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ORIGINAL CONTRIBUTION

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A study on the surface free energy of modified silica fillers and poly(ethylene terephthalate) fibers by inverse gas chromatography

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Abstract The surface free energy of modified silica fillers and poly(ethylene terephthalate) (PET) fibers was analyzed by inverse gas chromatography in order to investigate the relationship between their surface characteristics and the performance of the composite formed from these materials. The adsorption isotherms of *n*-heptane and 1-propanol were determined by the elution-peak-maximum method. The dispersive and polar components of the surface free energy were determined by use of the Young–Dupré equation and the Fowkes equation on the basis of the saturated spreading pressure derived from the Gibbs adsorption equation. The acidity and the basicity of the surface were estimated by the specific retention volume of each probe molecule with different donor number and acceptor number. It was found that the dispersive component of the surface free energy for modified silica fillers was mostly lower than that for original silica filler. The polar component of the surface free energy for ethylene glycol modified silica filler became large, while that for *n*-butanol modified silica filler decreased remarkably. It was also found that original silica filler exhibited high acidity, while modified silica fillers exhibited low acidity. Although these methods have been applied to PET fibers, the surface free energy could not be determined quantitatively because of the surface change during the pretreatment of PET fibers. It was observed that the polar component of the surface free energy decreased when the pretreatment was made at a temperature higher than the glass-transition temperature of PET. It became clear that the interaction between modified silica fillers and PET fibers correlated well with the basicity of the fillers, but not with their acidity.

Key words Surface free energy · Silica · Modification · Poly(ethylene terephthalate) · Interaction of composite interface

Introduction

Inorganic fillers, which are manufactured by dry or wet processes, have been used to improve heat resistance, mechanical properties, and the coefficient of friction for plastics [1]. Especially, since silica fillers are generally added to poly(ethylene terephthalate) (PET) fibers or films in order to improve the aforementioned properties, it is important to analyze the interaction factor between them.

In this study, the surface free energy of modified silica and PET fibers was analyzed in order to estimate the relationship between the surface free energy and the interaction of the composite formed from these materials. Inverse gas chromatography (IGC) is believed to be an efficient method to evaluate the surface free energy of solids [2–12] and in fact has been successfully applied to fillers and fibers [13–22]. Previous studies using the IGC method have indicated the surface free energy of modified silica fillers [13, 17, 20], polyethylene fiber [15], and nylon fiber [21], but have never quantitatively analyzed the surface free energy of PET nor the relationship between the surface free energy of modified silica fillers and their interaction with PET. In the present study, silica fillers with submicron diameters made by the wet process were investigated in order to determine their surface free energy and to clarify their interaction with PET. IGC with a finite concentration system was used to evaluate the surface free energy of modified silica fillers and PET fibers on the basis of the retention theory of gas chromatography and the concept for the work of adhesion. Moreover, IGC with an infinite dilution system was used to evaluate the acid–base property of modified fillers. In order to estimate the composite performance between the silica filler and PET, the internal haze value of the PET film stretched biaxially was measured.

Experimental

Original silica filler (W-N) was prepared by acetone-cleaning, centrifugation, and vacuum-drying of the water dispersion of spherical silica made from water glass and had a mean diameter of 0.55 μm. The agents used for the surface modification of the silica filler are shown in Table 1. Ethylene glycol modified silica filler (W-E) was obtained by a procedure where W-N was treated in ethylene glycol at the boiling point for 2 h with the water generated being excluded. *n*-Butanol modified silica filler (W-B) was obtained by treating W-N with *n*-butanol in an autoclave at 523 K for 16 h. The modified silica fillers, W-*N*-[3-(trimethoxysilyl)propyl]-*N′*-(4-vinylbenzyl)ethylenediamine hydrochloride (VSSM), W-3-glycidoxypropyltrimethoxysilane (GPSM), and W-vinyltrimethoxysilane (VTSM) were obtained through a procedure where W-N (10 g) was agitated with the corresponding coupling agent (0.1 g) and water (1 g) at 363 K for 1 h and then at 403 K for 1 h. The modified fillers were finally cleaned using acetone, centrifuged, and vacuum-dried.

PET fiber (PN) of approximately 5-μm diameter was melt-spun without spin-finish (lubricant). PET fiber (PW) of almost the same diameter was melt-spun with water in order to avoid fiber electrification. PN-50 refers the PN treated at 50 °C (323 K).

