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Ink Repellent Coatings Consisting of Silicone–Acrylic Block Copolymer for Ink Jet Printers

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Various silicone–acrylic block copolymers were prepared by a free radical copolymerization technique, in which we used poly(dimethylsiloxane) containing azo groups as a macromolecular initiator in reactions with acrylic monomers, including functional monomers. The copolymer solutions were coated onto substrates by using various application methods and subsequently cured by using either crosslinking agents or UV light. Advancing (θ_A) and receding (θ_R) contact angles of the resulting films were measured in various inks. These films were found to be hard enough to form a nozzle face, and exhibited over 80° of θ_A and 60° of θ_R when in an ink, which are superior values to those observed for 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 in various inks at 60°C for 4 weeks. The durability of the films was outstanding. The excellent properties were found to be attributable to the formation of a microdomain structure, and to be influenced by domain spacing rather than silicone content.

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Introduction

Ink repellency has been the most important performance indicator for the nozzle face material of ink jet printers because it controls the ease of removal of residual inks and dusts from the nozzle face, of which both factors closely relate to achieving the correct on-target impact of an ink droplet. Increasing demand for higher image quality has accelerated the development of coatings with improved ink repellency. Silicone resin is a preferred binder because of its excellent water repellency as well as its lack of impact on the environment. This study aims at achieving the following properties for nozzle face coatings: i) easy application; ii) ink resistance; iii) film hardness. A crosslinked material system would be the most appropriate solution, but the hardness and resistance of crosslinked silicone films are usually insufficient for the requirements of the application.

Our strategy was to utilize block copolymers consisting of silicone and acrylic chains, in which the acrylic chain is able to crosslink. The microscopic images of the crosslinked 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 was superior to that of films consisting of crosslinked silicone. Moreover, it was found that the density of domain distribution in the films significantly influenced the ink repellency properties.

Experimental

Preparation of Polymers

Poly(dimethylsiloxanes) containing azo groups, as illustrated in Fig. 1, were used as a macromolecular initiator (VPS, Wako Pure Chemicals Ind. Ltd.). The characteristics of VPSs used are listed in Table I. The VPS, acrylic monomers and a solvent were weighed in flask, and stirred at 120°C for 5 h. The functional group, molecular weight, and silicone content of the polymers are tabulated in Table II. As comparative samples, a graft copolymer, prepared by the copolymerization of a methacryloxy terminated poly(dimethylsiloxane) (Mn = 1,000, Silaplane FM-0711, Chisso Corp.), and a pure acrylic resin obtained by a conventional method were used in this experiment.

Coatings, Application, and Curing

The thermosetting coatings were prepared by mixing with hydroxy containing polymers and melamine-form-

TABLE I. Macromolecular Initiator

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

TABLE II. Acrylic, Block and Graft Copolymers

Code	Functional group	Mn	MWD	Silicone segment wt%	Silicone segment 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	—

