Morphogenetic Study of Particle Domains in Thermoreversible Recording Media Composed of Polymeric Films with Dispersed Fatty Acids

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Received March 12, 1996. Revised Manuscript Received August 20, 1996⊗

We have studied the morphogenetic conditions of particle domains in thermoreversible recording media composed of polymeric films with dispersed fatty acids. These recording media have two different optical states, transparent or light scattering, depending on the thermal history. These states can be selected repeatedly by controlling the heating temperature and can be recycled repeatedly. The essential requirement for this reversible behavior is the formation of small particle domains of the fatty acids, because a supercooling of the fatty acids occurs only when the small particle domains have been formed and plays a key role in the thermoreversibility. Morphological structures in the polymeric films formed using various polymers and behenic acid were observed by a transmission electron microscope. On the other hand, the surface tension of the polymers and the fatty acids was measured by the contact angle method. By studying the relationship between the morphological structures and the surface tension, it was revealed that proper immiscibility between the polymers and the fatty acids is required for forming the small particle domains of the fatty acids in the polymeric film. We also report on the influence of the solvent on forming the particle domains.

Introduction

Materials used as reversible recording media are now attracting attention from environmental as well as technological viewpoints, because they would conserve plastic products such as cards and sheets used for an overhead projector, and by offering superior functionality, they would find new markets.

Ueno et al. showed that in a polymer having cholesteric liquid crystals as the pendant group, the pendant liquid crystals have two different alignments depending on the cooling rate when the polymer is cooled to room temperature after being heated to 90−100 °C. They also demonstrated that the polymers align in a planar conformation during slow cooling, whereas they align in a random conformation during rapid cooling.[1]

Two-component materials composed of some polymers and liquid crystals make up another group of candidates for thermoreversible materials. Mcintyre et al. reported on the thermoreversible behavior of a mixture of a polymer and a nematic-type liquid crystal *N*-(4-ethoxybenzylidene)-4-*n*-butylaniline,[2] and Takahashi et al. reported on thermooptical effects of a mixture of a polymer and 4-alkoxy-3-chlorobenzoic acid.[3] These polymeric films can assume either a transparent or light-scattering state depending on the method of heating and cooling. Although some promising thermoreversible materials have been reported, most of them require careful control of the cooling rate, which, as mentioned above, requires complicated devices for the recording and erasing.

A thermoreversible recording material composed of a polymer matrix with a dispersed low molecular weight compound may be promising for practical use,[4] because the two optically different states (transparent and light-scattering states) can be selected using only temperature; control of the cooling or heating rate is not necessary.

In a previous paper,[5] we have proposed the assumption that the thermoreversible response of a recording material composed of a polymer matrix with a dispersed fatty acid is caused by a production of voids in the light-scattering state and disappearance of the voids in the transparent state. Furthermore, the mechanistic study of this thermal response suggested the conditions required for such thermoreversible characteristics: the glass transition temperature of the matrix is between two crystallizing temperatures of the fatty acid in the matrix. The two crystallizing temperatures of the fatty

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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S0897-4756(96)00193-7 CCC: $14.00

Table 1. Surface Tension and Its Components of Test Liquids[6–8]

test liquid	$\gamma_L{}^d$ (dyn/cm)	$\gamma_L{}^x$ (dyn/cm)	γ_L (dyn/cm)	ref
n-octane	21.8	0.0	21.8	6
n-decane	23.9	0.0	23.9	6
n-dodecane	25.4	0.0	25.4	6
n-hexadecane	27.6	0.0	27.6	6
dipropylene glycol	29.4	4.5	33.9	7
polyethylene glycol	29.9	13.6	43.5	7
diethylene glycol	31.7	12.7	44.4	7
ethylene glycol	30.1	17.6	47.7	7
formamide	32.3	26.0	58.3	8
glycerol	34.0	30.0	64.0	8

acid play a key role in the thermoreversibility. The fatty acid in the matrix crystallizes at a temperature just below the melting point of the fatty acid when it is cooled after being heated to a temperature that is slightly below the melting point, whereas the fatty acid crystallizes around 30 °C lower than the melting point when it is cooled after being heated to a temperature higher than the melting point. Fatty acids themselves do not show a supercooling phenomenon that the crystallizing temperatures are around 30 °C lower than the melting points. The supercooling of fatty acids occurs only when the fatty acids formed particles dispersed in the polymer matrix.

