

Ink-Repellent Coatings Composed of Silicone-Acrylic Block Copolymer for Ink Jet Printer

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Abstract

The silicone-acrylic block copolymers were prepared by free radical copolymerization, in which we used polydimethylsiloxane containing azo groups as a macromolecular initiator and acrylic monomers including functional monomers. The copolymer solutions were coated on substrates by various application methods, subsequently cured with either cross-linking agents or UV light. Advancing (θ_A) and receding (θ_R) contact angles of the resulting films were measured in various inks. The films were hard enough for a nozzle face, exhibited over 80° of θ_A and 60° of θ_R in an ink, which were superior to those of silicone or fluorinated coating films. The ink-resistance of the films was evaluated by changes in θ_A and θ_R before and after soaking the films into inks at 60°C for 4 weeks. The durability of the films were outstanding. The excellent properties were found to be caused by microdomain structure and to be influenced by domain spacing rather than silicone content.

Introduction

Ink-repellency has been the most important performance for nozzle face of ink jet printers, because it imparts the easily removal of residual inks and dusts from nozzle face, and subsequently dictates the accurate ink hits to the mark. Increasing demands for higher image quality has accelerated the development of coating with improved repellency. Silicone resin is a preferable binder because of excellent water-repellency as well as no impact on environment. The study protocol for the nozzle face coatings entails the followings: i) easy application; ii) ink-resistance; iii) film hardness. Cross-linking system would be most applicable, but hardness and resistance of cross-linked silicone films were usually insufficient.

Our strategy was to utilize block copolymers consist of silicone resin and acrylic resin, in which acrylic resin was able to cross-link. The microscopic images of the cross-linked films showed many spherical microdomains consisting of silicone. The resistance properties and hardness of the films were sufficient for nozzle face coatings, and their ink-repellency were more excellent than that of a film consisting of cross-linked silicone. Moreover, it was found that the density of domain distribution in the films significantly influenced on the ink-repellency.

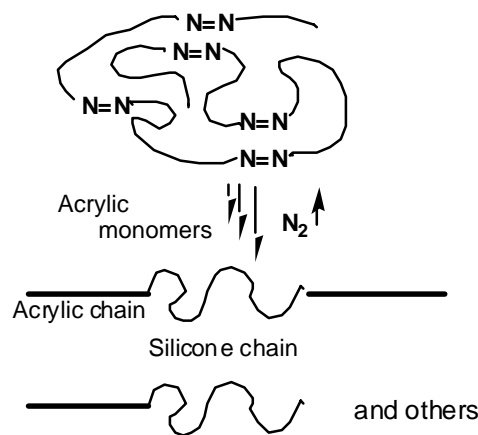


Figure 1. Preparation of silicone-acrylic block copolymers

Experimental

Preparation of Polymers

Polydimethylsiloxanes containing azo groups, illustrated in Fig. 1, were used as a macromolecular initiator (VPS, Wako Pure Chemicals Ind. Ltd.). Characteristic of VPSs used are listed in Table 1. VPS, acrylic monomers and a solvent were weighted in flask, and stirred at 120°C for 5 hours. Functionalities, molecular weight, and silicone content of polymers are tabulated in Table 2. As comparative samples, a graft copolymer prepared by the copolymerization of macromonomer of polydimethylsiloxane ($M_n=1,000$, Silaplane FM-0711, Chisso Corp.) and pure acrylic resin obtained by a conventional method were also used in this experiment.

Table 1. Macromolecular Initiator

VPS	Mn of silicone segment	Total Mn
0501	5,000	37,800
1001	10,000	87,600

Table 2. Acrylic, Block and Graft Copolymers

Code group	Functional		Silicone segment	
	Mn	MWD	wt%	Mn
Block 1 hydroxy	18,300	3.68	22	5,000
Block 2 hydroxy	15,500	5.54	24	10,000
Block 3 epoxy	18,600	2.96	22	5,000
Graft hydroxy	9,100	2.38	22	1,000
Acrylic hydroxy	4,500	1.86	0	--

Coatings, Application, and Curing

The thermosetting coatings were prepared by mixing with hydroxy-containing polymers and melamine-formaldehyde (MF) resin as a cross-linker. An UV-curable coating was prepared by mixing with Block 3 and cationic photoinitiator. Fluorinated acrylic emulsion and moisture-curable silicone resin were used as a reference.

Coatings were cast on glass plate (24 x 55 x 0.2 mm) by dip coating and applied for contact angle measurement after curing. Morphological observation called for free film samples cured on glass or polypropylene plates, after coated by splay or spin coating.

