

Effect of the Concentration of Dye on the Physical Property of Dye-Based Polyurethane Ionomer

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SYNOPSIS

We have successfully prepared Congo Red-based polyurethane ionomers at our lab, and these ionomer structures have been proven by infrared (IR) spectra. For a dye-based polyurethane ionomer molecule solution, the surface tension was found to decrease, but the number-average particle size was found to increase with increasing concentration of Congo Red employed to prepare this ionomer molecule. Interestingly, the number-average particle size of dye-based polyurethane ionomer molecules decreases with increasing concentration of Congo Red in the presence of other dyes (i.e., Remajol Brilliant Blue R and Amaranth), as a result of Congo Red intramolecular interaction. It is important to point out that the addition of a fixed concentration of Amaranth to prepare Congo Red-based polyurethane ionomer molecules will significantly enhance the tensile strength but will decrease the elongation of this ionomer molecule. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

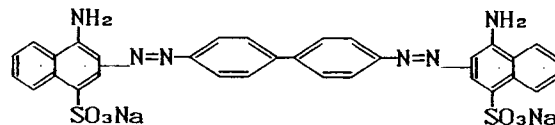
In recent years, since environmental protection became increasingly important, the resin industry gradually transferred from oil-based to water-based resins.¹⁻⁷ The development of water-based colored resins is one of the major targets for the chemical industry.

In general, reactive dyes can react with toluene diisocyanate in the presence of other additives to form water-based colored resins used for textile, leather, and other industries, and this will greatly reduce environmental pollution. In addition, increasing the coloration and adhesion of water-based color resins on leather or textile is useful in upgrading the technology of resins, for dyestuff, pigment, and other industries. Almost no literature concerning the synthesis and physical properties of water-based color resins has been published so far. Therefore, we attempted to explore this unique way to prepare water-based color resins and to further study their physical properties.

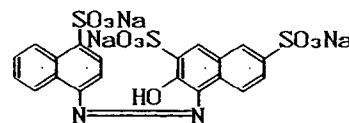
EXPERIMENTAL

Material

N,N-Dimethylacetamide (analyzed reagent) and dimethylolpropionic acid were purchased from J.T. Baker Chemicals (USA) and Alcolaco Industrial Chemicals (USA), respectively. Toluene diisocyanate, triethylamine, diethylenetriamine, and acetone were obtained from Merck Co. Congo Red,



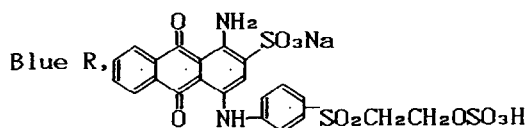
and Amaranth,



were supplied by Janssen Chemical (USA). Polyester (made by the reaction of adipic acid with 1,6-

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hexanediol and diethylene glycol) with a molecular weight of 2000 (OH number \approx 56) and Remajol Brilliant Blue R,

