

A Study of Colored Siloxane-Based Polyurethane Ionomer

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Received 12 August 1997; accepted 10 December 1997

ABSTRACT: The reaction of dye with toluene diisocyanate and dimethyldichlorosilane in the presence of other additives to form a colored siloxane-based polyurethane (PU) ionomer has been proven to occur by infrared spectra. In aqueous solution, the number-average particle size for the colored siloxane-based PU ionomer was found to increase with an increase in the NCO-to-OH ratio, dye concentration, and dimethyldichlorosilane concentration, as a result of increased free volume of the ionomer molecules. It is worthy to note that the amount of air diffusing into the film cast from colored siloxane-based PU ionomer was found to increase with an increase in the concentration of dimethyldichlorosilane instead of raising the ratio of NCO to OH or the concentration of dye, as a result of the formation of more porosities. In addition, the tensile strength of this film will be strengthened by raising the NCO/OH ratio or the concentration of dimethyldichlorosilane, whereas the elongation, on the other hand, can be substantially increased with increasing the concentration of dye instead of increasing the concentration of dimethyldichlorosilane for use in the PU ionomer system. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2097–2105, 1998

Key words: colored siloxane-based PU ionomer; infrared spectra; toluene diisocyanate; dimethyldichlorosilane

INTRODUCTION

In recent years, environmental protection becomes increasingly important, and the organic solvent used as a diluent for the resin industry is gradually being replaced by a nonpollutant solvent. In this respect, the development of a colored siloxane-based polyurethane (PU) ionomer becomes important at present.

In 1971, Ziegel¹ studied the diffusivity of the permeability of respective oxygen, nitrogen, and argon into 4 different kinds of polyurethane membranes. McBride et al.² further investigated the diffusivity of respective hydrogen, oxygen, and carbon dioxide into 3 kinds of polyurethane membranes and found that the diffusivity of gas decreases with an increase in the amount of hard segment of polyurethane

membrane and with an increase in the molecular weight of gas as well. Polyurethane resins, due to their unique properties, have been intensively utilized in the area of membrane and play an important role in the resin industry.

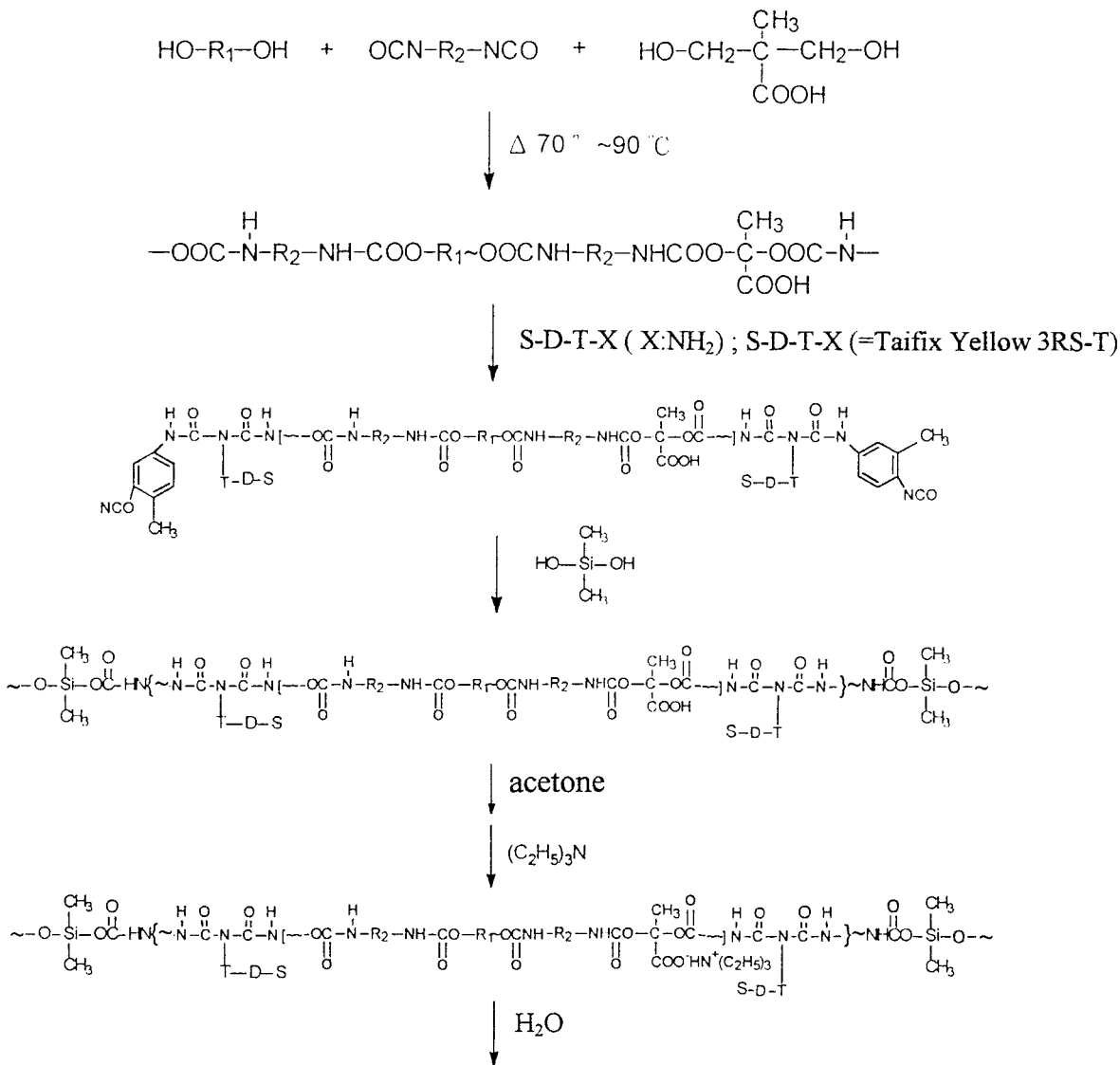
Increasing the concentration and adhesion of the colored siloxane-based polyurethane ionomer^{3–13} on leather or textiles or materials from another industry is useful in upgrading the technology for dye-stuff, leather, pigment, resin, and other materials. Presently, almost no literature concerning the synthesis and physical properties of the colored siloxane-based polyurethane ionomer has been published so far. For this reason, we attempted to develop the unique way for preparing colored siloxane-based polyurethane ionomers and to study further their physical properties.