The specific surface area of the samples was determined by the Kr adsorption isotherm measured volumetrically at 77 K. The number of silanol groups was determined by the reaction with thionyl chloride [23, 24] and the number of modified groups on the silica fillers was calculated from the elemental analysis results.

IGC measurements were carried out with a modified gas chromatograph (Honma Riken Co.) with a thermal conductivity detector at finite concentration or with a flame ionization detector at infinite dilution, both in He carrier gas. About 0.5 g of the sample was packed in the stainless steel column (40-cm long, inner diameter 4 mm). The flow rate was measured using a soap-film meter and was corrected for pressure drop and temperature change in the column by use of the James–Martin factor.

The adsorption isotherm in the finite concentration system was determined by the elution-peak-maximum method [25–27] at 313 and 323 K, at a flow rate of 10 cm^3/min for *n*-heptane and 20–50 cm^3/min for 1-propanol. The measurements in the infinite dilution system were carried out at 373 K and at a flow rate of 20 cm^3 min^{-1}.

The silica fillers were pretreated at 473 K for 12 h in He gas at a flow rate of 50 cm^3 min^{-1} and the PET fibers were pretreated at 323, 343, and 363 K for 12 h in He gas. He carrier gas was dehydrated through a molecular sieve 4-A trap before entering the column.

The degree of crystallinity (χ) of the PET sample was calculated using Eq. (1),

$$\chi = 100(\rho - \rho_a)/(\rho_c - \rho_a) \tag{1}$$

where the crystal density (ρ_c) is 1455 kg/m^3, the amorphous density (ρ_a) is 1335 kg/m^3, and the sample density (ρ) was measured by the density gradient tube method [28].

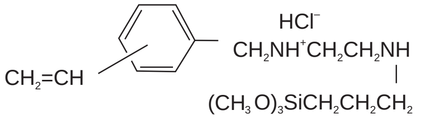
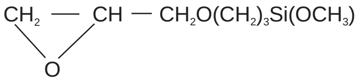
In order to evaluate the interaction between the silica fillers and PET, the internal haze value of the PET film containing 1 wt% of the original or modified silica fillers which was stretched biaxially 3 times at 363 K was measured and compared. The internal haze value was measured based on the method in ASTM D1003 by putting the film into tetralin so as to obtain only the haze value increased by the internal void without the influence of surface haze. The internal void generation is thought to be due to the fact that the PET–filler interface is broken when the interaction between the filler and PET molecules is less than the force to stretch PET molecules.

Theory

The adsorption isotherm can be obtained by integration [4, 6, 8],

$$q = 1/wRT \int_0^P V_N \, dp \ , \tag{2}$$

Table 1 Agents used for the surface modification

Abbreviation	Name	Molecular formula
W-N	–	–
W-E	Ethylene glycol	$HO\text{-}CH_2CH_2\text{-}OH$
W-B	*n*-Butanol	$CH_3CH_2CH_2CH_2\text{-}OH$
W-VSSM	*N*-[3-(trimethoxysilyl)propyl]-*N′*-(4-vinylbenzyl) ethylenediamine hydrochloride	
W-GPSM	3-glycidoxypropyl trimethoxysilane	
W-VTSM	Vinyltrimethoxysilane	$CH_2{=}CH\text{-}Si\ (OCH_3)_3$

where q is the amount of the probe adsorbed expressed in moles per gram, w is the weight of the solid, p is the vapor pressure of the probe that could be determined from the probe chromatogram, R and T are the gas constant and temperature, and V_N is the probe retention volume. On the basis of the relationship between p and q, the spreading pressure, π, could be calculated by use of the Gibbs adsorption equation.

Equation (3) is derived from the Young–Dupré equation and the Fowkes equation [29],

$$\pi + \gamma_L(1 + \cos\theta) = 2(\gamma_S^D \gamma_L^D)^{1/2} + 2(\gamma_S^P \gamma_L^P)^{1/2} \ , \qquad (3)$$

where γ_L is surface free energy of the probe, superscripts D and P mean the dispersive component and the polar component, and θ is the contact angle of the probe on the solid. Under the condition of saturation adsorption, the contact angle can be considered to be zero; therefore, values of γ_S^D and γ_S^P could be calculated by determining the spreading pressure at saturation adsorption, π_0, from adsorption isotherms of both *n*-heptane and 1-propanol. The specific surface area determined by Kr adsorption was applied to calculate the spreading pressure. The isosteric heat of adsorption, Q_{ST}, was calculated by use of Clausius–Clapeyron equation.

