Preparation of Hybrid Polyester with Uniformly Dispersed Silica Particles

Shinji Yamaguchi

Fiber Research & Development Department, Kuraray Co., Ltd., Sakazu, Kurashiki, 710-8622, Japan

Abstract : The alkaline-etching of polyester fiber has improved the feeling of the cloth and of the dyed goods. In the process, the control of dispersion state of inorganic micro particle in polyester became extremely important. After a few types of colloidal silica's were added to ethylene glycol, the polymerization were carried out under several conditions. It was concluded that, for achieving better dispersion of silica particles in polyester matrix, colloidal silica which was stable in basic circumstance and the lower esterification temperature were preferable. The particle dispersion was observed by the transmission electron microscopy. After measurement of distances between the particle centers, the dispersion state was analyzed using Rayleigh's statistics which allow us to evaluate the dispersion state whether the particles aggregated or the particles dispersed uniformly.

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1. Introduction

In Material science and technology, hybridization combining inorganic with organic materials in micro scale has created various new functions. This trend also directed to the fiber technology. Recently polyester has often been spun with micro inorganic particles, which were subsequently dissolved with alkaline chemicals leaving concaves and convexes on the fiber surface. This rugged surface improved the properties of polyester fabrics, such as the feeling and deepening of color [1] so that this treatment is generally called as the silk-like processing [2]. It is important in this processing that the fine particles distribute uniformly in polymer matrix. In this study, we developed the techniques for making the uniform particle distribution during polymerization, and the method for quantitative analysis of the particle dispersibility is proposed.

2. Theory

Let us assume that spherical particles distribute uniformly in polymer matrix as in Fig.1. From the geometry, number of particles in 1 unit volume N is expressed as

$$N = 3\alpha\rho_1 / 4\pi\rho_2 r^3 \quad (1)$$

where

$$\rho_1 = \rho_p\rho_2 / \{ \rho_2(1-\alpha) + \rho_p\alpha \} \quad (2)$$

 ρ_1 ; hybrid polymer density

ρ_p and ρ_2 are densities of matrix polymer and spherical particle respectively. r is radius of the particle, and α is weight fraction of particle in the hybrid polymer. Distance between the particle centers L can be expressed as follows.

$$L = N^{-1/3} \quad (3)$$

Fig.1 Schematic picture of inter-particle distance in perfect (uniform) dispersion.

Theoretical relation between L and r was calculated assuming that ρ_p for polyester was 1.38 g/cm^3 and ρ_2 for silica particle 2.20 g/cm^3 . Figure 2 shows that L is also dependent upon r . When silica content α

exceeds 80 wt%, L approach the particle diameter, i.e., the particles start to aggregate each other.

Fig.2 Calculated distance (L) of particle's-center vs content of silica in polyester.

We discussed here on an ideal case of particle distribution but, in practice, the particles do not take uniform distribution in polymer matrix. It is well known that the assembly set which has a dissymmetry distribution can be conveniently analyzed by Rayleigh's distribution [3]. The probability density function of Rayleigh distribution can be written as

$$p(\tau) = 2\tau / \lambda^2 \exp(-\tau^2 / \lambda^2) \quad (4)$$

where λ is a distributional parameter.
So the distribution function is

$$p(L) = \int_0^L p(\tau) d\tau = 1 - \exp(-L^2 / \lambda^2) \quad (5)$$

Finally equation 5 is transformed to

$$L^2 = -\lambda^2 \ln(1 - p(L)) \quad (6)$$

After cumulative frequency $p(L)$ is obtained from the relative frequency, it would be confirmed whether as far as Rayleigh's statistics is hold, L^2 and logarithm of $(1 - p(L))$ should keep a proportional relation. In the case, λ expresses a parameter for the dispersion state of the particles distributed.

3. Experimental

Polyester was prepared by the direct polymerization of terephthalic acid and ethylene glycol. Before esterification, colloidal silica was added to ethylene glycol at concentration of 3 wt%. Several types of colloidal silica were used (Table 1). L-AM was

smaller particles with narrow distribution in the particle size. This was used for calibration of detectability of particle distribution by the transmission electron microscopy (TEM).

Table 1 Properties of colloidal silica's

Sample	SiO ₂ content wt%	Particle size (nm)	pH	$\xi - P^{a)}$ (mv)
L-AM	30	14	9	
A;acid type	20	45	4	-13
B;basic type	20	45	9.5 ~ 11	-46
C;basic type	40	45	10	-48

^{a)} $\xi - P$: ξ - potential measurement(PEN-KEM)

The particle diameters are mean values determined by TEM and BET absorption methods.