The reaction of dye (that is, Taifix Red HE-3BT, Taifix Yellow 3RS-T, and Taifix Black B-T) with toluene diisocyanate and dimethyldichlorosilane in the presence of other additives is expected to form the colored siloxane-based polyurethane

This article was presented at the 36th IUPAC Congress, Geneva, 17–22 August 1997.

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Journal of Applied Polymer Science, Vol. 69, 2097–2105 (1998)
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Scheme 1

ionomer, and the possible structure of this ionomer is given in Scheme 1.

Material

Taifix Red HE-3BT ($\text{C}_{44}\text{H}_{24}\text{N}_{14}\text{O}_{20}\text{Cl}_2\text{S}_6\text{Na}_6$), Taifix Yellow 3RS-T ($\text{C}_{28}\text{H}_{20}\text{N}_9\text{O}_{16}\text{Na}_4\text{Cl}$), and Taifix Black B-T ($\text{C}_{26}\text{H}_{23}\text{N}_5\text{O}_{18}\text{S}_6\text{Na}_2$) were purchased from Taitan Industries Corporation (Taiwan). Dimethyldichlorosilane (DMDCS) and toluene diisocyanate (TDI) were obtained from Aldrich Chemical Co., Inc. (USA). Dimethylol propionic acid (DMPA) and *N,N*-dimethylacetamide (DMAC) were purchased from Alcolac Industrial Chemicals (USA) and J. T. Baker Chemicals (USA), respectively. Triethylamine, diethylenetriamine,

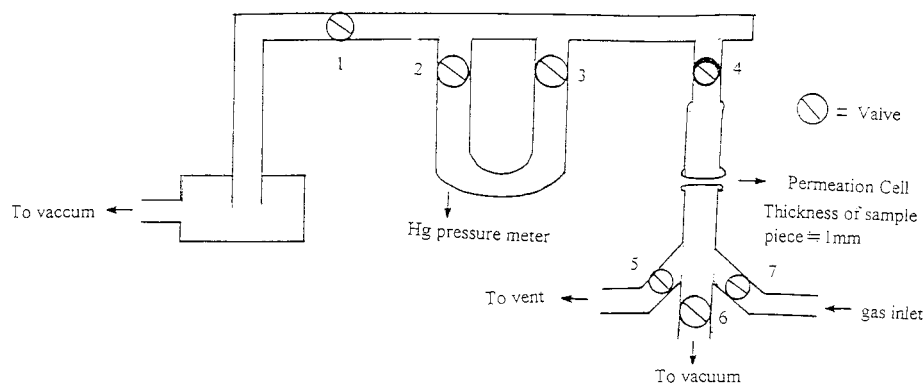
and acetone were supplied by Merck Co. (USA). Polypropylene glycol with an average molecular weight of 2000 (OH number ≈ 56.0) and epoxy resin (BE-501, E.W. ≈ 508) was received from Chiunglong Petrochemical Co. (Taiwan) and Chang Chun Petrochemical Co., Ltd. (Taiwan), respectively. All of these chemicals were used without further purification.

Method

A 0.018 equivalent of polypropylene glycol (PPG) with an average molecular weight of 2000, 0.003 equivalent of PPG (molecular weight ≈ 700), 0.00675 equivalent of epoxy resin (BE-501, E.W. ≈ 508), and 0.06 equivalent of dimethylol propi-

onic acid (DMPA) were charged to a 1000-mL four-necked reaction kettle equipped with a stirrer, thermometer, and condenser containing 20 g of *N,N*-dimethylacetamide under agitation at 70°C. Subsequently, 0.132 equivalent of TDI and 0.1–0.8 g of dye were added, respectively, in the presence of 0.2% (by weight) dibutyltin dilaurate and then reacted at around 81°C for about 2 h to form NCO-terminated PU prepolymer. A 0.03 equivalent of triethylamine was then reacted with this NCO-terminated PU prepolymer dissolved in 65 g acetone to form amine-neutralized NCO-terminated PU prepolymer. The amine-neutralized PU prepolymer further reacted immediately with hydrolytes of dimethyl dichlorosilane, and 170 g water was then added to form the colored siloxane-based PU ionomer. The acetone

was completely removed from the colored siloxane-based polyurethane ionomer by an evaporation technique. The final colored siloxane-based PU ionomer had an approximately 20% solid content. A dynamic light scattering spectrophotometer DLS-700 (Otsuka Electronic Co., Japan) was used to explore the number-average particle sizes of colored siloxane-based PU ionomers present in aqueous solution. The colored siloxane-based PU ionomer aqueous solution with 20% solids was poured into a polypropylene dish to 1 mm thickness and dried in oven at 60°C; it was used for tensile and elongation testing by an Instron 1130 (USA) and for the air permeation testing of this film by using an apparatus similar to the Yanaco Gas Permeability Analyzer Model GTR-10 briefly, as follows.