The thermosetting coatings were cured at 150°C for 30 minutes. The UV-curable coatings were exposed to an UV-light (120mJ/cm²) after pre-baking at 80°C for 10 minutes, and sequentially post-baked at 200°C for 1 hour.

Measurements

Dynamic contact angles, advancing (θ_A) and receding (θ_R) ones, based on Wilhelmy plate technique¹⁾, were measured at 20°C by a tensile tester (DCA-100, Orientec Co.). Commercially available three cyan inks, ink A, B, and C, soled by different manufactures were used for the measurement and durability test.

The morphology of the resulting films were observed by transmission electron microscopy (TEM, JEM-2000FXII, JEOL). Ultrathin sections of the specimens were obtained with ULTRACUT S (Reichert-nissei) and stained with ruthenium oxide to enhance contrast.

Durability Test

Durability test of films against the inks were performed by soaking them into the inks at 60°C for 4 weeks. The durability was evaluated by the changes in θ_A and θ_R before and after soak.

Results and Discussion

Performance of Block Polymer

The θ_A and θ_R of ink A for various coatings films before and after soaking in ink A were listed in Table 3. Pure acrylic film showed remarkably low θ_R . The hardness of fluorinated coating and silicone films were insufficient for a nozzle face coating. Furthermore, the silicone films showed low θ_R before soaking test, and fluorinated coating one had no adequate ink-resistance. Neither of these films satisfied the requirement for nozzle face coatings.

Table 3. θ_A and θ_R of Ink A for Materials Before and After Soaking in Ink A at 60°C

Binder	Cross-linking system	Silicone content wt%	P.H. ^{a)}	Initial		After 4 weeks	
				θ_A	θ_R	θ_A	θ_R
Block 1	-OH/MF	15	H	90	62	85	53
Block 3	Epoxy /H ⁺	7	H	84	61	81	50
Silicone	-SiOR	~100	<6B	88	48	91	56
Fluorinated	none	-	2B	97	78	50	17
Acrylic	-OH/MF	0	HB	80	24	65	8

a) pencil hardness

In spite of low silicone content below 10 wt%, the films prepared with Block 1/MF or Block 3/H⁺ maintained high values of θ_A and θ_R even after the soaking test and were hard enough to withstand a friction. Taking these results into consideration, these coatings well meet the purpose as an ink-repellent coatings for ink jet printer.

Dependence of Inks

The ink-resistance of the film prepared with Block 1 and MF resin was evaluated by soaking it in various inks. The changes in θ_A and θ_R are shown in Figure 2. Both values depended on the kind of inks and slightly decreased for only initial soaking period regardless of the kind of inks. The values of surface tension of ink A, B, and C were 37.1, 30.6, and 29.3 dyn/cm, respectively. Hence, it is considered that the difference in θ_A and θ_R is due to the amount and the kind of surfactants in the inks. After the coated plate was pulled up from ink C which showed the lowest θ_R , no mark and drop of the ink was observed on the surface.

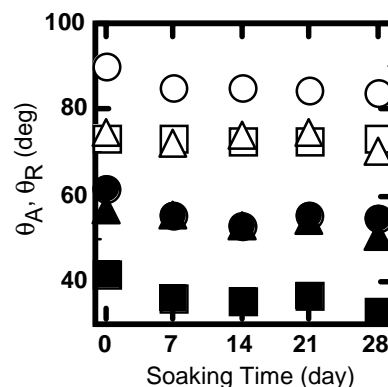


Figure 2. The change in advancing (θ_A) and receding (θ_R) contact angle of inks by soak in inks at 60°C. Filled and open symbols denote θ_A and θ_R . Circle, triangle, and square symbols denote the values of ink A, ink B, and ink C, respectively

Dependence of Molecular Structure

It is known that the θ_A would be more closely associated with high contact angle regions while θ_R would be more closely associated with low ones.²⁾ Cassie derived the following equation.³⁾

$$\cos\theta = \sigma_1 \cos\theta_1 + \sigma_2 \cos\theta_2 \quad (1)$$

where θ is the apparent contact angle, σ_1 and σ_2 are the fraction of the surface having the intrinsic angle θ_1 and θ_2 .

The film prepared from Block 1/MF contained 85 wt% of acrylic/MF component which belongs to relatively low contact angle reasions. Assuming that eq.1 applies in θ_R , the θ_R s for Block 1/MF before and after soaking test should come close to θ_R s for Acrylic/MF in Table 3, respectively, which was in conflict with our results. This may be due to an unique molecular structure such as a block copolymer. Hence the dependence of molecular structures onto θ_1 and θ_2 has been studied.