According to the Fowkes proposition [30–32] based on Lewis acid–base interaction or electron acceptor–donor interaction, the acidity and the basicity of the surface could be estimated from the logarithm of the specific retention volume of each probe molecule with different donor number (DN) and acceptor number (AN) in the infinite dilution system. The ability of a molecule to donate or accept electrons was defined by Gutmann [33] as the molar enthalpy of the reaction of the molecule with $SbCl_5$ (DN) [34] or the relative NMR chemical shift of ^{31}P in triethylphosphine oxide, $(C_2H_5)_3PO$, in the solvent of the respective molecule (AN) [35], respectively. DN and AN values [33] of all probes used in the experiments are presented in Table 2. It was also proposed that the specific interaction, I_{SP}, could be evaluated by comparing the specific retention volume of an *n*-alkane with that of the probe which has the same saturation vapor pressure as an imaginary *n*-alkane. I_{SP} was then defined as Eq. (4), the difference in ordinates between the logarithm of the specific retention volume of each probe plotted against its vapor pressure and the corresponding point of the reference line obtained from those of the alkane.

$$I_{SP} = RT \ln V_N - RT \ln V_N(\text{ref}) \ . \qquad (4)$$

Several reports demonstrated that there could be a linear relationship between the specific interaction of the fibers with probe molecules and their DN and AN [36, 37].

Table 2 Donor number (*DN*) and acceptor number (*AN*) of probe molecules used [33]

Molecules	DN	AN
n-Alkane	0	0
Benzene	0.1	8.2
Nitromethane	2.7	20.5
Acetonitrile	14.1	19.3
Methyl ethyl ester	17.1	9.3
Diethyl ether	19.2	3.9
Tetrahydrofuran	20.0	8.0
Carbon tetrachloride	0	8.6
Dichloromethane	0	20.4
Chloroform	0	23.1

Results and discussion

The specific surface area and the number of silanol groups or modification groups are shown in Table 3. It is considered that more than two-thirds of the total silanol groups were modified by ethylene glycol, *n*-butanol, and vinyltrimethoxysilane. The specific surface area of the original silica filler agreed well with the geometrical surface area (5.0 m^2/g).

The adsorption isotherms of *n*-heptane and 1-propanol for original silica filler and for modified silica fillers are shown in Fig. 1. The adsorption amount of 1-propanol for W-N is larger than that for *n*-heptane, which suggests that silanol groups on the silica filler interact specifically with hydroxyl groups of 1-propanol. The adsorption amount of *n*-heptane for modified silica decreased to some extent except for W-VSSM, suggesting that the surface activity decreased with the introduction of an organic chain on the surface. In the case of W-VSSM, an enhancement in the dispersion force by surface styryl groups and bipolar ions may be responsible for the increased adsorption of *n*-heptane. The adsorption amount of 1-propanol for W-N is almost equal to that for W-E, but is much larger than that for W-B. This is because alcoholic hydroxyl and butyl groups were generated on the former and the latter surface, respectively. The adsorption amount of 1-propanol decreased on W-GPSM and W-VTSM, but that on W-VSSM was almost equal to that on W-N. These results may be explained by the low polarity of VTSM group and a small number of attached GPSM

Table 3 The specific surface area and number of attached groups of original and modified silica fillers

Sample	Specific surface area (m^2/g)	Number of groups (number/nm^2)
W-N	5.5	6.0
W-E	4.8	4.0
W-B	4.5	4.7
W-VSSM	5.7	1.7
W-GPSM	6.0	2.4
W-VTSM	5.7	4.4

groups. The VSSM group, including bipolar ions, has a higher polarity though the number of groups attached is small.

As shown in Fig. 2, the isosteric heat of adsorption of 1-propanol for W-B was low at the initial stage of adsorption because of weak interaction and thereafter approached the heat of liquefaction, which corresponded to the result of the adsorption isotherm. The initial heat of adsorption of *n*-heptane for W-VSSM was high, while that of 1-propanol was similar to that for W-N. These results, together with the finding that the heat of adsorption of 1-propanol for W-VTSM was low, also reflected the adsorption isotherm behavior. The large isosteric heats of adsorption of 1-propanol at the initial stage and their decrease afterward for W-GPSM must be caused by both a small number of modified groups and high interaction with 1-propanol of modified groups.