To examine air permeated through the colored siloxane-based PU ionomer film, an air having a high partial pressure is allowed to diffuse into the one side of PU ionomer film, while the other side of this film is placed under low partial pressure or vacuum. During the measurements, valves (labeled 1, 2, and 6) are closed, but valves 5 and 7 are open. In this condition, the volume of air that permeated through the colored siloxane-based PU ionomer film is able to be measured through the variation of the low-pressure side by using a Hg pressure meter.

The experimental error for the above experiments was estimated to be within ± 0.5 .

RESULTS AND DISCUSSIONS

The infrared (IR) spectra for TDI, C. I. Reactive Black-5, and hydrolyte of dimethyldichlorosilane are given in Figures 1–3. The reaction of toluene

diisocyanate with dimethylol propionic acid, polypropylene glycol, epoxy resin, dimethyldichlorosilane, and dyes in the presence of other additives to form NCO-terminated PU prepolymer is illustrated by the formation of the absorbance peaks at around 1540 (NHCO), 3300 (NH), 1720 (C=O), 1100 (—Si—O—CH₂—), 1250 (—Si—CH₃), and 1360 cm⁻¹ (S=O) and by a substantially decreased absorbance peak at around 2275 cm⁻¹ (NCO), given in Figure 4 in comparison to that of Figures 1–3. These results demonstrate that the reaction of TDI with dimethylol propionic acid, polypropylene glycol, C. I. Reactive Black-5, dimethyldichlorosilane, and other additives does indeed form the colored siloxane-based polyurethane ionomer. For the colored siloxane-based polyurethane ionomer molecule in aqueous solution, the number-average particle size of this ionomer molecule increases drastically with an increase in the concentration for the various dyes investigated, as described in Figure 5. Increased

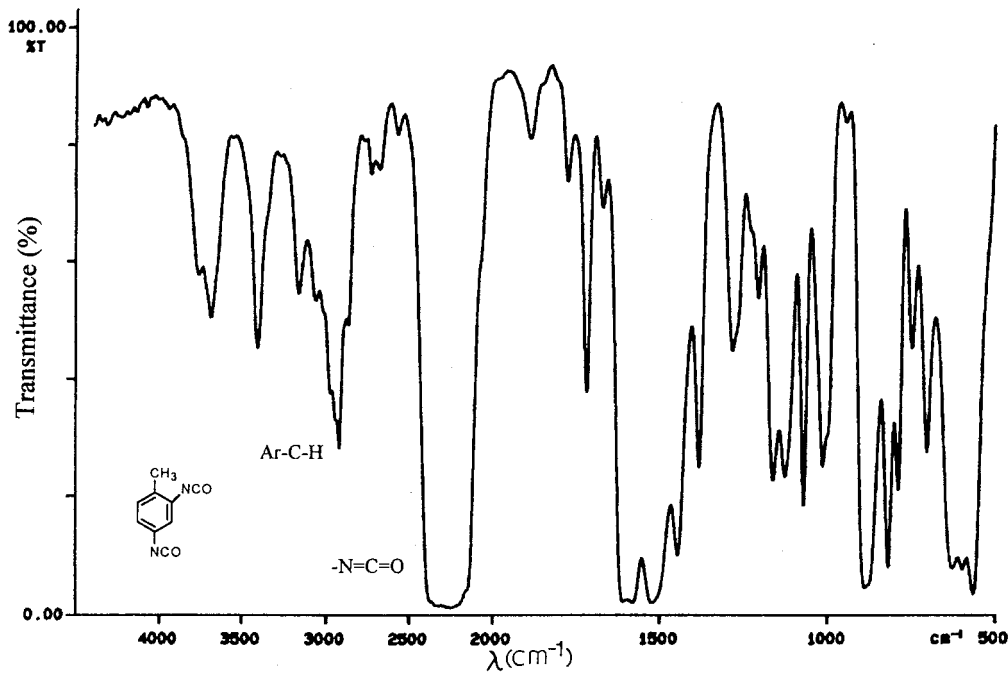


Figure 1 Spectra of isophorone diisocyanate at $25 \pm 0.05^\circ\text{C}$.

dye concentration may force the colored siloxane-based PU ionomer molecules to form hydrogen bonding with the surrounding water molecules and make the free volume of these ionomer molecules become large. This is the reason why the

number-average partial size of the colored siloxane-based PU ionomer molecule increases dramatically with an increase in the concentration of dyes. For the colored siloxane-based PU ionomer, the plots of the number-average particle sizes as

