STUDY ON HIGHER DISPERSION OF TITANIUM DIOXIDE PARTICLES DURING POLYMERIZATION OF POLY (ETHYLENE TEREPHTHALATE) (PET)

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Abstract

Zeta (ζ)-potential of TiO_2 particles in the BHET/ EG mixture as an alternative material of PET with various additives for PET polymerization such as metallic salts, phosphoric acid and alkyl phosphates was investigated by electrophoretic mobility method. The dispersion stability of TiO_2/BHET/EG suspension was influenced due to the decreasing ζ -potential in absolute value by the addition of metal acetates as well as phosphates. The addition of $K_5P_3O_{10}$ in the TiO_2/BHET/EG suspension restrained the change of ζ -potential from negative to positive, resulting in higher dispersion of TiO_2 particles in it. It was proved in the actual polymerization of PET that the addition of $K_5P_3O_{10}$ is so effective for the dispersion of TiO_2 particles in PET, even if in the presence of metallic salts, phosphoric acid and its alkyl phosphates.

1. Introduction

Poly (ethylene terephthalate) (PET) is an excellent commercial thermoplastic polymer, which is now used in lots of fields. Its physical and chemical properties are improved by the incorporation of inorganic particles such as titanium dioxide (TiO_2), silica (SiO_2) and calcium carbonate ($CaCO_3$). PET is also endowed with new functions by the addition of inorganic particles. TiO_2 has been added and dispersed as a light scattering agent and an ultraviolet light absorbent in PET.

Good dispersion of TiO_2 particles in a polymer is very important for the achievement of high performance as well as a highly efficient afterward-processing on its practical use. The incorporation of inorganic particles such as TiO_2 into PET is usually carried out by either melt-mixing or in-situ polymerization method. The uniform and productive dispersion of submicron inorganic particles with the size of less than 1μm into a polymer by melt mixing is very difficult because of high viscosity of the polymer. In the case of in-situ polymerization of PET, TiO_2 is pre-dispersed in ethylene glycol (EG) and the obtained suspension of EG/TiO_2 is added to participate in the PET polymerization process. Though good dispersion of TiO_2 is obtained in EG by the various methods, the TiO_2 particles often aggregates due to the reaction temperature and the additives during the polymerization of PET.

In the previous paper, the effect of additives such as metal acetate salt, phosphate ester, Sb_2O_3 and amine on ζ-potential of TiO_2 particles in EG has been investigated with the electrophoresis method [1]. It was concluded that the addition of metal acetate salts and phosphate esters neutralizes the negative charges on TiO_2 particle surfaces, which results in the decrease of electrical repulsion forces between TiO_2 particles to be dispersed in EG and PET, while the addition of TEA in the TiO_2/EG suspension leads to the increase of ζ-potential in absolute value, resulting in the improvement of the TiO_2 dispersion. In addition, it was confirmed by model experiments and actual PET polymerization that TEA has a strong ability to disperse TiO_2 particles, even if in the presence of aggregation accelerators such as metal salts and phosphoric acid. However, EG was used as a model of PET in the previous paper, where the effect of the terephthalic acid unit (benzene ring) in PET was not considered.

In this work, by using bis(hydroxyethyl terephthalate) (BHET)/EG solution instead of EG as a model of PET, the effect of additives such as metal acetate salt, phosphate ester and salt on ζ-potential of TiO_2 particles has been investigated with the electrophoresis method. In addition, the influence of the polymerization conditions on the dispersion of TiO_2 particles in PET is discussed on the basis of the above results.

2. Experimental

2.1. Reagents and materials

TiO_2 (TA-300, anatase type) was supplied by Fuji Titanium Industry Co. Ltd. Terephthalic acid (TPA) and ethylene glycol (EG) of fiber grade were purchased. Bis (hydroxyethyl terephthalate) (BHET) was prepared by the transesterification of dimethyl terephthalate (DMT) with EG and purified by the recrystallization with water. All other reagents, phosphoric acid (($HO)_3PO$) (PA), trimethyl phosphate (($CH_3O)_3PO$) (TMPA), triethyl phosphate (($C_2H_5O)_3PO$) (TEPA), potassium polyphosphate ($K_5P_3O_{10}$), cobalt acetate ($Co(OAc)_2$), calcium acetate ($Ca(OAc)_2$), antimony trioxide (Sb_2O_3)) were of analytic grade and used without any further purification.