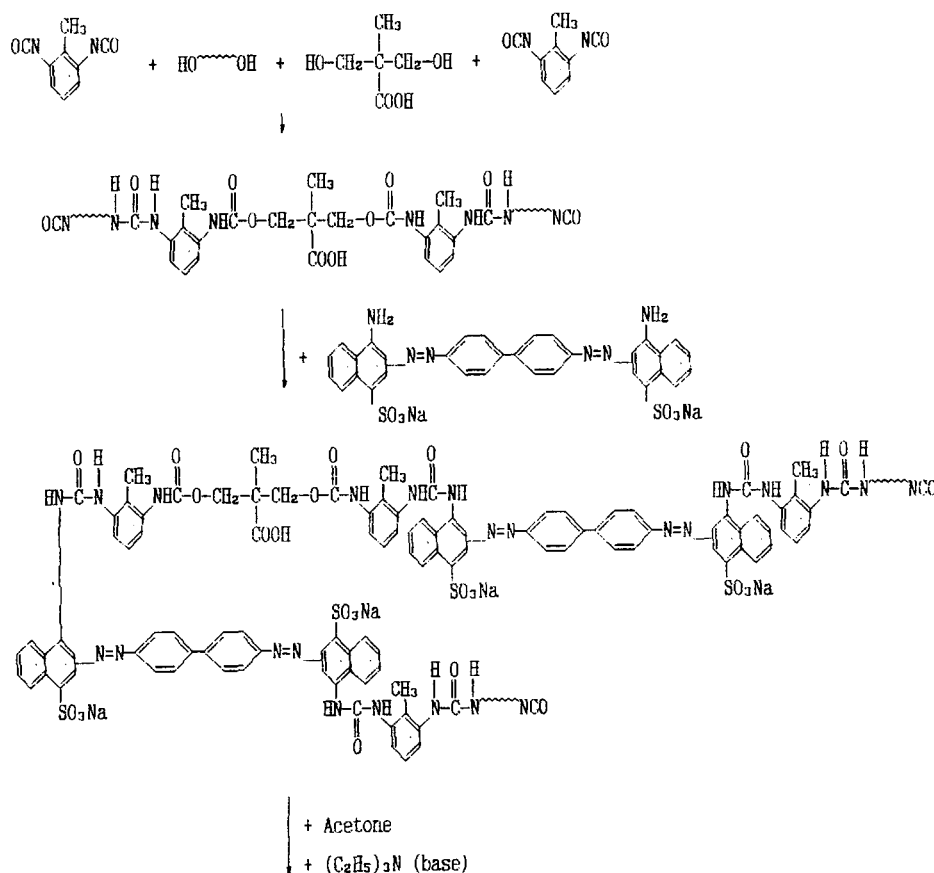


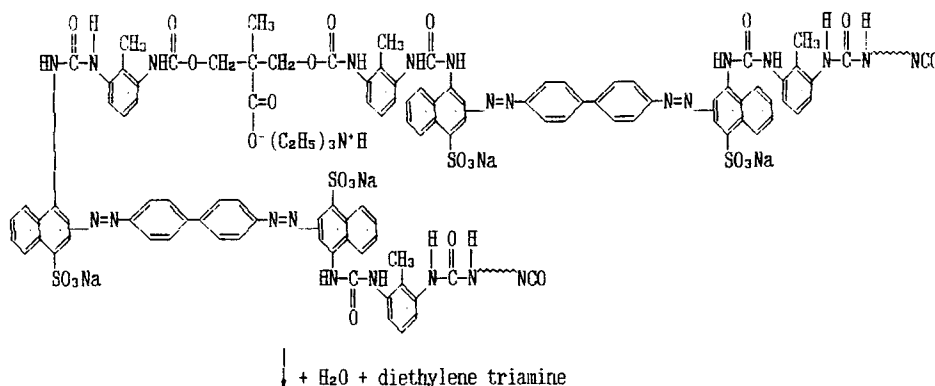
were received from Tai Chin Chemical Industry Co. (Taiwan) and Sigma Chemical Co. (USA), respectively. All these chemicals were used without further purification.

Method

Congo Red polyurethane (PU) ionomers were made in two steps: First, 6.2 g dimethylolpropionic acid was added to a 1000 mL four-necked Pyrex glass flask equipped with a stirrer, thermometer,

and condenser containing 17 g *N,N*-dimethylacetamide and 23 g polyester under agitation with a speed of 400 rpm. Subsequently, 15 g of toluene diisocyanate (TDI) and respective amounts of Congo Red, Amaranth, and Remajol Brilliant Blue R (0.2, 0.5, 0.8, and 1.2 g) were added slowly and then reacted in the presence of 0.2% (by weight) dibutyltin dilaurate at 80–85°C for about 3 h in the above flask. Second, triethylamine (4.6 g) was added (the equivalent amount of triethylamine based on dimethylolpropionic acid used in preparing quaternized isocyanate-containing prepolymer) and reacted with PU prepolymer dissolved in 56 g acetone as an organic solvent at 600 rpm for about 30 min to form quaternized isocyanate-containing prepolymers. These quaternized isocyanate-containing prepolymers reacted further with approximately 300 g water in the presence of a small amount of diethylenetriamine to form Congo Red PU ionomers and their possible structure is given as follows:





Congo Red based polyurethane ionomers

To convert Congo Red-based charged PU ionomer liquids into the aqueous phase, acetone, the organic solvent, was removed by blowing it out *in vacuo*. The surface tension and average particle size of these Congo Red-based PU ionomer aqueous solutions with 30% solids were examined at room temperature using a FACE surface tensiometer, CBVP-A3 type (Kyowa Interface Science Co., Japan), and a dynamic light scattering spectrophotometer DLS-700 (Otsuka Electronics Co., Japan), respectively. A Congo Red-based PU ionomer aqueous solution with 10% solids was poured into a polypropylene dish to 1 mm thickness dried in oven at 60°C and was used for tensile and elongation testing by an Instron 1130 (USA) at room temperature. The experimental error for the above measurements was estimated to be within ± 0.5 .