This paper describes the necessary conditions for the fatty acids and polymers and the influence of the solvent for forming small domains of fatty acids in the polymeric layer that is an essential condition for the supercooling phenomenon of fatty acids. The details of the supercooling phenomenon will be reported in a next paper.

Experimental Section

Materials. Poly(vinyl chloride), polystyrene (PS, Mw = 96 000), poly(propylene chlorinated), polybutadiene, and poly(vinyl isobutyl ether) were obtained from Aldrich Co., Ltd. A copolymer of vinyl chloride and vinyl acetate (P(VC-VAc), Mn = 20 000, molar ratio of copolymerization = 86/14) and phenoxy resin were purchased from Union Carbide Chemicals and Plastics Co., Ltd. Chlorinated poly(vinyl chloride) was purchased from Sekisui Chemical Co., Ltd. Cellulose acetate was purchased from Eastman Kodak Co. Polysulfone (commercial name P3500NT) was purchased from Nissan Chemical Industries, Ltd. Polycarbonate (PC, commercial name L1250) was purchased from Teijin, Ltd. Epoxy resin was purchased from Yuka Shell Epoxy Co., Ltd. Polyester (commercial name V200) was purchased from Toyobo Co., Ltd. A copolymer of vinylidene chloride and acrylonitrile was purchased from Asahi Chemical Industry Co., Ltd. Polyurethane (commercial name MS-5500) was purchased from Mitsubishi Heavy Industries, Ltd.

Behenic acid (BA) and stearic acid (SA) were available from Sigma Chemical Co. and were 99% pure. Tetrahydrofuran (THF) and toluene were purchased from Kanto Chemical Co., Inc.

N-Octane, *n*-decane, *n*-dodecane, *n*-hexadecane, dipropylene glycol, diethylene glycol, ethylene glycol, formamide, and glycerol were purchased from Tokyo Kasei Kogyo Co., Ltd. In Table 1, the test liquid, the dispersion component of the surface tension ($\gamma_L{}^d$), the summing component of the polar component and hydrogen-bonding component ($\gamma_L{}^x$), and the surface tension (γ_L) at room temperature are listed. The values given in Table 1 were obtained from the literature.[6–8]

Table 2. Components of Solubility Parameter and Boiling Temperature of Solvents[9]

solvent	δ_d (cal/cm^3)$^{1/2}$	δ_x (cal/cm^3)$^{1/2}$	boiling temp (°C)
tetrahydrofuran	8.22	4.80	65.4
methyl ethyl ketone	7.77	5.06	79.6
dioxane	9.30	3.71	101.3
methyl isobutyl ketone	7.49	3.61	115.1

Methyl ethyl ketone (MEK), dioxane, and methyl isobutyl ketone (MIBK) were obtained from Tokyo Kasei Kogyo Co., Ltd. In Table 2, the solvent, the dispersion component of the solubility parameter (δ_d), the summing component of the polar component and hydrogen-bonding component (δ_x), and the boiling temperature which are quoted from the literature[9] are shown.

Measurement. We prepared a series of recording layers by various combinations of the matrix polymer and BA as the low molecular weight material. The polymer and BA were dissolved in a mixture of THF and toluene for evaluation of morphological structures and thermal responses. P(VC-VAc) and SA were dissolved in various solvents for evaluation of the solvent effect. We coated a transparent poly(ethylene terephthalate) (PET) film support with the solution using a wire bar. The coated films were dried at 110 °C to form a recording layer about 10 μm thick. The thickness of the layers was measured with a contact thickness micrometer (K351C/K107C) from Anritsu Corp.

Various polymer films for contact angle measurements were prepared by dissolving the polymers in a mixture of THF and toluene and then coating on glass plates using an applicator. The coated films were dried at 110 °C to form a polymer layer about 10 μm thick. Fatty acid layers were prepared on glass plates using a vacuum evaporation (degree of vacuum 10^{-6}–10^{-5} mmHg, evaporation time about 10 min) and were about 1000 Å thick.

We measured the transparency of the film at various temperatures with a Thermo-system (FP80HT/FP82HT) from Mettler-Toledo AG and a Nikon Optiphoto2 microscope. The temperature was varied continuously at the rate of 2 °C/min.

We observed the microscopic structure of the recording layer with a Hitachi H-500H TEM. The layer was stained by exposing it to OsO_4 vapor for 12 h, fixed with two-pack epoxy from Sony Chemicals Co., and sliced with a RMC MT6000-XL microtome to prepare a 1200–1300 Å thin film.