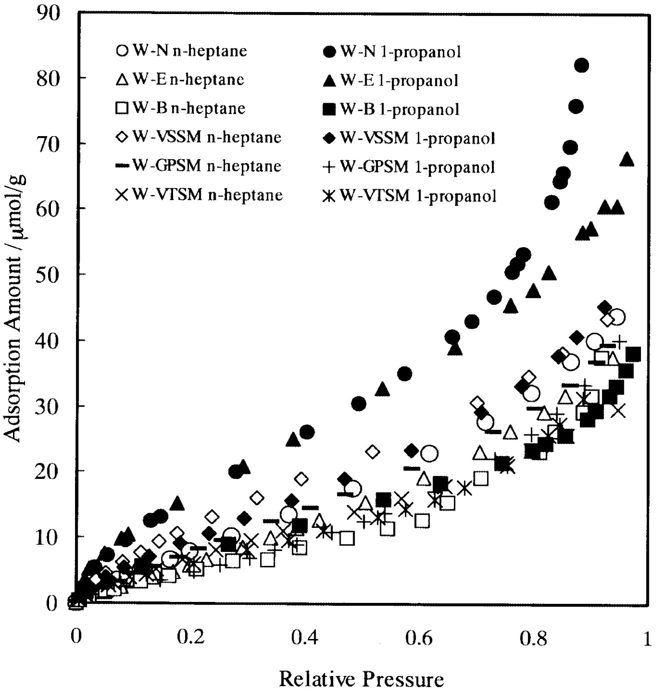


Fig. 1 The adsorption isotherms for original and modified silica fillers

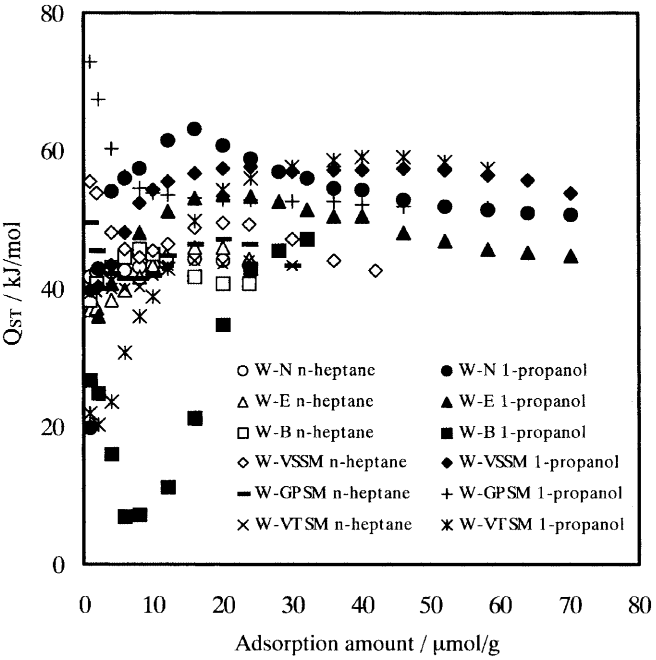


Fig. 2 The isosteric heats of adsorption for original and modified silica fillers

Values of π_0, γ_S^D and γ_S^P calculated by the aforementioned method are shown in Table 4. By introducing an organic component on the surface of the fillers, all γ_S^D decreased except for W-VSSM with styryl groups and bipolar ions. The γ_S^P values of W-N and W-E were large and those of W-B as well as the fillers modified by silane coupling agents were very small. In particular the γ_S^P of W-GPSM was the smallest regardless of the small number of attached chains, which can be interpreted by the fact that long organic chains of GPSM prevented the probe molecules from adsorbing on the residual silanol groups on the silica fillers.