The other 3 colloidal silica's have larger particle size but their decentralization pH ranges were different each other. After mixing terephthalic acid and ethylene glycol at mole ratio of 1.5 with 0.035 wt% of antimony oxide, esterification was carried out at 250 °C at internal pressure of 0.117 MPa, subsequently polymerized under reduced pressure at 285 °C. Polymerization was stopped at time when the intrinsic viscosity of the reactant reached 0.65-0.67 (dl/g) (intrinsic viscosity measured in equal weight mixture solvent of the phenol and tetrachloroethane at 30 °C). In order to examine influence of the reaction temperature on the coagulation state of silica particles, esterifications were carried out at temperatures 10 °C above and also below 250 °C (the standard esterification temperature). Colloidal silica generally forms stable decentralization by repulsive force of the surface silanol groups [4]. It is well known that decentralization state is metastable in the pH range of 2- 4, and stable in the pH range of 8- 10, but silica is apt to aggregate near isoelectric point [5]. In this study, we dispersed the colloidal silica in ethylene glycol and polymerized with terephthalic acid. Though the colloidal silica was dispersed homogeneously in ethylene glycol, following problems might happen on the esterification. (1) Addition of terephthalic acid decreased pH of the reaction system, and might induce aggregation of the particles. (2) Heating the reactants

up to ca. 250 °C facilitated coagulation of the silica particles. (3) Dehydration for increasing degree of esterification and polymerization also changed the stable decentralization. The details were written in the patents [6-8]. Thus it is necessary to ascertain whether the reaction system keeps the uniform dispersion of the colloidal silica throughout the polymerization.

Ultrathin sections of silica hybrid polyester were cut with a diamond knife in the ultramicrotome (Lica Co.: Reichert ULTRACUT-S). Thickness of the section was controlled to be ca. 80 nm. The sections were then observed by a transmission electron microscope (TEM, Hitachi Ltd : H-800N-A) at magnification of 20,000. The photographs were enlarged twice (x40,000), and the distances between particle centers were measured with calipers.

L was obtained directly from the TEM photographs as follows. The accuracy was ± 2.5 nm.

(1) Three particles in the shorter distance from the particle at an arbitrary position were selected and the distance L between the particles were measured.

Number of the distance measurements = 3^1

(2) The other 3 particles were selected for each particle previously selected and the distances were measured.

Number of the distance measurements = $3^1 + 3^2$

(3) The measurement was repeated until the total number of the distance measurements became 300 or more.

$$3^1 + 3^2 + \dots + 3^{n-1} + 3^n > 300 \text{ or more}$$

4. Result and Discussion

4.1 Reliability of TEM in measuring the inter-particle distance

TEM of ultrathin section of silica(L-AM)polyester hybrid is shown in Fig.3. Number of silica particles observed within unit area was 1180 pieces / μm^2 on the average. On the other hand, the number of silica particles in unit volume was calculated to be 1.32×10^{16} pieces/ cm^3 using the equation (1). This value reduces to 1056 pieces/ μm^2 when observed in projection of the ultrathin section with thickness of 80 nm. For this particle diameter (14nm), the average inter-particle distance was calculated to be 42 nm which is shorter than the thickness of the ultrathin section. So there remained a possibility of inaccuracy in the particle counting that plural particles might

overlapped somewhere and might be observed as one particle, but we actually obtained good coincidence in the density between the observation and the estimation.

With the other larger particles, the overlapping should decrease because L become larger than the thickness, leading to higher reliability of this method.

Thus we can use this TEM observation for analysis of the particle dispersion in the following silica hybrid polyesters.

Fig.3 TEM of silica(L-AM) hybrid polyester.

4.2 Dependency of the particle dispersion on the colloidal silica property.

Figures 4, 5 and 6 are TEM's of the silica hybrid polyesters prepared with A, B and C types of colloidal silica, respectively. Particle coagulation is clearly observed on TEM of the silica hybrid polyester prepared with A type of colloidal silica which was metastable in acidic circumstance. On the contrary, on both with B and C types, particles were apparently observed isolating. But closer observation revealed that the particles with more silica content (from C-type colloidal silica) coagulated a little more than that from B-type.

Generally, the colloidal silica forms sol in stable at lower concentration but tends to coagulate with higher concentration. Esterification which inevitably accompanied dehydration increased the concentration of the colloidal silica in the reaction system, hence the metastable A-type colloidal silica was segregated. This factor would also be applied to the particle formation from B- and C-types colloidal silica(NaOH, though they were stable in alkaline circumstance).