2.2. Preparation of TiO₂/BHET/EG suspension with additives

BHET/EG (0.05 mol/L), phosphoric compound/EG (0.5 mol/L), metal compound/EG (0.05 mol/L) and TiO_2/EG (0.5wt %) suspension were prepared. BHET/EG solution was mixed well with the TiO_2/EG suspension with a stirrer, and a suitable amount of the additive/EG solution was put into the obtained mixture. The TiO_2/BHET/additive/EG mixtures were applied for the following electrophoresis measurement.

2.3. Preparation of PET

PET was prepared from TPA and EG with the incorporation of TiO_2/EG suspension and additives/EG solution according to the conventional polycondensation method (TPA/EG method). The target of intrinsic viscosity was 0.62 dl/g and the concentration of TiO_2 in PET was 0.5wt%. All the additives were added together with EG monomer. The number of TiO_2 particles with the size of larger than 5 μm (aggregates) in a unit area of PET was measured by means of an optical microscope.

2.4. Measurements of ξ-potential of TiO₂ particles

The measurements of ξ-potential of TiO$_2$ particles in the TiO$_2$/BHET/additive/EG suspensions were carried out according to the previous paper [1, 2].

3. Results and discussion

3.1. Effect of BHET on ζ-potential of TiO₂ particles and their dispersibility

Fig.1 shows the effect of BHET on the ξ-potential and dispersion behavior of TiO$_2$ particles. TiO$_2$ particles dispersed in EG exhibited ζ-potential of -72mV. Absolute value of their ζ-potential decreased to a small absolute value with the increase of BHET. Our previous paper revealed that TiO$_2$/EG suspension with the absolute values of ζ-potential below 30 mv aggregated easily, possibly due to the lack of electric repulsion between TiO$_2$ particles. The reason why TiO$_2$/BHET/EG suspension showed good dispersion stability lies in the adsorption of BHET on TiO$_2$. Adsorbed BHET possibly prevents from the aggregation of TiO$_2$ particles. Then it is presumed that PET oligomer and polymer adsorb easily on TiO$_2$ particles during PET polymerization, which contributes to the dispersion of TiO$_2$ particles.
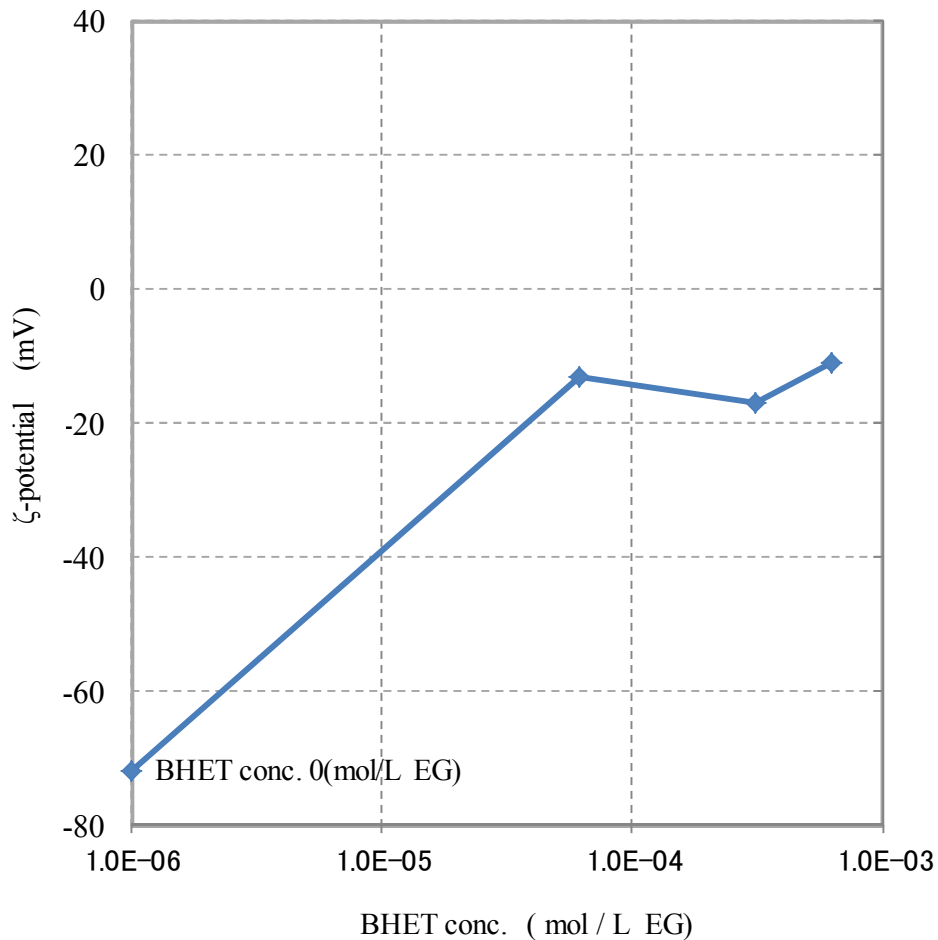