Differential scanning calorimetry (DSC) measurements were performed for samples of about 5 mg using the DSC 3100, a Mac Science DSC. The samples were measured after being heated to a temperature higher than the melting point of the low molecular weight material and cooled to room temperature. The scanning rate was 2 °C/min. The recording layer prepared on the substrate was peeled off and used for DSC.

We obtained the surface tension and its components of the polymers and the fatty acids by measuring contact angles using test liquids whose components (dispersion, polar, and hydrogen-bonding components) were known. The test liquids and their surface tensions and components are listed in Table 1. The contact angles were measured at room temperature with a contact angle meter (CA-D) from Kyowa Kaimenkagaku Co., Ltd. About 5 μL of the test liquid was dropped onto the polymers and the fatty acids. We allowed the drops to stand for a while and started the measurements after the contact angle became stable. The same measurements were repeated three times for the same sample and test liquid without changing the conditions.

Results and Discussion

Morphological Structures and Thermal Responses of the Polymeric Films Using Various Polymers. We observed recording films sliced thin and

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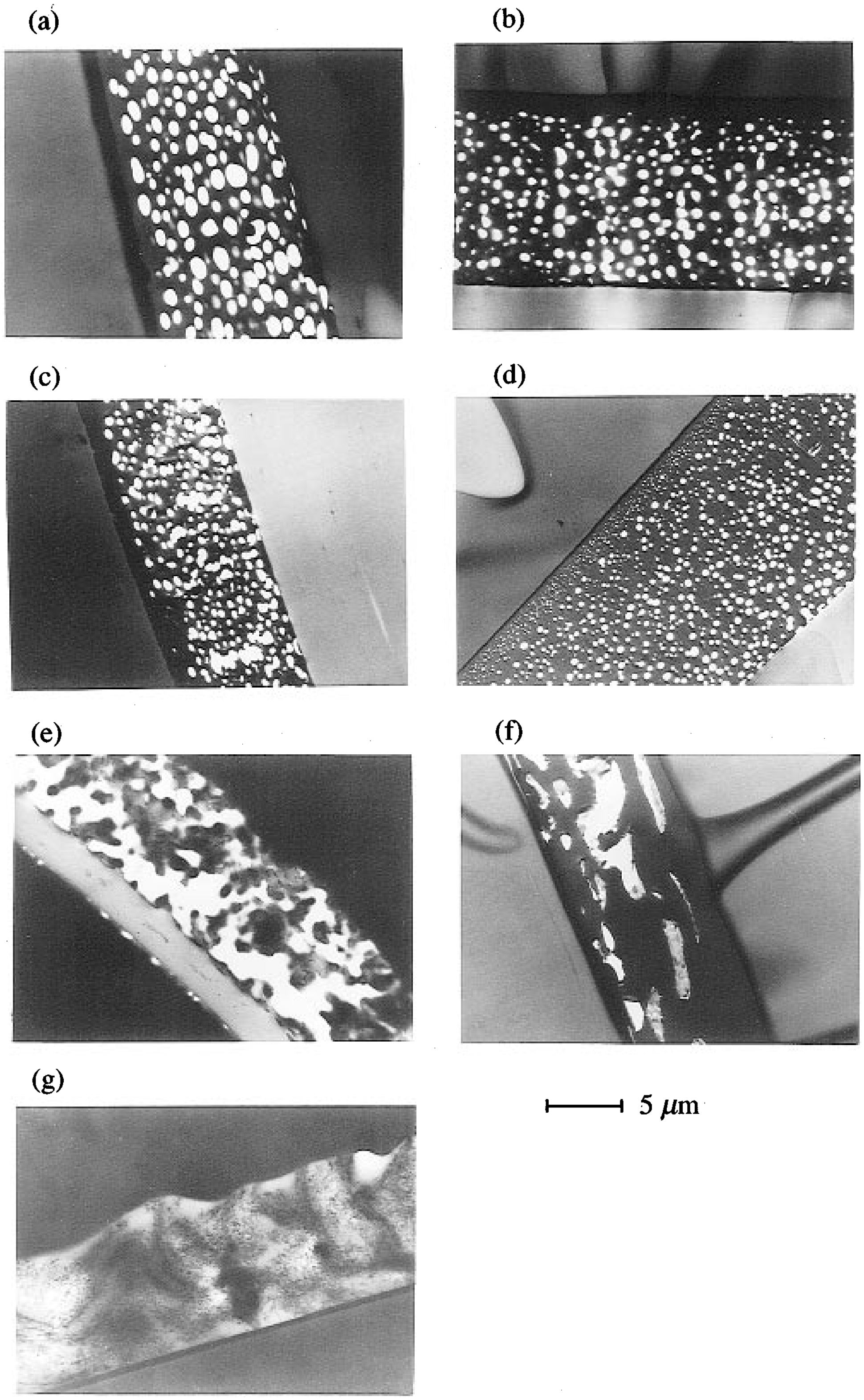

