta \cos\theta) \quad (1)$$

Where D is mean grain size, λ is the wavelength ($Cu K_\alpha$), β is the full width at the half-maximum (FWHM) and θ is the diffraction angle. Figure 1 shows the XRD pattern of TiO_2 nanoparicles, the average particle size of these nanoparticles was found to be 32nm.

Non-isothermal crystallization kinetics of TiO_2 nanoparticle filled composites of PET has been studied using NETZSCH DSC 204 F1 Phoenix. The samples were heated up to 300 °C with different heating rates (5, 10, 15 and 20K/min)and held for 5 min to remove its previous thermal history. The crystallization behavior has been investigated by cooling these samples from 300 to 30 °C with the same cooling rate corresponding to that particular heating rate.

The crystallization peaks after melting pristine PET and 1 wt% TiO_2 nanocomposites at different cooling rates are shown in figure 2. As cooling rate increased, the crystallization onset, peak and end temperatures, T_s, T_p and T_e, shift to lower temperature for all samples. The fact influencing the occurrence of crystallization is nucleation and growth process. When PET and its nanocomposites were cooled through its melting temperature, due to heterogeneous nucleation, growth of new phase particles plays a major role in lowering the crystallization temperature.

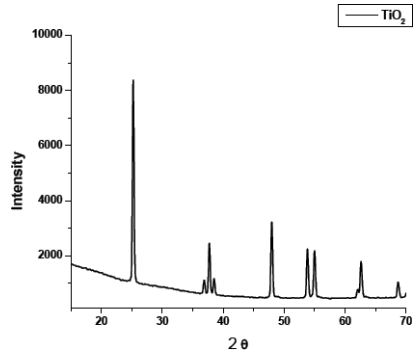

Figure 1: XRD pattern of TiO_2 nanoparticles prepared by chemical method.

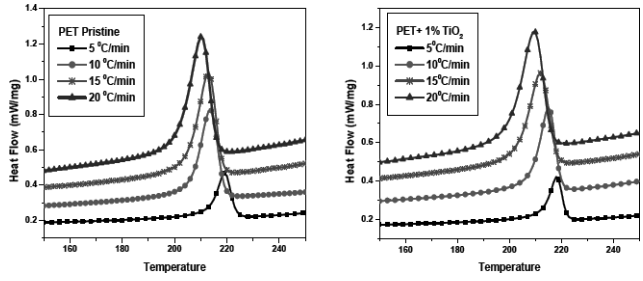

Figure 2: DSC thermograms of pristine and PET+ 1 wt% TiO_2 nanocomposites.

The overall crystallization time, t_c, can be determined as followed [8]:

$$t_c = \frac{T_s - T_e}{a} \tag{2}$$

Where a is the cooling rate, T_s is the initial crystallization temperature, and T_e is final crystallization temperature. Due to heterogeneous nucleation effect, inclusion of TiO_2 nanoparticle in PET matrix may cause to reduce the overall crystallization time as well as the increment in cooling rate also results to lower t_c. Figure 3 represents the overall crystallization time of PET-TiO_2 nanocomposites at various cooling rates. The values of crystallization parameters have been listed in table 1.

The absolute crystallinity fraction X_c at different cooling rates can be calculated using following relation [8]:

$$X_c = \frac{\Delta H_c}{\Delta H_f^0 \, W_{polymer}} \times 100 \tag{3}$$

Where ΔH_f^0 ~ 140 J g^{-1} and $W_{polymer}$ is the weight fraction of the polymer matrix.

Table 1: Crystallization parameters of PET-TiO_2 nanocomposites.

Sample	Cooling rate ($^{\circ}C\ min^{-1}$)	T_m($^{\circ}C$)	T_s($^{\circ}C$)	T_p($^{\circ}C$)	T_e($^{\circ}C$)	H_c(Jg^{-1})	X_c (%)
Pristine PET	5	253.7	214.54	219.25	222.71	15.96	11.4
	10	253.43	207.78	213.53	217.79	18.14	12.9
	15	253.8	205.77	213.11	217.65	18.43	13.2
	20	252.62	202.03	210.24	215.71	18.85	13.3
PET + 1% TiO_2	5	246.86	214.00	218.22	221.51	13.75	9.72
	10	253.7	209.73	215.13	219.11	15.8	11.1
	15	253.92	204.49	211.95	217.23	16.12	11.4
	20	252.98	201.08	209.45	215.24	17.25	12.1
PET + 2% TiO_2	5	253.37	215.74	220.11	223.53	14.95	10.5
	10	253.78	210.02	215.53	220.45	16.63	11.7
	15	253.23	205.11	212.03	216.90	17.78	12.4
	20	253.81	200.92	209.29	214.58	19.74	13.8
PET + 3% TiO_2	5	245.1	212.85	217.36	220.90	14.5	10.0
	10	252.93	208.58	214.23	218.40	14.88	10.3
	15	254.68	204.54	211.39	216.37	15.5	10.7
	20	254.36	200.81	208.83	214.16	18.36	12.7

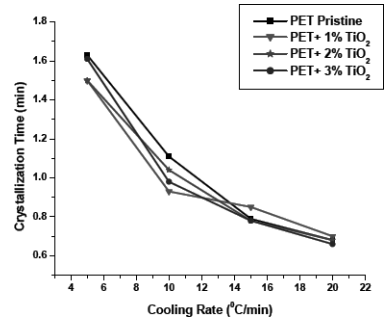

Figure 3: Overall crystallization time for PET-TiO_2 nanocomposites at various cooling rates.

As listed in table 1, the degree of crystallinity has been increased by addition of TiO_2 filler content. This may be explained as TiO_2 nanoparticles were working as nucleation agent in PET matrix under non isothermal crystallization condition [8].

4. CONCLUSION

TiO_2 nanoparticles were synthesized using chemical method and average particle size was determined 32 nm with the help of XRD. PET-TiO_2 nanocomposites were prepared

by solution casting method and non-isothermal crystallization behavior was carried out using DSC. The thermograms reveal that crystallization temperature shifts to lower temperature with increasing cooling rate. The nucleation and growth process causes to lower overall crystallization time and increase the absolute degree of crystallinity with inclusion of TiO_2 content.

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