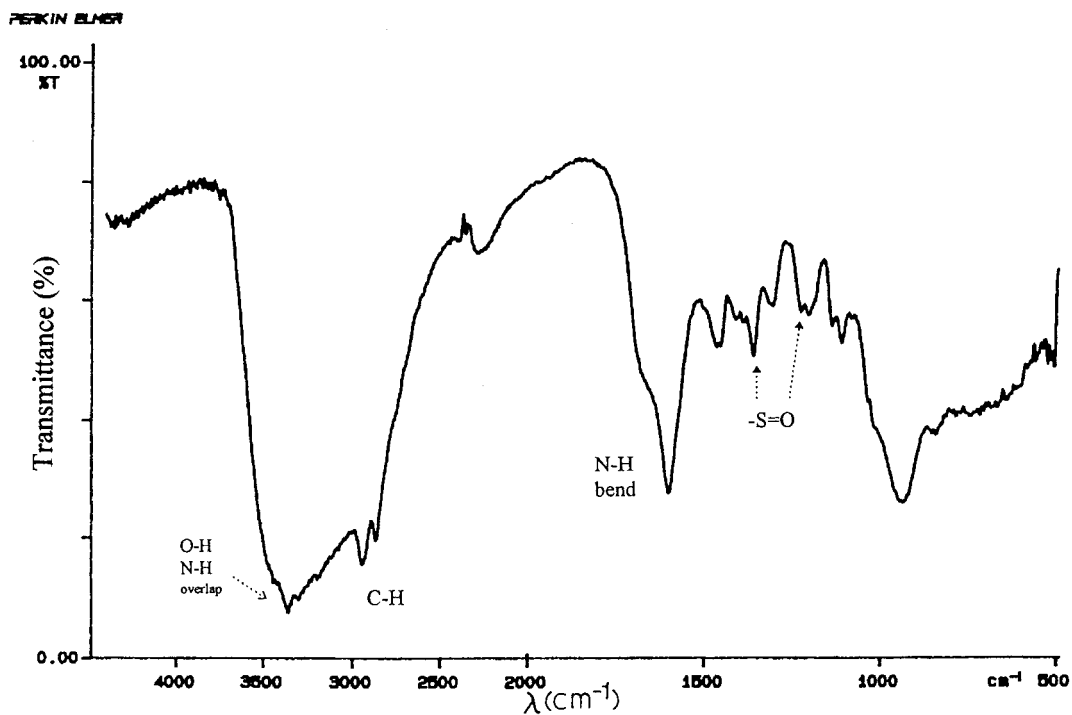


Figure 2 Spectra of the C. I. Reactive Black-5 at $25 \pm 0.05^\circ\text{C}$.

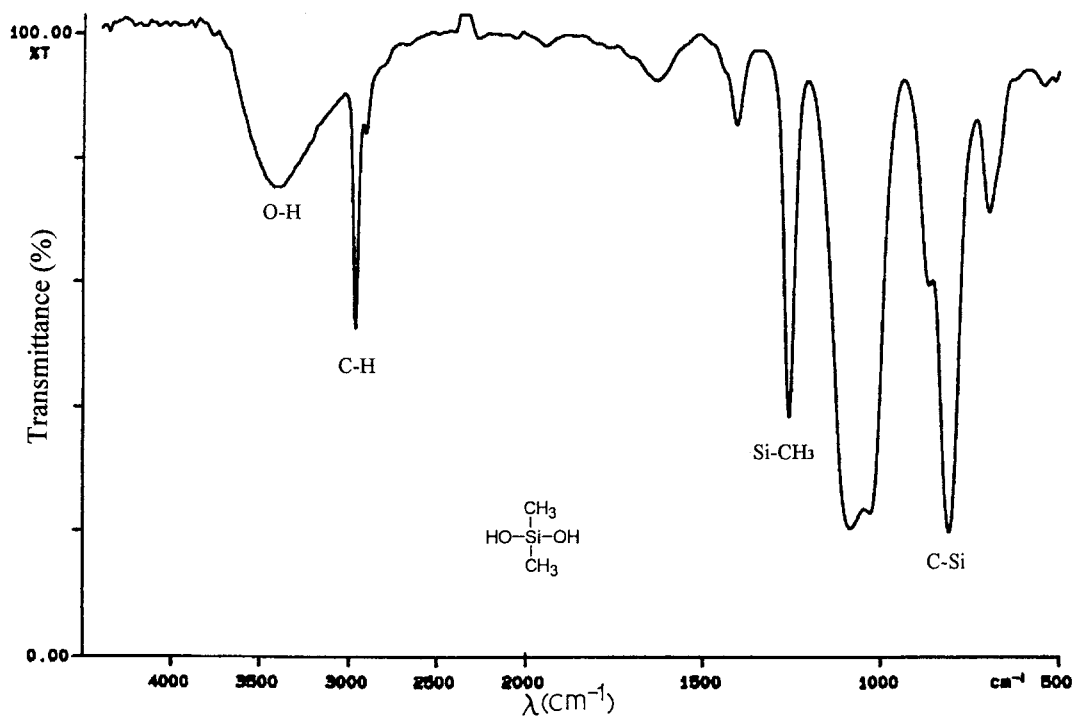


Figure 3 Spectra of the hydrolyte of dimethyl dichlorosilane at $25 \pm 0.05^\circ\text{C}$.

a function of the ratio of NCO/OH and of the concentration of DMDCS, respectively, are given in Figures 6 and 7. Figures 6 and 7 indicate that,

for the colored siloxane-based PU ionomer system, the number-average particle size increases drastically with an increase in the ratio of NCO/OH or