The cured films were prepared from silicone-acrylic block copolymer (Block 1) or Silicone-acrylic graft copolymer (Graft) with MF resin. The film abbreviated as Acrylic in Table 4 was obtained from acrylic resin, MF resin, and homo-polydimethylsiloxane. The results of soaking test in ink A for these films were listed in Table 4. The initial θ_A and θ_R for the film of Acrylic / MF / silicone system were lower than those for the others. These low values were presumably caused by an incomplete fixing of silicone into the matrix.

The θ_R after soaking test for the films of Block 1/ MF system became higher than those of Acrylic/MF/silicone and Graft/MF systems. Figure 3 shows an electron micrograph of a ca. 40-nm-thick ultrathin section of the cured film of Block 2/ MF system. The white area in the micrograph corresponds to the acrylic chain/MF phases while the silicone phases are stained by ruthenium oxide and appear dark. The diameter of silicone spheres was estimated from micrograph to be about 20 nm and the value for Block 1/MF system also found to be approximately 12nm. On the other hand, no micromorphology was observed in the cured film prepared from Graft / MF. Since no silicone grafts is fixed structurally, polar components such as carbonyl group may be easily oriented to the film surface, consequently, result in remarkable decrease of θ_R after soaking test.

Table 4. Effect of molecular structure on θ_A and θ_R

Code	Silicone content wt%	Initial		After 4 weeks	
		θ_A	θ_R	θ_A	θ_R
Block 1	15	95	62	85	55
Graft	15	86	58	84	29
Acrylic ^{b)}	5	76	36	78	25

a) Melamine-formaldehyde curing system b) homopoly-dimethylsiloxane was added to acrylic resin in Table 1.

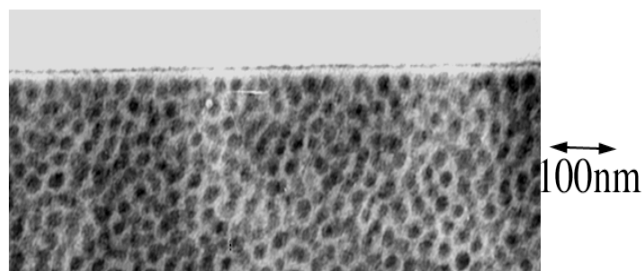


Figure 3. An electron micrograph of a thin section of Block 2/MF sample, showing the air-polymer interface.

In Figure 3, ca. 3-nm-thick ultrathin layer colored dark was observed at the air-polymer interface. The X-ray photoelectron spectroscopic analysis confirmed that the layer consists of silicone. As shown in Figure 2, every values of θ_A and θ_R initially decreased and remained constant during soaking test. It may be because the films obtained from silicone-acrylic block copolymer / MF resin have an orderly micromorphology from air-side to substrate-side surface after the ultrathin layer is taken away from the surface for initial period of soaking test.

These results suggest that the value of θ_R after soaking test is closely related to micromorphology of a film surface which is due to unique molecular structure of block copolymers. It is, however, not still clear the reason why the value of θ_R after soaking test for block copolymers /MF resin system is much higher than that for acrylic/MF resin system though the former film has 85 wt% of component of acrylic chain/MF.

Dependence of Morphology

By numerical calculation process Johnson and Dettre⁴⁾ suggested that contact angle hysteresis ($\theta_A - \theta_R$) on a heterogeneous surface appears above a certain width between adjacent fractions of different surface energy. This means that microdomain structure would affect the values of θ_A and θ_R .

In the study of binary mixture of poly(isoprene-block-styrene) and homo polystyrene⁵⁾, homo polystyrene having a lower molecular weight than that of polystyrene block is known to be solubilized into microdomains composed of polystyrene block, causing a change in microdomain spacing. On the basis of the fact, acrylic resin was added to Block 1 or Block 2, as showing in Table 5, in order to control domain spacing.