The specific retention volumes of *n*-alkanes at infinite dilution were found to change linearly with their saturated vapor pressure for each filler; therefore, I_{SP}, could be calculated according to Eq. (4) for polar probes. By plotting I_{SP} values of each probe molecule against its DN, an almost linear relationship was obtained as shown in Fig. 3. The slope indicates the acceptance of electrons on the surfaces of the silica fillers, in other words, the acidity. As shown clearly, the original silica, W-N, exhibits the highest acidity, while W-E and W-GPSM exhibit lower acidity. The electron-accepting properties of W-VTSM and W-VSSM can be explained by the fact that the *s* orbital property in the sp^3 hybrid orbital of the common vinyl group of VTSM and VSSM is greater than that in sp^2; thereby, the carbon atom of the vinyl group tends to be electronegative and the terminal hydrogen atom is easily released as a proton. On comparing these results with the results for modified glass fiber reported previously [37], the acidities of the modified silica fillers correspond to those of the

Table 4 Surface free energy of original and modified silica fillers

Sample	π_0 (mJ/m^2)		γ_S^D (mJ/m^2)	γ_S^P (mJ/m^2)
	n-Heptane	1-Propanol		
W-N	20	40	44	49
W-E	18	42	41	61
W-B	15	21	37	12
W-VSSM	25	37	52	26
W-GPSM	17	21	39	9
W-VTSM	15	24	36	18

glass fibers modified by the same or almost similar silane coupling agents; however, there is a great difference between the acidity of the original silica filler and that of the original glass fiber due to the difference in the surface activity caused by the difference in the method of manufacture or pretreatment.

The plots of I_{SP} values against AN are shown in Fig. 4. Although it was rather difficult to set a linear relation because of the lack of available data and also of their scattering, the slopes clearly differed depending on the sample. It was found that the slopes of W-GPSM and W-N were greater, in other words, more basic, while that of W-E was the least. The basicity of W-GPSM is ascribed to the high electron donating ability of the oxygen atom in the glycidoxy group. The polar component, γ_S^P, of the surface free energy for W-E was found to be large, but both its acidity and basicity were found to be small. This can be ascribed to the polar, but neither acidic nor basic, property of the alcoholic hydroxyl group; however, more experiments are needed to determine more quantitatively the acidic or basic property.

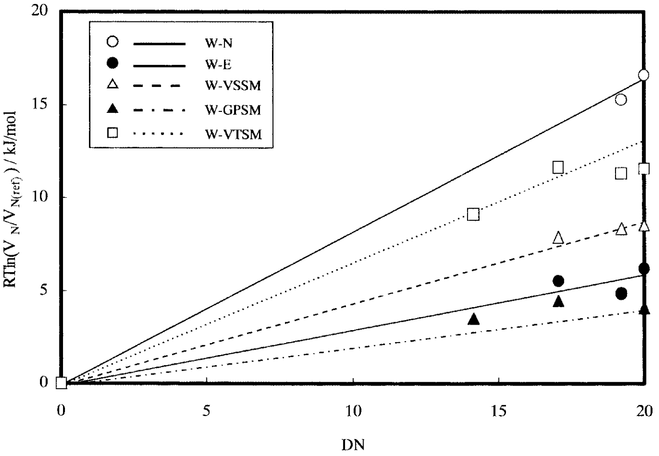


Fig. 3 The relationship of the specific interaction, I_{SP}, with donor number (*DN*) of probe molecules for original and modified silica fillers

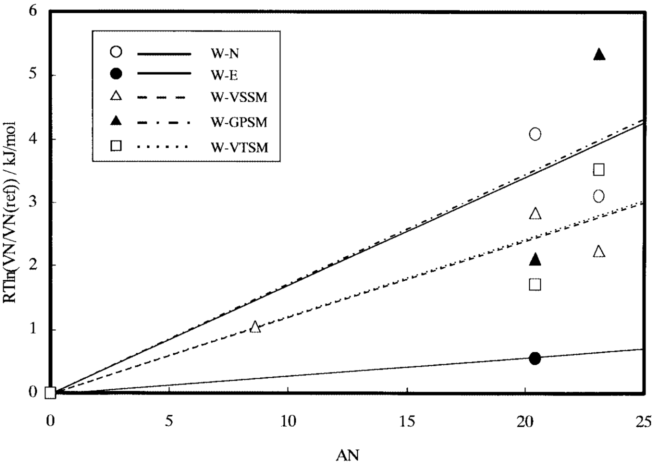


Fig. 4 The relationship of I_{SP} with acceptor number (*AN*) of probe molecules for original and modified silica fillers