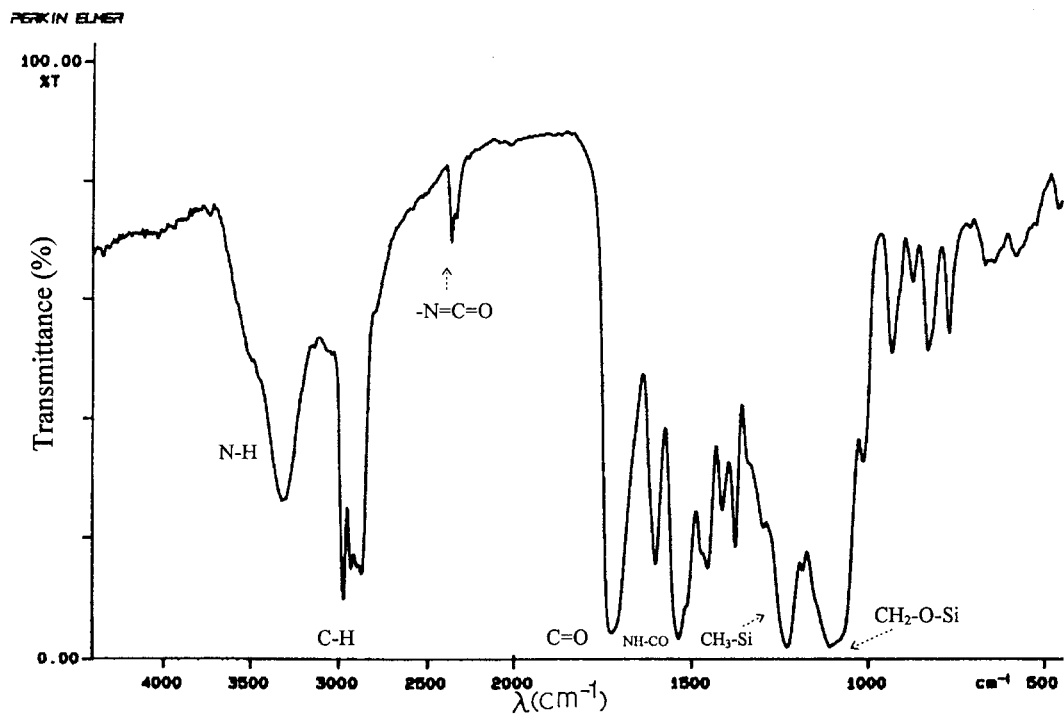


Figure 4 Spectra of the colored NCO-terminated siloxane-based polyurethane prepolymer formed after around 2 h reactive, at $25 \pm 0.05^\circ\text{C}$.

the concentration of DMDCS. The reason for this behavior is the same as described in Figure 5.

To evaluate the air permeability of film made by the colored siloxane-based PU ionomer, we have fully investigated the amount of air permeated through a unit area of this film as a function of the ratio of NCO to OH and of the concentration of dye and DMDCS, respectively, given in Figures 8–10. Figure 8 clearly indicates that the amount of air permeated through the film increasing with increasing the concentration of DMDCS is possibly due to more porosities formed. Contrarily, the amount of air diffusing into the film appears to decrease with increasing the concentration of dye and the ratio of NCO to OH, given in Figure 9. In fact, the increased concentration of dye attached to the backbone of the PU ionomer molecule enables the ionomer molecule to have more functional groups, which may help to increase the intramolecular and/or intermolecular interaction of these ionomer molecules. This interaction is likely to decrease the porosities of ionomer molecules to be formed and, on the other hand, reduces the amount of air diffusing into the film, as shown in Figure 10.

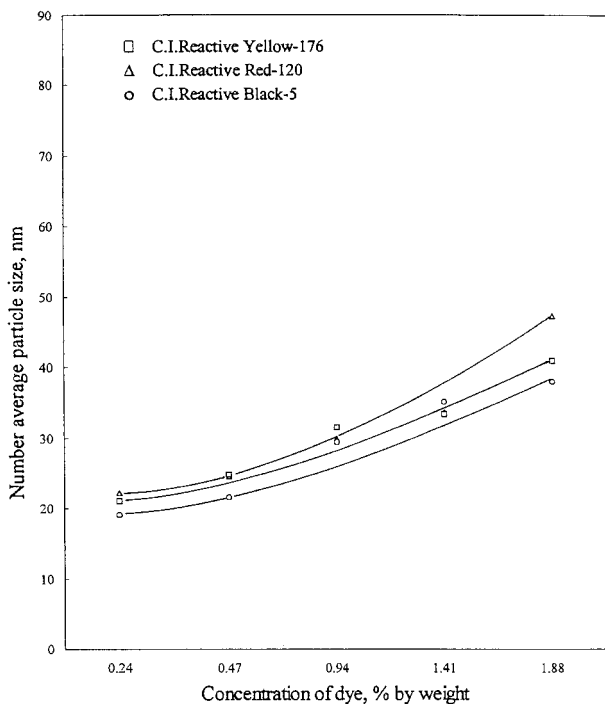


Figure 5 Plot of the number-average particle size versus the respective concentration of C. I. Reactive Red-120, C. I. Reactive Yellow-176, and C. I. Reactive Black-5 for use to prepare the percentage (by weight) of gas-permeable, water-soluble, dye-based polyurethane ionomer, at $25 \pm 0.05^\circ\text{C}$.

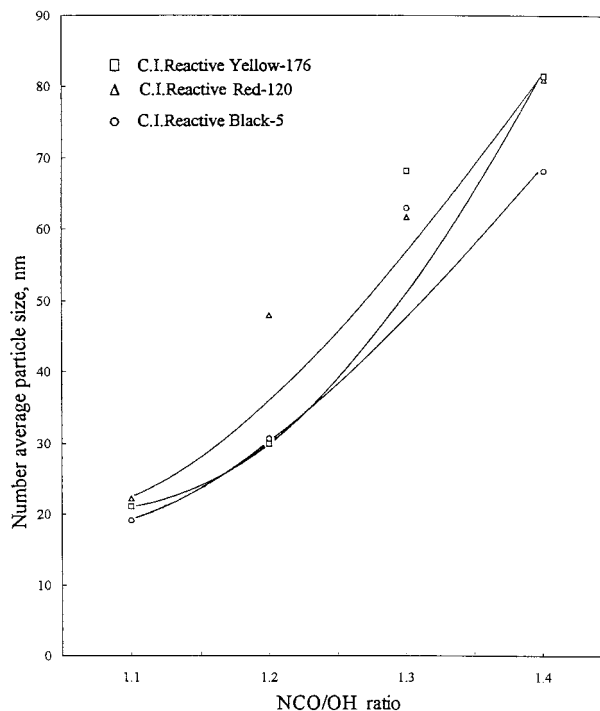


Figure 6 Plot of the number-average particle size versus the ratio of NCO/OH for use to prepare the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