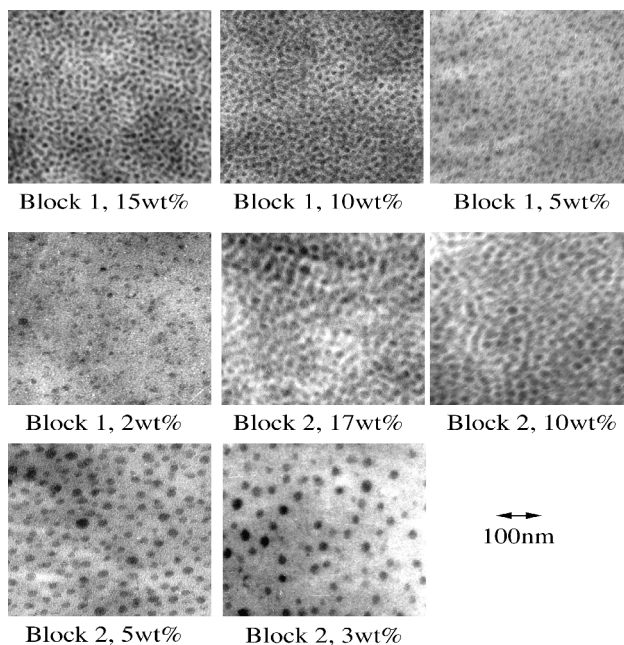


Figure 4. Electron micrographs of thin sections. The values in wt % denote silicone content of each sample

Figure 4 shows electron micrographs of the resulting films. The area fraction of acrylic domain increased with increasing the weight fraction of added acrylic resin. Even in low silicone content, the spherical microdomains were still conserved, but dispersed randomly in the matrix. The microdomain size was dependent on silicone chain length and independent of silicone content. The domain spacing

and domain size were roughly estimated from the micrographs. These result and the value of θ_A and θ_R of ink A for the films before and after soaking test in ink A are summarized in Table 5.

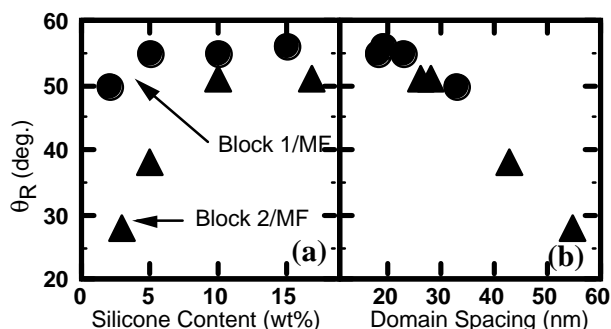


Figure 5. Relationship between (a) silicone content or (b) domain spacing and θ_R after soak in ink A for 4 weeks.

Table 5. Domain Size and Domain Spacing

Formulation ^{a)} Block no.	Acrylic wt%	Silicone After content wt%	Domain				Spacing nm	Size nm
			Initial θ_A	Initial θ_R	4 weeks θ_A	4 weeks θ_R		
1, 70	-	15	87	61	88	56	19	12
1, 46	24	10	84	63	84	55	18	
1, 23	47	5	82	65	82	55	23	
1, 8	62	2	84	61	84	50	33	
2, 70	-	17	80	66	84	51	26	20
2, 40	30	10	80	67	87	51	28	
2, 20	50	5	80	68	84	38	43	
2, 12	58	3	84	61	82	28	55	

a)30wt% of melamine-formaldehyde resin was added.

The values of θ_A for all films were over 80° and unchanged by soaking test in ink A for 4 weeks. The values of θ_R for a few films decreased by soaking test although all of initial values of θ_R were over 60° . Figure 5(a) shows the relationship between silicone content of the films and θ_R after soaking test. The value of θ_R after soaking test decreased below a certain critical weight fraction of

silicone, which depended on domain size. Figure 5(b) shows the relationship between roughly estimated microdomain spacing of the films and θ_R after soaking test. The value of θ_R after soaking test remarkably decreased below about 30 nm in the domain spacing regardless of the domain size. Similar results were obtained in the cases of ink B and C. These results suggest that the value of θ_R is dependent on domain spacing rather than silicone content, and independent of low contact angle region such as Acrylic chain/MF so long as the silicone microdomain spacing is shorter than about 30 nm in this study.

Conclusion

The present silicone-acrylic block copolymers have provided thermo- or UV-curable coatings which were preferable for a nozzle face of ink jet printers. Their excellent ink-repellency and ink-resistance were found to result from micromorphology and silicone domain spacing of the films. We believe that these coatings are widely applicable.

References

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Biography

Masatoshi Ohata received his Bachelor and Master degree in Engineering from Kyoto Institute of Technology in Japan in 1982 and 1984, respectively. Since 1984 he has worked in Resin Center at Nippon Paint Co. Ltd. in Japan. During From 1985 to 1988, he worked in Technical University of Nagaoka in Japan, as a contract researcher. His work has primarily focused on the preparation of functional polymers by living anionic or free radical polymerization and their application in coating fields.