The surface properties of PET fibers were also evaluated. The specific surface areas of PN and PW determined by Kr adsorption were 0.59 and 0.49 m^2/g, respectively, which are not different from the geometrical surface areas (0.56–0.90 m^2/g). The adsorption isotherms are shown in Fig. 5, which indicates that the isotherms of *n*-heptane were of type II with a little knee and those of 1-propanol were of type III. With an increase in the pretreatment temperature, the adsorption amount of all PET samples decreased. The adsorption amount of *n*-heptane for PN was greater and was less affected by increasing the pretreatment temperature than that for PW. As for 1-propanol, no difference between PN50 and PW50 was observed at low equilibrium pressure, while the adsorption amount of PW50 became greater at high pressure than that of PN50. The adsorption amount of PW decreased much more with an increase in the pretreatment temperature. Two explanations can be offered for this finding. First, the decrease may be ascribed to the decrease in the specific surface areas. It was found that the specific surface areas shown in Table 5, which were calculated from the isotherms of *n*-heptane and 1-propanol determined by IGC as well as the Kr adsorption isotherm, decreased with an increase

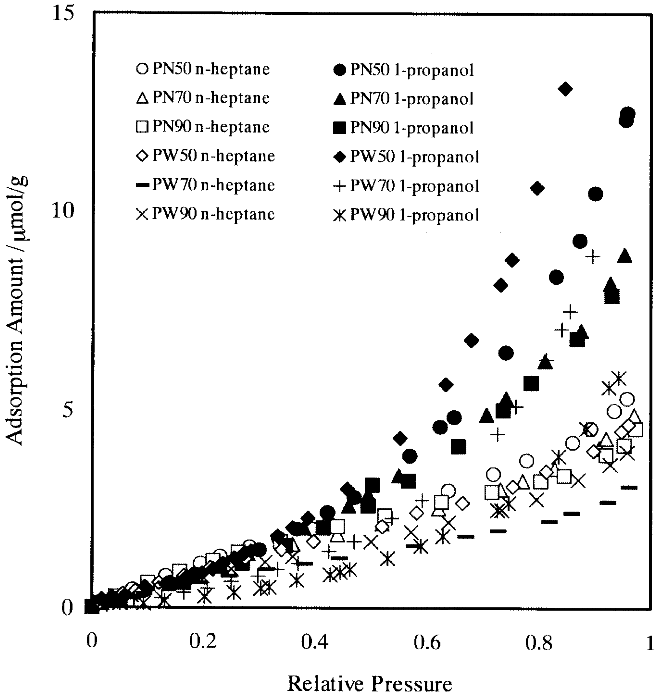


Fig. 5 The adsorption isotherms for poly(ethylene terephthalate) fibers

Table 5 Specific surface areas calculated by each probe molecule and degree of crystallinity for poly(ethylene terephthalate) (*PET*) fibers

Sample	S_{GC} 1-Heptane (mJ/m_2)	S_{GC} 1-Propanol (m^2/g)	S_{Kr} (m^2/g)	Degree of crystallinity (%)
PN-50	0.51	0.46	0.59	< 1
PN-70	0.44	0.42	0.40	< 1
PN-90	0.45	0.41	0.39	8
PW-50	0.38	[a]	0.49	< 1
PW-70	0.32	[a]	0.32	6
PW-90	0.26	[a]	0.28	10

[a] It was difficult to make a Brunauer-Emmett-Teller plot from the adsorption amount of 1-propanol for PW

in the pretreatment temperature, especially at pretreatment above 343 K. It was also observed by scanning electron microscopy that the surface of the fibers pretreated at 323 K was rough, while it became smooth when the fibers were pretreated at 363 K. The second explanation that is related to the first would be the crystallinity of the fibers shown in Table 5.

The dispersive component, γ_S^D, and the polar component, γ_S^P, of the surface free energy of PET fibers are shown in Table 6. With an increase in the pretreatment temperature, the dispersive component values increased and the polar component values decreased. These results can be ascribed to the crystallization of PET, which agreed with the change in the surface free energy calculated from the contact angle for the stretched PET film [38]. It should be noted that the polar component of the surface free energy decreased significantly for PN70 (degree of crystallinity: 8%) pretreated at 363 K and for PW70 (6%) and PW90 (10%) pretreated at 343 and 363 K, respectively. It may also be ascribed to the crystallization of the surface since the pretreatment temperature was higher than the glass-transition temperature (T_g) of 351 K for PN and 341 K for PW. The decrease in T_g for PW was considered to be caused by water intrusion. On the other hand, a tailing was observed in the IGC measurement of PET at infinite dilution, which may be ascribed to the probe intrusion in fibers.