Fig.4 TEM of silica(A-type) hybrid polyester polymerized at 250 °C (at the standard esterification temperature).

Fig.5 TEM of silica(B-type) hybrid polyester.

Fig.6 TEM of silica(C-type) hybrid polyester.

4.3 Influence of esterification temperature on the particle dispersion in the polymer matrix

TEM's of silica(B-type) hybrid polyesters prepared at 240 °C and 260 °C are shown in Figs.7 and 8, respectively. Comparison of these figures and Fig.5 shows that silica particles aggregated more and more with increasing the esterification temperature. Thus esterification at low temperature using B-type colloidal silica gave us the best distribution of silica particles in the polyester matrix.

Fig.7 TEM of silica(B-type) hybrid polyester esterificated at 240 °C (10 °C below the standard esterification temperature).

Fig.8 TEM of silica(B-type) hybrid polyester at 260 °C (10 °C above the standard esterification temperature)

4.4 Distribution analysis of the silica particles

It should be examined whether the particle distributions were able to be adjusted to the Rayleigh's distribution statistics as a set. By enlarging the TEM, the distance between silica particles was measured according to the method mentioned in the experimental part. Figure 9 shows a histogram of frequency of the best dispersion of particles shown in Fig.7.

Fig.9 Distribution of silica particles in silica hybrid polyester prepared at 240 °C.

Fig.10 Accumulation of relative frequency at 240 °C on low temperature condition

Figure 10 is the cumulative frequency derived from Fig.9.

For the analysis L^2 plotted against $\ln(1-p(L))$ according to equation (6). Fig.11 clearly shows a straight line. As mentioned above, this specimen has no aggregation, the Rayleigh's relation can be applied to the analysis of a system with particle distribution without aggregation.

Fig.11 Plot of $L^2 - \ln(1-p(L))$ using data of Fig. 10 according to Rayleigh's distribution.

From the slope, the distribution parameter λ was determined to be 67.1 nm. On the other hand, in the case of silica hybrid polyester prepared at higher temperature, Fig.12 shows the plot of $L^2 - \ln(1 - p(L))$ deviated from a straight line, i.e., the particle aggregation made the line curved.

Figures 13, 14 and 15 show histograms of L in the silica hybrid polyesters prepared with A-, B- and C-types colloidal silica's at the standard esterification temperature (at 250 °C). Frequency at L lesser than the particle diameter means the aggregation of the particles.

In Fig.15, the distribution curve is unsymmetrical being extremely inclined toward left side. This means

that silica(C-type) hybrid polyester contained many two particle coagulation. As for the silica(A-type) hybrid polyester, the histogram has two maximum peaks one of which located at less than the particle diameter and the other extended long toward the right side. Here there are many aggregations and the aggregations were distributed widely. In order to analyze these distributions more quantitatively, we plotted the L^2 as a function of $\ln(1-p(L))$.

Fig.12 Plot of $L^2 - \ln(1-p(L))$ in the case of silica hybrid polyester prepared at 260 °C.

Fig.13 Distribution of silica particles in silica (A-type) hybrid polyester prepared at 250 °C.

Fig.14 Distribution of silica particles in silica (B-type) hybrid polyester prepared at 250 °C.

Fig.15 Distribution of silica particles in silica (C-type) hybrid polyester prepared at 250 °C.

The deviation from linearity became larger in the order of B , A , and C types. Though it was not so easy to understand the particle distribution state from the relative frequency histograms, this method where the deviation from the Rayleigh's distribution is used as a criterion give us clearer understanding of the particle distribution state.

Fig.16 Comparison of plots of $L^2 - \ln(1-p(L))$ among 3 types of silica hybrid polyesters.

5. Conclusion

Silica hybrid polyester was prepared by the direct polymerization of terephthalic acid and ethylene glycol mixed with a small amount of colloidal silica. In order to obtain good dispersibility of the silica particles, the polymerization was carried out at several temperatures using various kinds of the colloidal silica.

A method for quantitative evaluation of the dispersion state of the silica in polyester was proposed.

1. In order to distribute silica particles uniformly in

polyester matrix, the colloidal silica should be diluted in ethylene glycol and stabilized in weak basic circumstance. Also, silica hybrid polyester with good silica particle dispersion was obtained by lowering the esterification temperature.

2. The silica particle dispersion in ultrathin section of the silica hybrid polyester was observed by TEM.

The distance between silica particle centers was measured from TEM photograph. Good dispersion state has been analyzed according to the Rayleigh's relation which can expressed numerically the distribution state. In the case that the system has particle aggregation, Rayleigh's plot deviated from a straight line.

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