Figure 1. TEM images of cross sections of films composed of polymer matrixes containing dispersed BA. Matrix (a) P(VC-VAc), (b) phenoxy resin, (c) polycarbonate, (d) polystyrene, (e) cellulose acetate, (f) polysulfone, and (g) poly(vinyl isobutyl ether).

stained with OsO_4 by TEM. Figure 1 shows typical examples of the TEM images of cross sections of the recording films composed of the BA and matrix polymer involving P(VC-VAc), phenoxy resin, PC, polystyrene, cellulose acetate, polysulfone, and poly(vinyl isobutyl ether). The bright and dark areas indicate BA and the matrix, respectively. Figure 1a−d clearly shows that BA is phase-separated from the matrix polymer to form small particle domains. However, in Figure 1e,f, although BA is also phase-separated from the matrixes, the domains are larger and some of them are fused together. In Figure 1g, the domains are not observed and the cross section shows a homogeneous state because the phase separation is not clearly observed. This indicates that BA is uniformly mixed with the matrix.

We studied the thermal response in terms of combinations of BA and polymer matrixes to clarify the

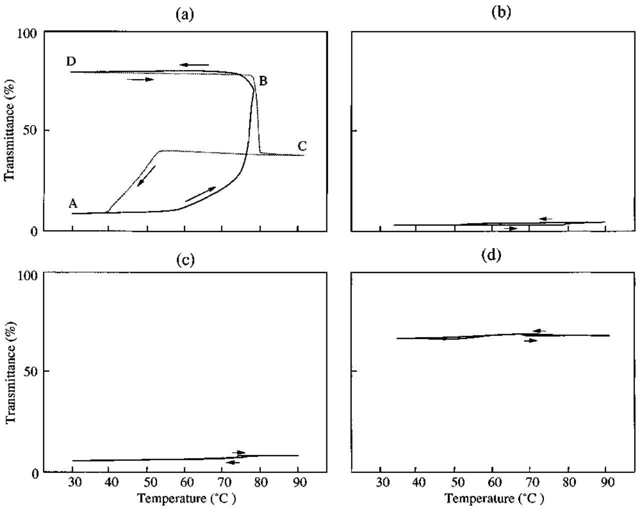

Figure 2. Changes in transmittance during heating and cooling of films composed of (a) P(VC-VAc), (b) polycarbonate, (c) cellulose acetate, and (d) poly(vinyl isobutyl ether) containing dispersed BA.

relationship between the morphological structure and thermal responses. Figure 2 shows the thermal responses of the BA and P(VC-VAc), polycarbonate, cellulose acetate, and poly(vinyl isobutyl ether) recording films. These films were typical examples of various morphological structures selected from Figure 1. In Figure 2a, when the recording film in the light-scattering state is heated to a temperature just below the melting point of BA (80.7 °C), it becomes transparent (A→B). This transparency is maintained after the film is cooled to room temperature (B→D). On the other hand, when the transparent film is heated to a temperature above the melting point of BA, it becomes translucent (D→B→C) and then reaches the light-scattering state after being cooled to room temperature (C→A). Similar thermoreversibility is exhibited in the BA and phenoxy resin film shown in Figure 1b.

On the other hand, in Figure 2b,c, the films show very slight thermoresponse, and the initial appearance of light scattering is almost unchanged. On the other hand, in Figure 2d, the initial appearance of transparency is almost unchanged. The BA and polystyrene and polysulfone films shown in Figure 1d,f show a very slight thermoresponse similar to those of Figure 2b,c.

In a previous paper,[5] we proposed that formation of particle domains is an essential condition for recording films exhibiting the reversible behavior, because a supercooling of the fatty acids occurs only when the small particle domains have been formed and plays a key role in the thermoreversibility. The results mentioned above support our proposition.