RESULTS AND DISCUSSION

The IR spectra for TDI and Congo Red (or Remajol Brilliant Blue R or Amaranth) are given in Figures 1 and 2, respectively. The reaction of toluene diisocyanate (TDI) with Congo Red (or Remajol Brilliant Blue R or Amaranth) to form Congo Red PU prepolymer is illustrated by the formation of the absorbance peaks at around 1540 cm^{-1} (NHCO), 3300 cm^{-1} (NH), 1720 cm^{-1} (C=O), and 1400 cm^{-1} (S=O) and by the almost total disappearance of the absorbance peak at around 2275 cm^{-1} (NCO), given in Figure 3 in comparison to that of Figures 1 and 2. These results suggest that the reaction of TDI with Congo Red, dimethylolpropionic acid, and polyester to form Congo Red PU prepolymer does, indeed, take place.

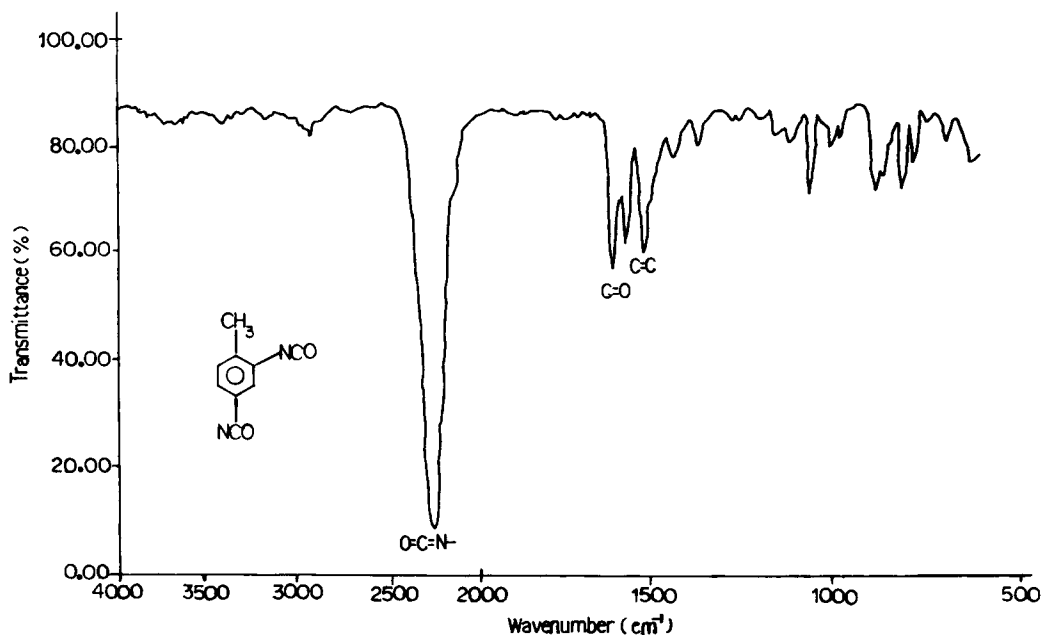


Figure 1 Spectra of toluene diisocyanate at $25 \pm 0.05^\circ\text{C}$.