In order to clarify the real interaction between the silica fillers and PET, the internal haze of the stretched PET film including the silica fillers was measured. As shown in Figs. 6 and 7, the internal haze properties were found to decrease almost linearly with an increase in the I_{sp}–AN slope (basicity) of the silica fillers. A monotonous correlation between the haze property and the I_{sp}–DN slope (acidity) was not found. Though the number of data is not necessarily sufficient, the interaction is thought to relate to the filler's basicity and PET's acidity. These results suggest that the carboxyl end group of PET interacts strongly with the electron-donating groups of the filler.

Table 6 Surface free energy of PET fibers

Sample	γ_S^D (mJ/m^2)	γ_S^P (mJ/m^2)
PN-50	48	19
PN-70	59	20
PN-90	66	9
PW-50	49	42
PW-70	68	5
PW-90	74	2

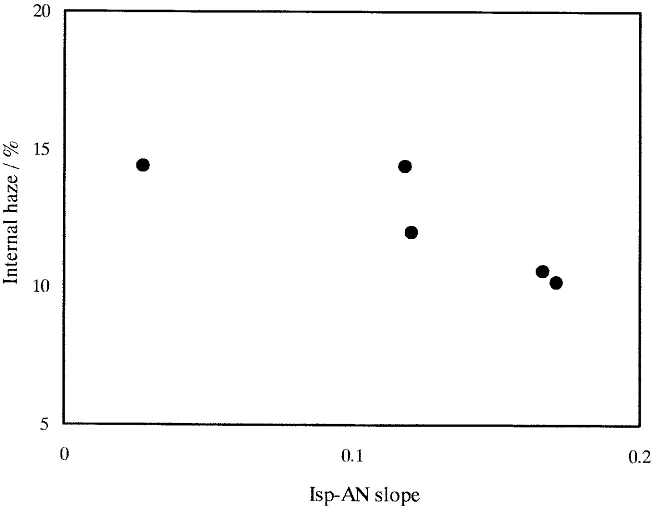


Fig. 6 The relationship of the internal haze with I_{sp}–AN slope (basicity) of silica fillers

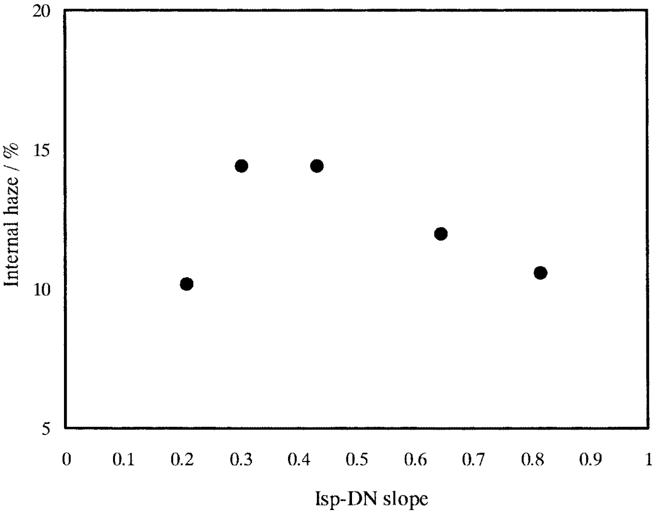


Fig. 7 The relationship of the internal haze with I_{sp}–DN slope (acidity) of silica fillers

Conclusions

The surface free energy of modified silica fillers and PET fibers were analyzed by IGC in order to investigate the relationship between their surface characteristics and their mutual interactions. It was found that the dispersive components of the surface free energy for all modified silica fillers were smaller than that for the original silica. The polar component of the surface free energy for ethylene glycol modified silica filler was rather large, while that for *n*-butanol modified silica filler was small. The polarity, the acidity, and the basicity of the silica fillers could be controlled by modification with various silane coupling agents. The original silica filler exhibited the highest acidic property and the silica filler modified with a silane coupling agent with a vinyl group had a relatively high acidity. The silica filler modified with a silane coupling agent with a glycidoxy group exhibited high basicity, suggesting the high electron donating ability of the oxygen atom of the glycidoxy group. The ethylene glycol modified silica filler exhibited rather polar properties, but these were neither acidic nor basic.

It was also found that the polar component of the surface free energy of PET fibers decreased on pretreatment above *T*g.

The interaction between PET fibers and modified silica fillers corresponded to the basicity of the fillers.

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