Figure 3 shows DSC curves of the BA and P(VC-VAc), PC, cellulose acetate, and poly(vinyl isobutyl ether) recording films measured on heating to 90 °C at which BA completely melts and cooling to room temperature from the temperature at which BA partially melts or 90 °C, respectively. The endothermic peaks appearing upon heating were due to melting of BA, and the exothermic peaks upon cooling were due to crystallization of BA.

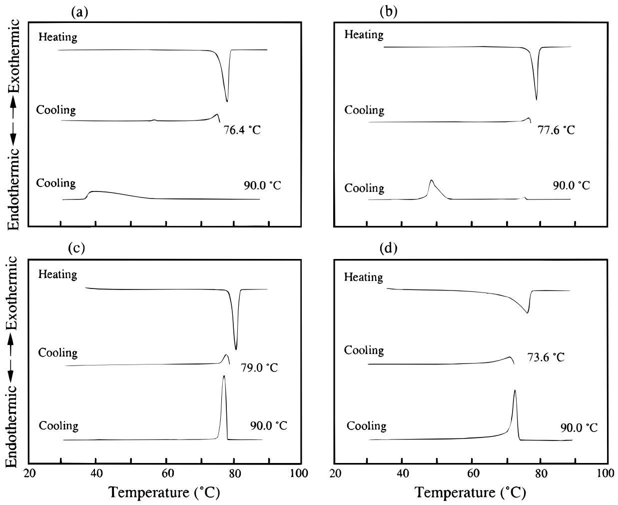

Figure 3. DSC curves of films composed of (a) P(VC-VAc), (b) polycarbonate, (c) cellulose acetate, and (d) poly(vinyl isobutyl ether) containing dispersed BA obtained by heating to 90.0 °C and cooling from the temperature at which BA partially melted and 90.0 °C.

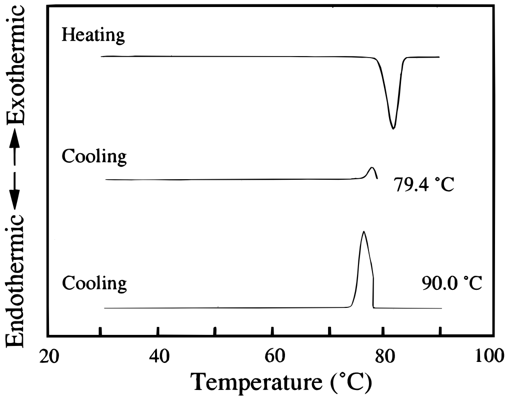

Figure 4. DSC curves of BA itself obtained by heating to 90.0 °C and cooling from the temperature at which BA partially melted and 90.0 °C.

In Figure 3a,b, although the exothermic peak appeared just below the melting point of BA on cooling from 76.4 or 77.6 °C, respectively, the temperature at which BA is partially melted, it appeared at lower temperature on cooling from 90.0 °C, which is apparently due to supercooling of the BA. On the other hand, in Figure 3c,d, the exothermic peak appeared just below the melting point of BA regardless of the starting temperature. Figure 4 shows DSC curves of BA itself measured on heating to 90 °C and cooling to room temperature from 79.4 °C at which BA partially melts or 90.0 °C in the same way as in Figure 3. As shown in this figure, BA itself did not show the supercooling phenomenon. The supercooling of BA observed occurred only when BA formed particle domains dispersed in the polymer matrix and seems to be a prerequisite for recording films exhibiting thermoreversibility.

The slight thermoresponse shown in Figure 2c,d seems to be caused by the slight depression in the crystallizing temperature due to the supercooling as indicated in Figure 3c,d, because the particle domains of BA were not formed. In Figure 2b, the reason for the thermoirreversibility of the BA and PC recording film despite the formation of BA particle domains is that the softening temperature of the PC is higher than the crystallizing temperature of BA.[5] We reported a degree of plasticization of the polymeric films with dispersed BA caused by a diffusion of BA into the polymer in