The tensile strength of self-cured films of the colored siloxane-based PU ionomer as a function of the ratio of NCO to OH and the concentration of dye and DMDCS is given in Figures 10–13. Figures 10–13 clearly show that, for the colored siloxane-based PU ionomer system, the tensile strength of dry film at the breaking point is seen to increase dramatically with an increase in the ratio of NCO to OH and the concentration of dye and DMDCS, respectively. For the colored siloxane-based PU ionomer molecule, increased intermolecular and/or intramolecular interaction resulting from more functional groups linked to the backbone of the ionomer molecule may greatly enhance the capability of crosslinking of the ionomer molecule. Thus, the tensile strength of the film made by the colored siloxane-based PU ionomer becomes stronger as the NCO/OH ratio, dye, and DMDCS concentration increase. In comparison of Figures 10–13, the tensile strength is seen to be stronger for the PU ionomer system with the increased NCO/OH ratio or the increased DMDCS concentration than for the PU ionomer system with increased dye concentration. This may be attributed to the functional groups of dye molecule attached to the backbone of the ionomer molecule generating strong intramolecular interac-

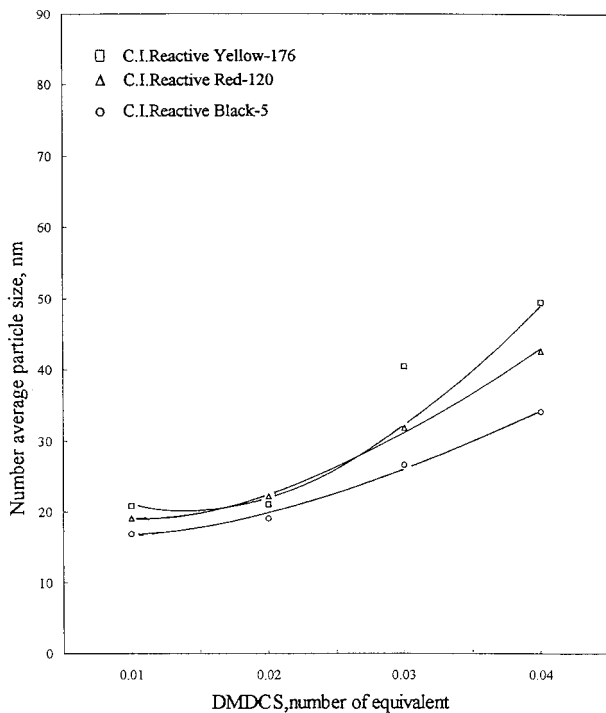


Figure 7 Plot of the number-average particle size versus the concentration of DMDCS for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

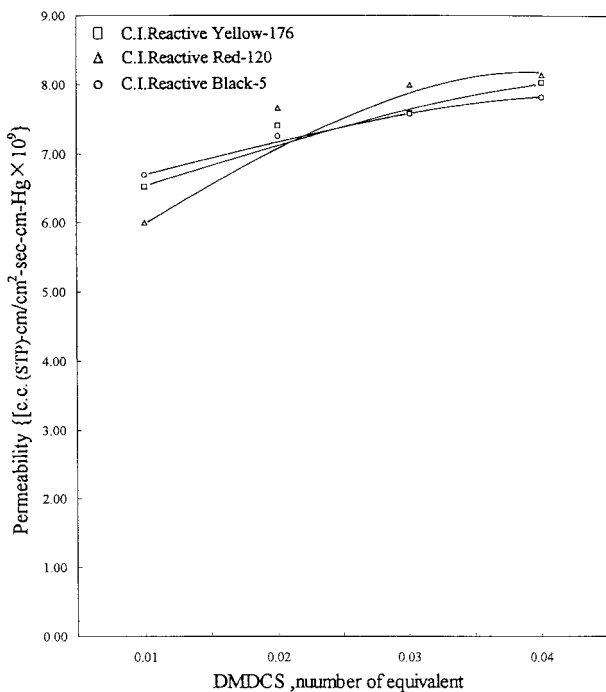


Figure 8 Plot of the permeability versus the concentration of DMDCS for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

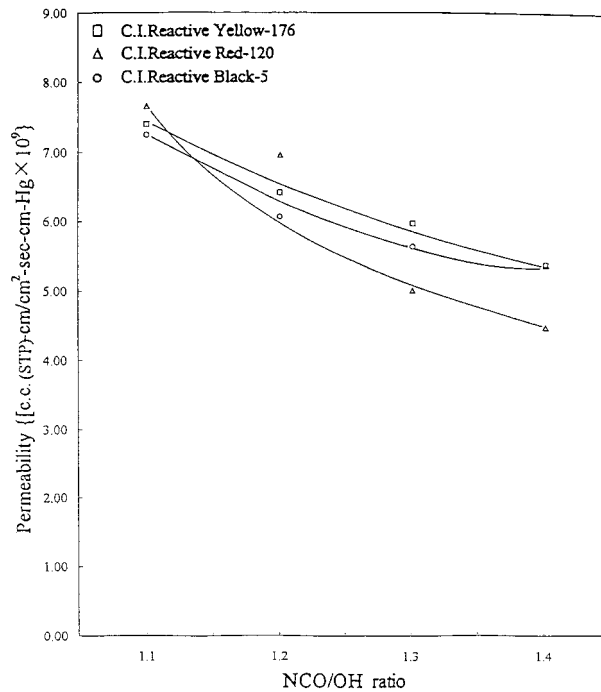


Figure 9 Plot of the permeability versus the ratio of NCO/OH for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