Figure 1. Effect of BHET on ζ-potential of TiO$_2$ particles

3.2. Effect of metallic compounds on ζ-potential and dispersibility of TiO$_2$ particles in the presence of BHET

It was reported that TiO$_2$ particles dispersed in EG exhibited ζ-potential of -72mV, and the addition of metallic salts such as Co(OAc)$_2$ and Ca(OAc)$_2$ changed ξ-potential from minus value to plus value (decrease of absolute value of ξ-potential) to bring about TiO$_2$ aggregation. Aggregation of TiO$_2$ particles was observed in the TiO$_2$/EG suspension when its ζ-potential was ranging from -30 mv to +30 mv. On the other hand the addition of Sb$_2$O$_3$ exhibited good dispersion behavior of TiO$_2$ particles in spite of a large change of ξ-potential [1].

Fig.2 shows the effect of metallic compounds such as Co(OAc)$_2$, Ca(OAc)$_2$ and Sb$_2$O$_3$ on the ξ-potential and dispersion behavior of TiO$_2$ particles in the TiO$_2$/BHET/EG suspension. The sign "ppt" shown in Fig.1 stands for the aggregation of TiO$_2$ in the suspension. In spite of the presence of BHET the ξ-potential value changed from negative to positive value ranging from -20 mV to +20 mV with the increase of metallic compounds at the conventional concentration (10^{-5}~10^{-4}mol/mol EG). In addition, while TiO$_2$ particles aggregates were observed in the BHET/EG suspension with Co(OAc)$_2$ and Ca(OAc)$_2$, they were dispersed well in the BHET/EG suspension with Sb$_2$O$_3$. As for Co(OAc)$_2$ and Ca(OAc)$_2$, there was little change in the ζ-potential values and dispersion behavior between in the presence and in the absence of BHET which means they adsorb strongly on the surface of TiO$_2$ than BHET. As for Sb$_2$O$_3$, the ξ-potential value came close to 0 mV with the increase of Sb$_2$O$_3$ without evolution of TiO$_2$ aggregates. Such ξ-potential and dispersion behaviors are the same with those of TiO$_2$ in the TiO$_2$/BHET/EG suspension, which means that Sb$_2$O$_3$ adsorbs on TiO$_2$ weaker than BHET. In conclusion, the order of adsorbing ability is as follows.