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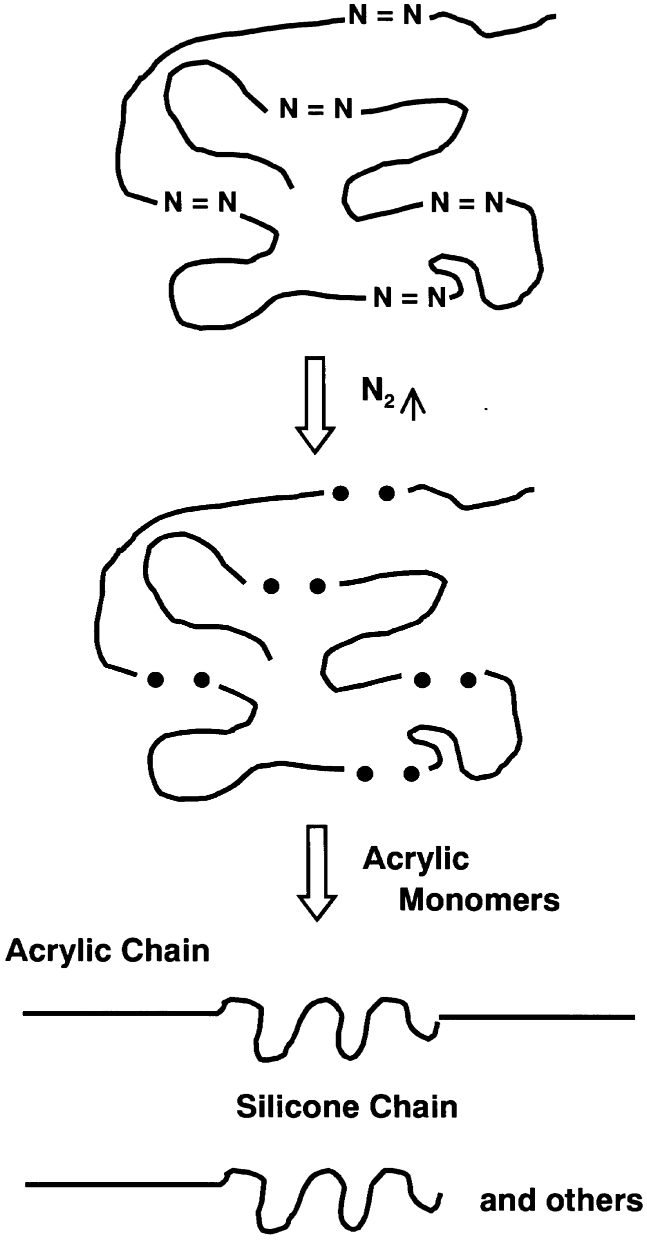


Figure 1. Preparation of silicone–acrylic block copolymers.

aldehyde (MF) resin as a crosslinking agent. A UV curable coating was prepared by mixing with Block 3 and a cationic photoinitiator. Fluorinated acrylic emulsion and a moisture curable silicone resin were used as a reference.

The coatings were cast onto a glass plate (24 × 55 × 0.2 mm) by dip coating, and applied for contact angle measurement after curing. Morphological observation called for free film samples cured on polypropylene or polytetrafluoroethylene plates, after coating by spray or spin coating methods.

The thermosetting coatings were cured at 150°C for 30 min. The UV curable coatings were exposed to a UV light (120mJ/cm^2) after pre-baking at 80°C for 10 min., and sequentially post-baked at 200°C for 1 h.

Measurements

Dynamic contact angles, advancing (θ_A) and receding (θ_R), based on the Wilhelmy plate technique,[1] were measured at 20°C by a tensile tester (DCA-100, Orientec Co.). Three commercially available cyan inks—inks A, B and C, sold by different manufacturers, were used for the measurement and durability tests.

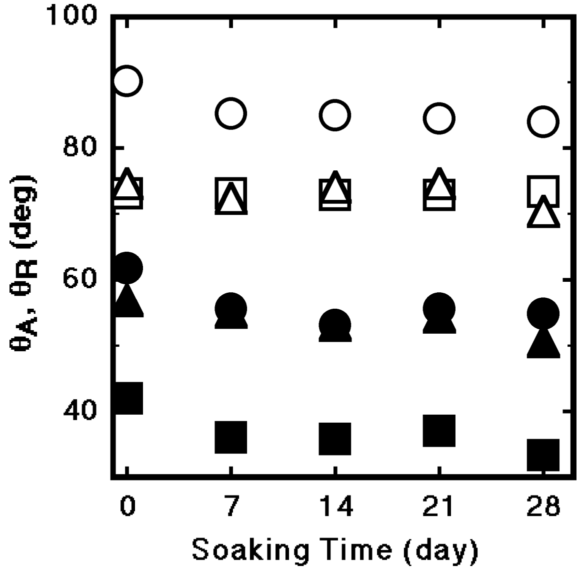


Figure 2. The change in advancing (θ_A) and receding (θ_R) contact angle of inks by soaking in the inks at 60°C. Open and filled symbols denote θ_A and θ_R, respectively. Circle, triangle, and square symbols denote the values of ink A, ink B and ink C, respectively.