Table 3. Components of Surface Tension and Glass Transition Temperature of Polymers

	polymer/fatty acid	$\gamma_S{}^d$ (dyn/cm)	$\gamma_S{}^x$ (dyn/cm)	glass transition temp (°C)
1	poly(vinyl chloride)	40.2	0.4	81
2	P(VC-VAc)	38.3	1.3	72
3	chlorinated poly(vinyl chloride)	36.0	2.2	83
4	phenoxy resin	45.5	0.6	84
5	epoxy resin	39.9	2.6	79
6	polyester	29.7	4.4	62
7	poly (vinylidene chloride-*co*-acrylonitrile)	31.2	2.3	15
8	polyurethane	30.4	5.2	36
9	polystyrene	28.6	2.3	107
10	polycarbonate	30.0	3.7	155
11	poly(propylene chlorinated)	32.2	3.7	139
12	polybutadiene	23.3	0.0	−95[a]
13	poly(vinylisobutyl ether)	22.4	0.0	−19
14	cellulose acetate	28.4	11.5	30−55[b]
15	polysulfone	27.1	7.4	189[b]
16	behenic acid	24.6	0.0	
17	stearic acid	23.4	0.0	

[a] Data supplied from manufactures. [b] The Society of Polymer Science, Japan Ed.; *Koubunshizairyoubinran*; Handbook for High Polymer Materials; Corona Publishing Co. Ltd.: Tokyo, 1973; p 1275.

previous paper.[5] The thermomechanical characteristics of the polymeric films with dispersed BA were almost the same as those of the pure polymers. This seems to indicate that BA does not mix the polymers when BA particles were formed in the polymers.

The supercooling of BA may be due to interaction between BA and the polymers because the interfacial area between particles of BA and the polymer matrix is large when BA formed particle domains. This will be reported in detail in a future paper.

Morphological Structures and Surface Tensions of Various Polymers and Fatty Acids. We studied the surface tension of various polymers and fatty acids. Fowkes has advanced the simple but illuminating hypothesis that the total free energy at a surface is the sum of contributions from the different intermolecular forces at the surface.[10] Owens et al.[11] and Schwarcz[12] proposed an expanded Fowkes' equation to include a hydrogen bonding and a polar term, respectively. By applying these propositions, the following equation is obtained in term of the separation of surface tension into dispersion and other components,

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L{}^d\,\gamma_S{}^d} - 2\sqrt{\gamma_L{}^x\,\gamma_S{}^x} \qquad (1)$$

where γ_{SL}, γ_L, and γ_S are the interfacial tension of the interface between liquid and solid, the surface tensions of liquid and solid, respectively and the superscripts d and x refer to the dispersion force and the other components which contain the hydrogen bonding force and the polar force components.

The work of adhesion, W_A, can be expressed as follows:

$$W_A = \gamma_L + \gamma_S - \gamma_{SL} \qquad (2)$$

The work of adhesion can also be expressed in terms of the contact angle θ:

$$W_A = \gamma_L(1 + \cos\theta) \qquad (3)$$

The work of adhesion was obtained by measuring the contact angle using test liquids whose surface tensions and components were known as shown in Table 1. The values of the contact angles for repeated measurements were within a maximum error of 5%.

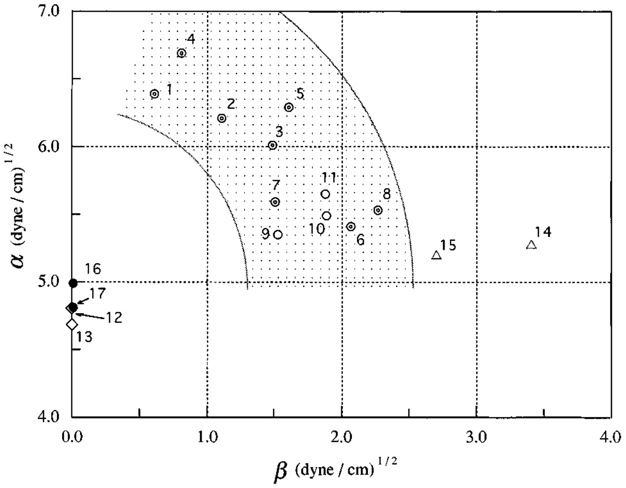

Figure 5. Square root of dispersion force component, α, versus square root of the other components, β, for various polymers and fatty acids. Refer to Table 3 for the numbers. A double circle and a single circle indicate formation of particles of BA in the polymeric film. The double circle indicates thermoreversibility but the single circle indicates thermoirreversibility. A triangle and a diamond indicate separation and compatibility between the polymer and BA, respectively, and both symbols indicate thermoirreversibility.