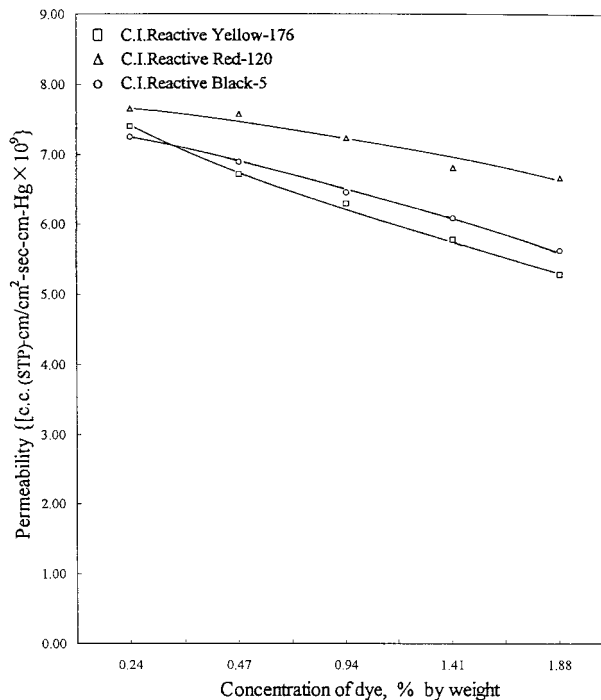


Figure 10 Plot of the permeability versus the respective concentration of C. I. Reactive Red-120, C. I. Reactive Yellow-176, and C. I. Reactive Black-5 for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer, at $25 \pm 0.05^\circ\text{C}$.

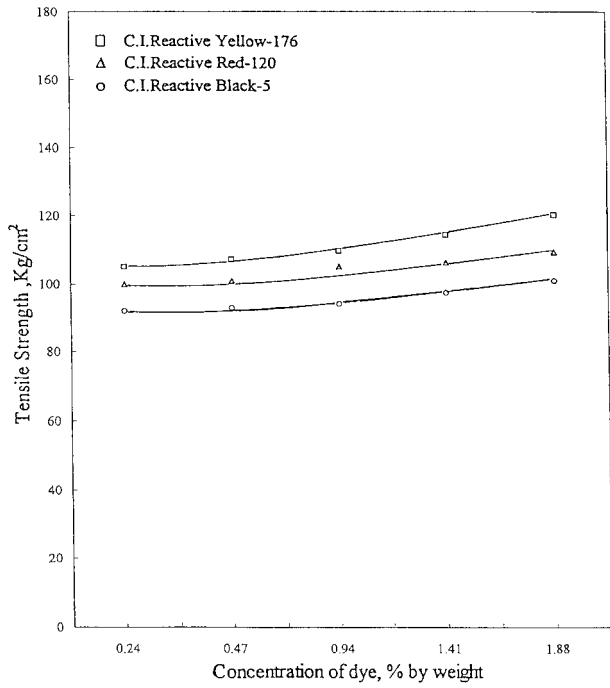


Figure 11 Polt of the tensile strength versus the respective concentration of C. I. Reactive Red-120, C. I. Reactive Yellow-176, and C. I. Reactive Black-5 for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer, at $25 \pm 0.05^\circ\text{C}$.

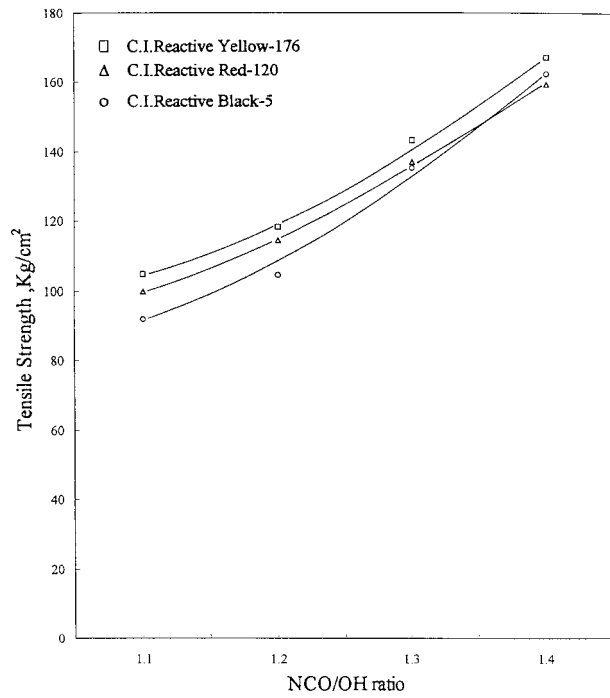


Figure 13 Polt of the tensile strength versus the ratio of NCO/OH for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

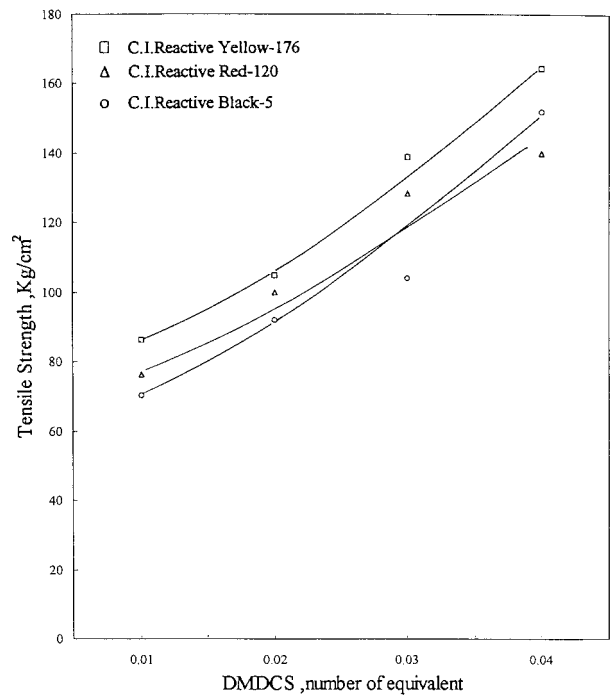


Figure 12 Polt of the tensile strength versus the concentration of DMDCS for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