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

Durability Test

Durability tests to gauge the resistance of the films against various inks were performed by soaking them in the inks at 60°C for 4 weeks. The durability was evaluated by monitoring changes in θ_A and θ_R before and after immersion.

Results

Dependence of Inks

The ink resistance of the film prepared with Block 1 and MF resin was evaluated by soaking it in various proprietary inks. The changes in θ_A and θ_R are shown in Fig. 2. Both values depended on the kind of inks that the films were subjected to. This particular film showed over 80° of θ_A and over 50° of θ_R in ink A, even after the durability test, while it showed only 40° of θ_R in ink C. However, no marks or droplets of the ink were observed on the surface after the film was pulled up from ink C. The values of surface tension of inks A, B, and C were 37.1, 30.6, and 29.3 dyn/cm, respectively. Hence, the dependence of θ_A and θ_R on the inks may be caused by differences in the type and amount of surfactants in the inks.

The θ_A and θ_R values decreased slightly only during the initial soaking period, and remained constant throughout the durability test. This slight decrease may be due to the removal of poly(dimethylsiloxane) from the film surface, as described below.

Performance of Block Polymer

The θ_A and θ_R values of ink A for the various film coatings before and after soaking in this ink are listed in Table III, together with their pencil hardness. The

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

	Crosslinking	Silicone content		Initial		After 4 weeks		
Binder	system	wt%	P.H.*	θ_A	θ_R	θ_A	θ_R	θ_{av}†
Block 1	–OH/MF	15	H	90	62	85	53	70
Block 3	Epoxy /H$^+$	7	H	84	61	81	50	66
Silicone	–SiOR	~100	<6B	88	48	91	56	74
Fluorinated	none	—	2B	97	78	50	17	37
Acrylic	–OH/MF	0	HB	80	24	65	8	45

* pencil hardness

† Averaged contact angles (θ_{av}) after immersion were calculated by the following equation. $\cos\theta_{av} = (\cos\theta_A + \cos\theta_R)/2$

crosslinked films prepared from Block 1 or Block 3 were much harder than fluorinated coating and silicone films. The excellent hardness of the present films is comparable to that of an automotive topcoat.

Pure acrylic film showed remarkably low θ_R. Fluorinated film initially showed highest values of θ_A and θ_R, but the values became lower after the durability test. On the other hand, the values of θ_A and θ_R for the crosslinked block copolymer system were similar to those of silicone film, even after durability test.

Various workers have developed non-wetting nozzle faces for ink jet recording heads by various methods,[2–5] such as plasma polymerization of fluorocarbons, coating of thermoplastic fluorinated polymers and thermal evaporation of fluorocarbon resins. Unfortunately, ink repellency properties in the present study cannot be directly compared with the previous results because the values of contact angles depend critically on the kinds of inks used, as mentioned before. Hence, the static contact angles of the present films with respect to water were measured. The resulting values were approximately 103°, which is close to that of poly(tetrafluoroethylene), 108°.[6]

Considering these results, the present coatings are very well suited to the purpose as ink repellent coatings for the nozzle faces of ink jet printers.

Discussion

Cassie has derived the following equation.[7]

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

where θ is the apparent contact angle and σ_1 and σ_2 are the fraction of the surface having the intrinsic angles θ_1 and θ_2. The present films prepared from silicone–acrylic block copolymer and MF resin contain no more than 15% silicone by weight. The bulk of the material consists of acrylic chains and MF resins, which are the same components found in Acrylic/MF film, which showed low θ_A after immersion and very low θ_R before and after immersion, as listed in Table III.

The theoretical contact angle of the present film was calculated by the Cassie equation, where the averaged contact angles[8,9] of silicone film and Acrylic/MF film after immersion were used, and where the area fraction of silicone was roughly estimated from the silicone content to be 0.15. The resulting value was 50°, which was much smaller than the observed value.