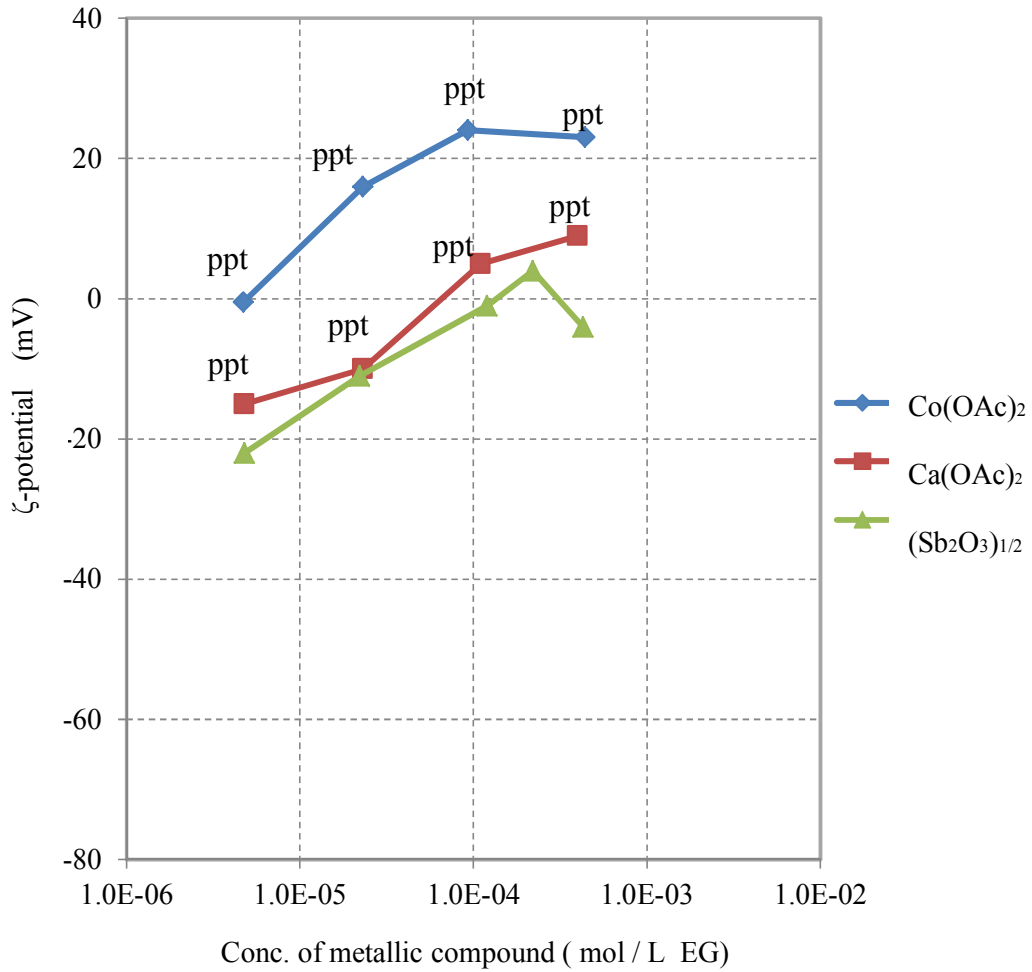(Strong adsorption)   Co(OAc)$_2$, Ca(OAc)$_2$ >>> BHET > Sb$_2$O$_3$ (weak adsorption)