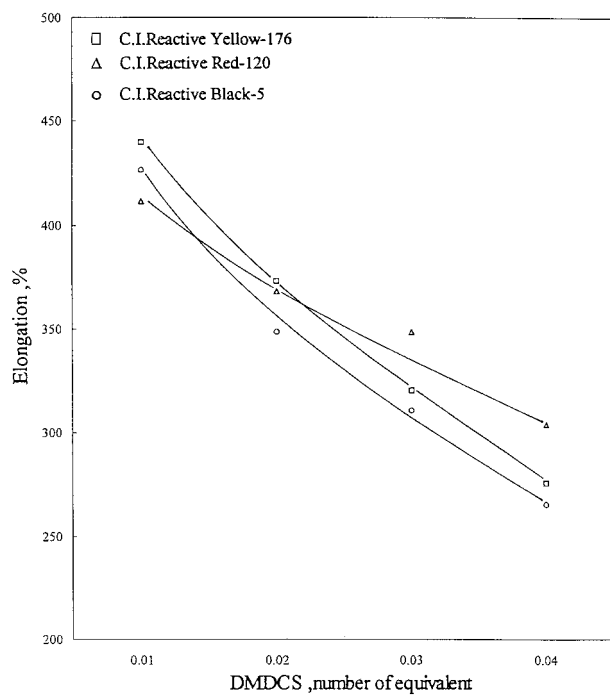


Figure 14 Polt of the elongation versus the concentration of DMDCS for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer with fixed dyes (0.24%), at $25 \pm 0.05^\circ\text{C}$.

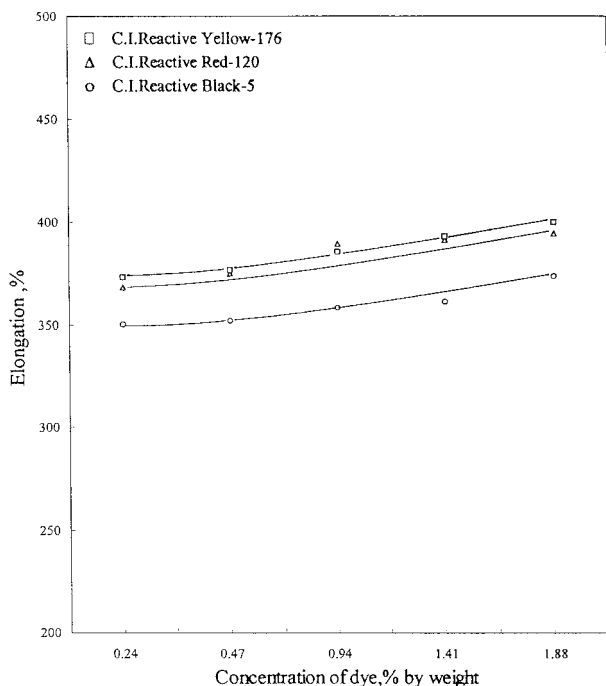


Figure 15 Plot of the elongation versus the respective concentration of C. I. Reactive Red-120, C. I. Reactive Yellow-176, and C. I. Reactive Black-5 for use in preparing the gas-permeable, water-soluble, dye-based polyurethane ionomer at $25 \pm 0.05^\circ\text{C}$.

tion, which possibly reduces the tensile strength of the film made by the PU ionomer prepared with increased dye concentration.

On the other hand, the elongation of dry film cast from the colored siloxane-based PU ionomer molecules at the breaking point appears to increase with an increase in the concentration of dye, but it appears to decrease with an increase in the concentration of DMDCS, as shown in Figures 14–15. For the colored siloxane-based PU ionomer system, the tensile strength due to more crosslinking formed, was found to be weaker for the ionomer system prepared with the increased concentration of dye than for the ionomer system prepared with the increased concentration of DMDCS, thus causing the elongation of the PU ionomer molecule with the concentration of dye instead of DMDCS to be higher.

CONCLUSION

The reaction of dye with toluene diisocyanate and dimethyldichlorosilane in the presence of other additives is expected to form colored siloxane-

based PU ionomers, and their structures have been proven by IR spectra. For the colored siloxane-based PU ionomer system, the number-average particle size was found to increase dramatically with increasing the ratio of NCO to OH or the concentration of dye or DMDCS, as a result of increased free volume of the ionomer molecules resulting from the hydrogen bonding effect and/or intermolecular interaction in aqueous solution.^{12–13} It is interesting to note that, for the colored siloxane-based PU ionomer system, the amount of air diffusing into the film was found to increase with increasing the concentration of DMDCS instead of raising the NCO/OH ratio or the concentration of dye, as a result of the formation of more porosities. Our experimental results clearly show that the increased concentration of DMDCS used in preparing colored siloxane-based PU ionomer molecules will substantially raise the amount of air permeated through the film cast from the colored siloxane-based PU ionomer. In addition, the tensile strength of these films will be strengthened by raising the NCO/OH ratio and the concentrations of DMDCS and dye, respectively; on the other hand, the elongation becomes higher for the ionomer system with increased concentration of dye instead of DMDCS.

The authors thank the National Science Council of the Republic of China for financial support of this research.

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