As mentioned below, the present film was found from observations of electron micrographs to form a micromorphology. The diameter of the silicone spheres, the domain spacing and the area fraction of the silicone domains on the film surface were roughly estimated to be 12nm, 19nm, and 0.24, respectively. By the use of the observed area fraction, the calculated contact angle was found to be 53°, which was smaller than the observed mean value. Hence we tried to find the reason why the present films showed high contact angles, as high as silicone film.

TABLE IV. Effect of Molecular Structure on θ_A and θ_R

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

* Melamine-formaldehyde resin curing system

† homopoly(dimethylsiloxane) was added to acrylic resin in Table I.

Dependence of Molecular Structure

We initially expected that the silicone chains, which were fixed in the matrix, would fill the film surface, because materials having low surface tension tend to rise to the surface. If this speculation is correct, a graft copolymer having a silicone branch will show the same performance as the block copolymer. Hence, we tested the ink repellency and ink resistance of a film prepared from a graft copolymer and MF resin, together with a film prepared from a mixture of poly(dimethylsiloxane), acrylic, and MF resin. The values of θ_A and θ_R before and after durability test for the films are listed in Table IV.

The θ_R of the film containing poly(dimethylsiloxane) was already low before the durability test. This result suggests that poly(dimethylsiloxane) was removed during the measurement, because no silicone chain was fixed in the matrix. In the case of the film consisting of the graft copolymer, the θ_R became lower after immersion. This may be due to a structural reorganization, i.e., polar chains appeared on the surface during the immersion, although silicone chains were fixed in the matrix. These results implied that the first hypothesis was incorrect.

Micromorphology

Block copolymers having mutually incompatible chains have been known to form micromorphology within the films. Therefore, we observed an approx. 40 nm thick ultra-thin section of the cured film prepared from Block 2 and MF resin by TEM. Figure 3 shows the electron micrograph. The white area in the micrograph corresponds to the acrylic chain and MF resin phases, while the silicone phases are stained by ruthenium oxide and appear dark. The spherical micromorphology can be observed from the airside to the substrate side. The

TABLE V. Domain Size and Domain Spacing

Formulation*			Silicone			After		Domain	
	Block	Acrylic	content	Initial		4 weeks		Spacing	Size
No	wt%	wt%	wt%	θ_A	θ_R	θ_A	θ_R	nm	nm
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	

* 30 wt% of melamine-formaldehyde resin was added.

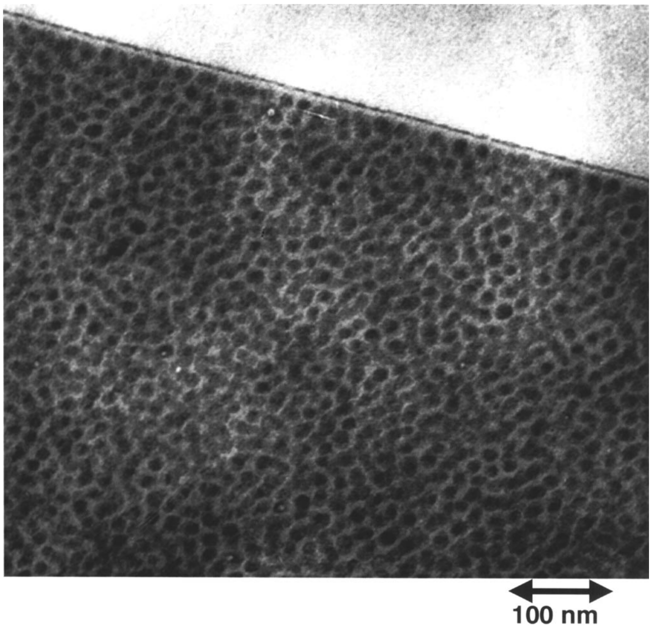


Figure 3. An electron micrograph of a thin section of Block 2/MF sample, showing the air–polymer interface.

diameter of the silicone spheres was estimated from the micrograph to be about 20 nm. The value for the film prepared from Block 1 and MF resin was also found to be approximately 12 nm. On the other hand, no micromorphology was observed in the cured film prepared from the graft copolymer and MF resin.