Figure 2. ξ-potential versus concentration of metallic compounds

3.3. Effect of phosphoric acid compounds on ζ-potential and dispersibility of TiO_2 particles in the presence of BHET

Fig.3 shows the effect of phosphoric acid compounds such as PA, TMPA, TEPA and $K_5P_3O_{10}$ on the ξ-potential and dispersion behavior of TiO_2 particles in the TiO_2/BHET/EG suspension. As for PA, TMPA and TEPA, the ξ-potential value changed from negative to positive value through 0 mV with their increase at the conventional concentration (10^{-5}~10^{-4}mol/mol EG), which ranged from -20 mV to +40 mV. There was no difference in the ξ-potential and dispersion behavior of TiO_2 particles between the TiO_2/BHET/EG suspension and TiO_2/EG suspension. The ξ-potential in TiO_2/EG suspension was not influenced by the addition of BHET, which revealed that PA, TMPA and TEPA adsorbed stronger than BHET to bring about the decrease of ξ-potential, resulting in the TiO_2 aggregation.
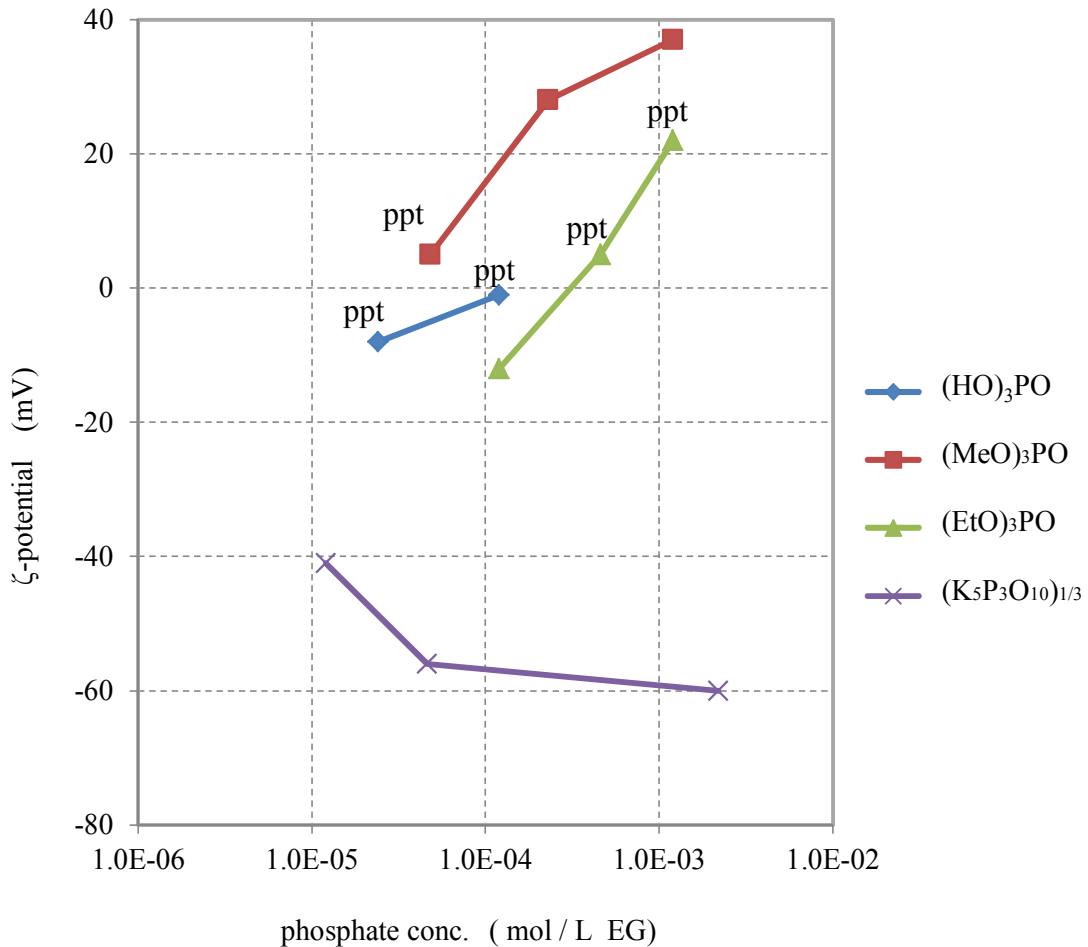
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Figure 3. ξ-potential versus concentration of metallic compounds