For the purpose of calculation of the surface tension components of polymers and fatty acids, it will be convenient to combine eq 1 with eq 2 to give

$$W_A/2\sqrt{\gamma_L{}^d} = \sqrt{\gamma_S{}^x}(\sqrt{\gamma_L{}^x}/\sqrt{\gamma_L{}^d}) + \sqrt{\gamma_S{}^d} \qquad (4)$$

The results were plotted with $W_A/2\sqrt{\gamma_L{}^d}$ as ordinate against $\sqrt{\gamma_L{}^x}/\sqrt{\gamma_L{}^d}$ as abscissa. The square root of the dispersion force component of the surface tension. $\sqrt{\gamma_S{}^d}$ (=α), was obtained from an intersection of the vertical axis and a regression line obtained by a least-squares method. The square root of the other components of the surface tension, $\sqrt{\gamma_S{}^x}$ (=β), was obtained from a slope of the regression line.

The dispersion force, $\gamma_S{}^d$, and the other force components, $\gamma_S{}^x$, of the polymers and the fatty acids were obtained by the method just mentioned. Table 3 sum-

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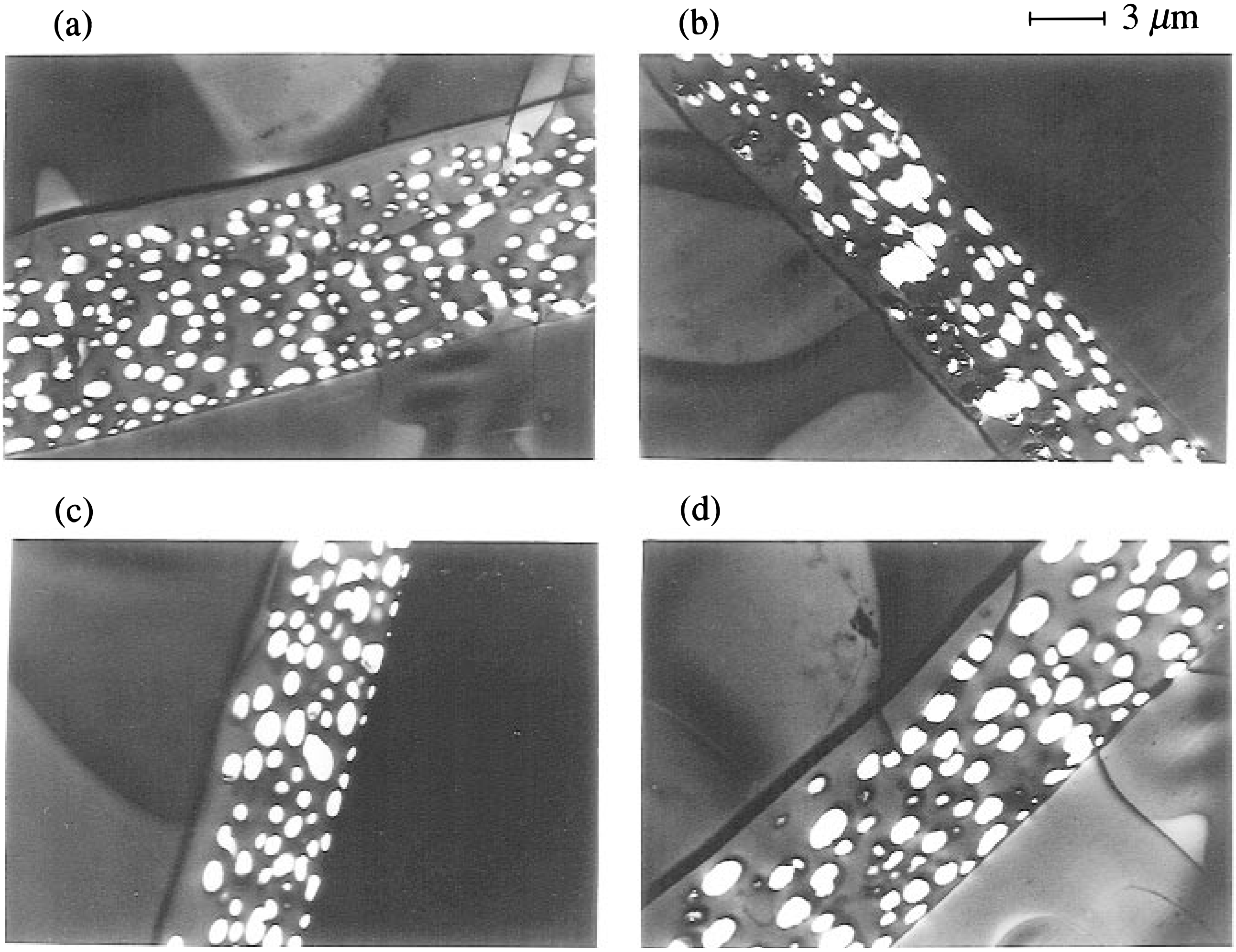

Figure 6. TEM images of cross sections of films composed of P(VC-VAc) containing dispersed SA which were formed using (a) THF, (b) MEK, (c) dioxane, and (d) MIBK.

marizes the dispersion force and the other force components and the glass transition temperatures of the polymers.