In Fig. 3, an ultra-thin dark colored layer, approximately 3 nm thick, was observed at the air–polymer interface. X-ray photoelectron spectroscopic analysis performed by changing the incident angles of the Xray confirmed that the layer consists of silicone. After the film was immersed in hexane, the layer could not be observed at the surface. This may be because the layer was composed of homopoly(dimethylsiloxane), formed as a by-product during the polymerization. As shown in Fig. 2, every value of θ_A and θ_R initially decreased and then remained constant during the soaking test. These results suggested that the high value of θ_R observed after the soaking test for the block copolymer system was closely related to the micromorphology after the ultrathin layer was removed from the surface during the initial period of immersion.

Dependence of Microdomain Spacing

By using a numerical calculation process, Johnson and Dettre[10] have 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 the microdomain structure would affect the values of contact angles.

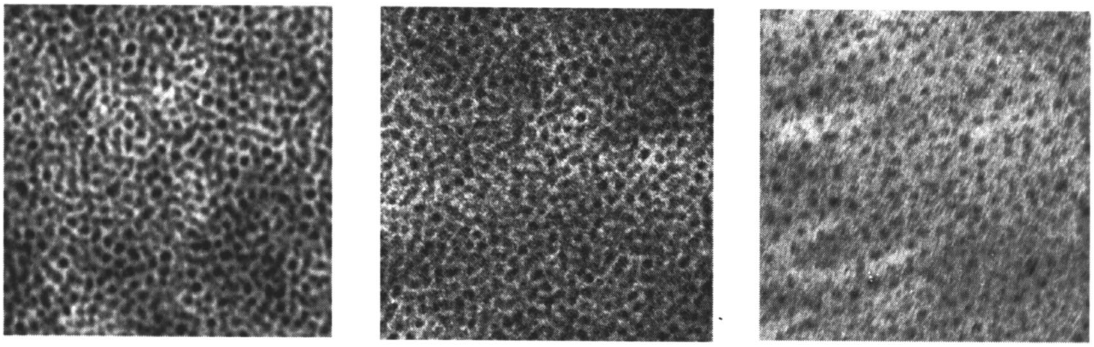
In a study of a binary mixture of poly(isoprene–block–styrene) and homo poly(styrene),[11] homo poly(styrene), which has a lower molecular weight than that of polystyrene block, was shown to be solubilized into microdomains composed of polystyrene block, causing a change in microdomain spacing. Based on this observation, acrylic resin was added to Block 1 or Block 2 to control the domain spacing, as showing in Table V.

Figure 4 shows electron micrographs of the resulting films. The domain spacing and domain size were roughly estimated from the micrographs. These results and the values of θ_A and θ_R with respect to ink A for the films before and after the soaking test in it are summarized in Table V.

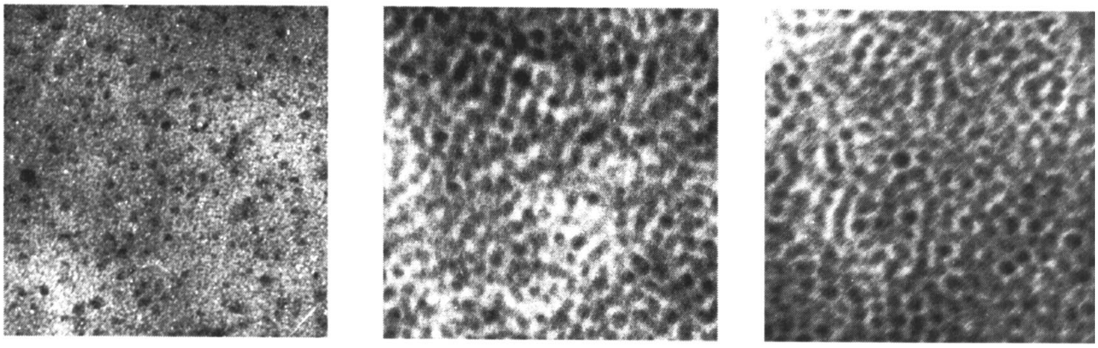
Even when there is a low silicone content, the spherical microdomains were still conserved, but dispersed randomly in the matrix. The microdomain size was dependent on silicone chain length and independent of silicone content. The space between silicone domains increased with increasing weight fraction of added acrylic resin.