3.4. Effect of $K_5P_3O_{10}$ on dispersion of TiO_2 in the TiO_2/BHET/EG suspension

Table 1 shows the ζ –potential values of TiO_2/EG and TiO_2/BHET/EG suspension added with $K_5P_3O_{10}$, where TiO_2 aggregation was not observed. The addition of $K_5P_3O_{10}$ in the TiO_2/BHET/EG suspension brought about a change of ζ –potential value to further negative value. Its ξ -potential in absolute value was increased by the addition of $K_5P_3O_{10}$ in spite of the presence of BHET, which means that $K_5P_3O_{10}$ adsorbs stronger on TiO_2 surface than BHET to stabilize more the TiO_2 suspension. The dispersion ability of $K_5P_3O_{10}$ to TiO_2 possibly resulted from the adsorption onto the surface of TiO_2 particles, which caused the increase of negative charge on it. $K_5P_3O_{10}$ yields possibly a thicker double layer to give more stable dispersion of TiO_2 particles in the suspension, which is due to a larger electrostatic repulsive force between two TiO_2 particles.

Table 1. Effect of $K_5P_3O_{10}$ addition on ζ-potential of TiO_2 particles

$K_5P_3O_{10}$ (mol/mol EG)	ζ -potential (mV)	
	EG	BHET/EG
0	-72	-17
1.2E-5	-75	-41
4.6E-5	-76	-56
2.2E-3	-72	-60

TiO_2/EG : 0.5 wt %, BHET/EG : 4.7×10^{-4} mol/mol EG

3.5. Effect of $K_5P_3O_{10}$ on dispersion of TiO_2 in the actual polymerization of PET

Preparation of PET was carried out with different kinds of additives according to the usual procedure. The number of PC-5μ in obtained PET was evaluated and the results were listed in Table 2. By the comparison of No.1 and No3 experiments, the addition of $K_5P_3O_{10}$ decreased the number of larger size particles (PC-5μ in PET) from 6 to 4. PET obtained in the No.2 experiment showed a large PC-5μ value (26), which was due to the aggregation of TiO_2 by the addition of Co(OAc)$_2$, Ca(OAc)$_2$ and TMPA. However, the number of PC-5μ was decreased from 26 to 9 by the introduction of $K_5P_3O_{10}$ as shown in the No.4 experiment. In summary, it was made clear that $K_5P_3O_{10}$ has a strong ability to control effectively the dispersion of TiO_2 particles during the polymerization of PET.

Table 2. PC-5μ of PET obtained with different additives

Exp. No.	Additives (TiO$_2$ / PET = 0.5 wt%)				PC-5μ in PET
	Co(OAc)$_2$ (mol%)	Ca(OAc)$_2$ (mol%)	(CH$_3$O)$_3$PO (mol%)	K$_5$P$_3$O$_{10}$ (mol%)	
1	0	0	0	0	6
2	0.0012	0.0021	0.0044	0	26
3	0	0	0	0.00009	4
4	0.0012	0.0021	0.0038	0.00009	9

Catalyst: Sb$_2$O$_3$ (0.025 mol%), Temp.: 275 ℃ Press.: 0.1 mmHg, Time: 1.5 h

3. Conclusion

The effect of additives used during polymerization of PET on the ζ-potential and aggregation behavior of TiO_2 particles was studied according to electrophoretic mobility method by using TiO_2/BHET/EG suspension as a model of TiO_2 added PET polymer. Since there was no difference in the ζ-potential and dispersion/aggregation behavior of TiO_2 particles between TiO_2//EG and TiO_2/BHET/EG suspensions, the existence of BHET dissolved in TiO_2/EG slurry has no influence on dispersion/aggregation behavior of TiO_2 particles.

The addition of $Co(OAc)_2$, $Ca(OAc)_2$ PA, TMPA and TEPA neutralizes the negative charges on TiO_2 particle surfaces, which results in the decrease of electrical repulsion forces between TiO_2 particles to be dispersed in EG and PET. The addition of $K_5P_3O_{10}$ in the TiO_2 /BHET/EG suspension leads to the increase of ζ-potential in absolute value, and contributes to the TiO_2 dispersion.

It was confirmed by the model experiments and actual PET polymerization that $K_5P_3O_{10}$ has a strong ability to disperse TiO_2 particles, even if in the presence of aggregation accelerators such as metal salts and phosphoric acid.

References

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