Pav et al. proposed that the wettability of damper rolls could be evaluated using the distance between two different points in a diagram of the square root of the dispersion component versus that of the polar component.[8] By applying this method, we studied the necessary conditions between fatty acids and polymers for forming small domains of fatty acids.

Figure 5 shows the square root of the dispersion force component, α, versus the square root of the other components, β, for various polymers and fatty acids. In this figure, each symbol indicates the morphological structure and the thermoreversibility of the polymeric films which were formed using BA and each polymer for numbers 1−15 indicated in Table 3. A double circle and a single circle indicate formation of particles of BA in the polymeric film. The double circle indicates thermoreversibility, but the single circle indicates thermoirreversibility. A triangle indicates separation between the polymer and fatty acid, but a diamond indicates compatibility, and both the triangle and the diamond indicate thermoirreversibility.

The distance between each polymer and fatty acid in this figure indicates the degree of miscibility. The degree of miscibility decreases as the distance becomes longer. As shown in Figure 5, the region in which the single and double circles are located is limited to a shaped portion enclosed by the two circular arcs drawn with a center at number 16, BA. In the inside of the left circular arc, the polymer is uniformly mixed with the fatty acid. On the other hand, on the outside of the right circular arc, the polymer is phase separated from the fatty acid.

Figure 5 indicates that proper immiscibility between the polymers and the fatty acid is required for forming small particle domains of the fatty acids in the polymeric film. When the miscibility between the polymer and the fatty acid becomes better, the fatty acids could not be separated from the polymer but will be mixed with the polymer and the domains will be not formed. On the other hand, when the miscibility becomes worse, the domains will become larger and some of them will be fused together, and the small domains will be not formed.

Influence of Solvents for Forming Small Particle Domains. We studied the influence of solvents on forming small particle domains of fatty acids in the polymeric film. Until the preceding subsection, we have investigated the morphogenesis of the polymeric films using the surface tension. However, in this subsection, we investigated the solvent effect for the morphogenesis of the polymeric films using solubility parameters instead of the surface tension, because the data of surface tension and its components of solvents in which the polymers and the fatty acids are dissolved did not exist. Influence of the dispersion force and the other components which contain the hydrogen-bonding force and the polar force components of solvents for the morphogenesis of the polymeric films can be also investigated using the solubility parameters in the same manner as the surface tension, because each component of the solubility parameter can be expressed in terms of each component of the surface tension as follows:[13]

$$\delta_a = (\gamma^a / K_a V_m{}^{1/3})^{1/2} \qquad (5)$$

where K and V_m are constant and molar volume, respectively, and the superscript and the subscript a refer to the dispersion force or the other components which contain the hydrogen-bonding force and the polar force components. Recording films were prepared using SA, P(VC-VAc), and the solvents shown in Table 2 which have various components of the solubility parameter.

Figure 6 shows the TEM images of cross sections of the recording films formed using THF, MEK, dioxane, and MIBK, which can dissolve both SA and P(VC-VAc). Comparing the TEM images for the four types of films, the particles of SA differ in the domain size. However, the morphological structure in which the small particle domains are formed agrees for the four types of films. This indicates that formation of small particle domains does not depend on the characteristics of the solubility parameter of the solvents used in this study.

Conclusions

We have clarified the necessary conditions between fatty acids and polymers to form small particle domains of fatty acids in the polymeric film. The formation of small particle domains is a prerequisite for recording films exhibiting thermoreversibility, because only when the small particle domains of the fatty acids are formed, a supercooling of the fatty acids occurs and plays a key role in the thermoreversibility. By observation of the morphological structures in the polymeric films and from measurements of the components of the surface tension of the polymers and the fatty acids, it was clarified that proper immiscibility between the polymers and the fatty acid is required for forming small particle domains of the fatty acids in the polymeric film. It was also revealed that the formation of small particle domains does not depend on the characteristics of the solvents used in this study (δ_d 7.49−9.30, δ_x 3.61−5.06) at least.

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