The values of θ_A for all films were over 80° and unchanged by the soaking test in ink A, even after 4 weeks. The values of θ_R for a few films were decreased considerably by the soaking test, although all of the initial values of θ_R were over 60°. Figure 5(a) shows the relationship between θ_R after the soaking test and the silicone content of two kinds of films that have different domain sizes. Both values of θ_R remained constant at higher silicone content, but decreased with decreasing silicone content from different critical points.

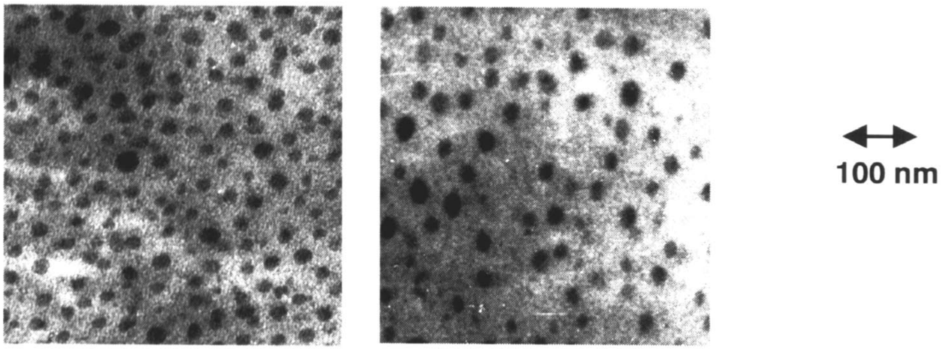
Figure 5(b) shows the relationship between θ_R after the soaking test and a roughly estimated microdomain spacing dimension for the films. Both values of θ_R decreased with increasing domain spacing from almost the same critical point, which was roughly from 20 nm to 30 nm. Similar results were obtained in the cases of inks B and C. These results suggested that the value of θ_R is dependent on domain spacing rather than silicone content, and independent of low contact angle regions such as Acrylic chain/MF resin, so long as the silicone microdomain spacing is shorter than about 30 nm for the material in this study.



Block 1, 15 wt% Block 1, 10 wt% Block 1, 5 wt%



Block 1, 2 wt% Block 2, 17 wt% Block 2, 10 wt%



Block 2, 5 wt% Block 2, 3 wt%

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

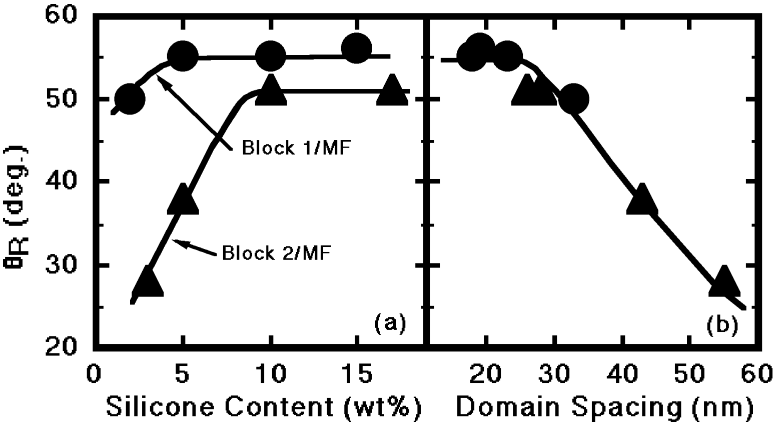


Figure 5. Relationship between (a) silicone content or (b) domain spacing and θ_R after soaking in ink A for 4 weeks. Circle and triangle symbols denote the values of the films prepared from Block 1/MF and Block 2/MF, respectively.

The decrease of θ_R after immersion may be due to the hydrolysis of acrylic and MF resins by inks. Further study is necessary to explain why inks neglected the acrylic/MF domain under the present conditions.

Conclusion

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

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