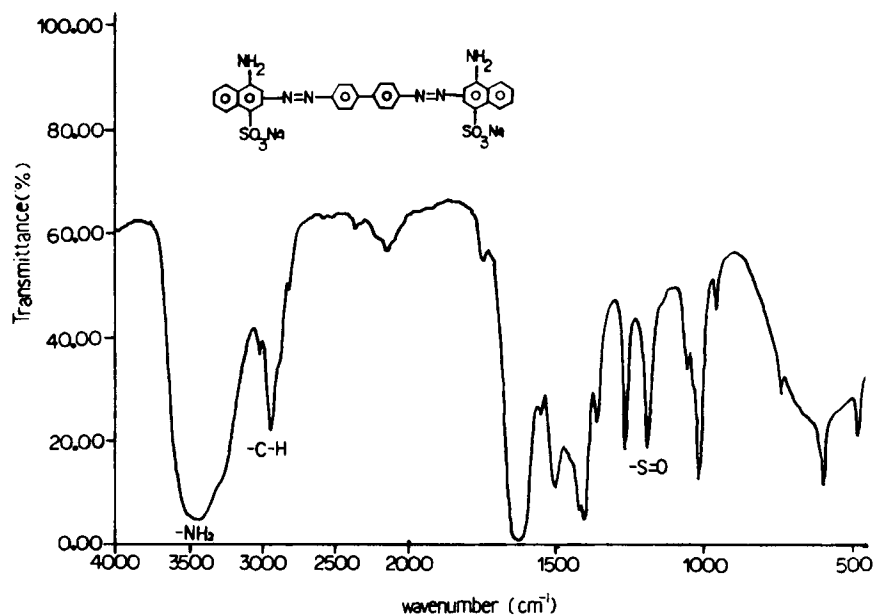


Figure 2 Spectra of Congo Red at $25 \pm 0.05^\circ\text{C}$.

The surface tension at room temperature as a function of the concentration of Congo Red, in the presence and absence of a fixed concentration of Remajol Brilliant Blue R or Amaranth used to prepare Congo Red-based PU ionomer, is given in Figure 4. Figure 4 clearly indicates that the surface tensions of Congo Red-based PU ionomer solution rapidly decrease with increasing concentration of Congo

Red as a result of the hydrophobicity of Congo Red-based PU ionomer adsorbed at the air-water interface. More interestingly, it appears that, in the presence of a fixed concentration of Remajol Brilliant Blue R or Amaranth, the surface tension of Congo Red-based PU ionomer solution decreases gradually with an increase of Congo Red's concentration and is seen to be slightly smaller than that of Congo

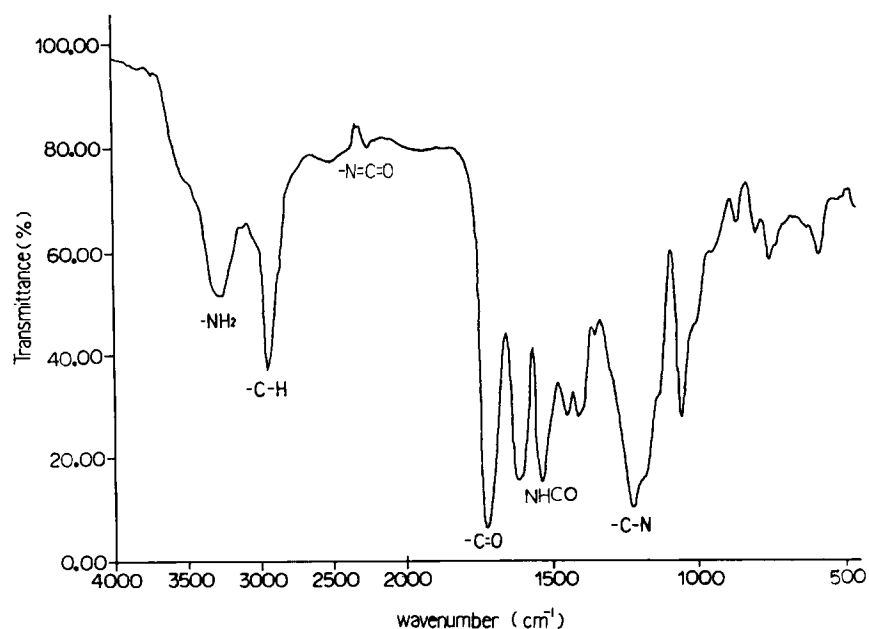


Figure 3 Spectra of Congo Red-based PU prepolymer formed after 30 min reaction, at $25 \pm 0.05^\circ\text{C}$.

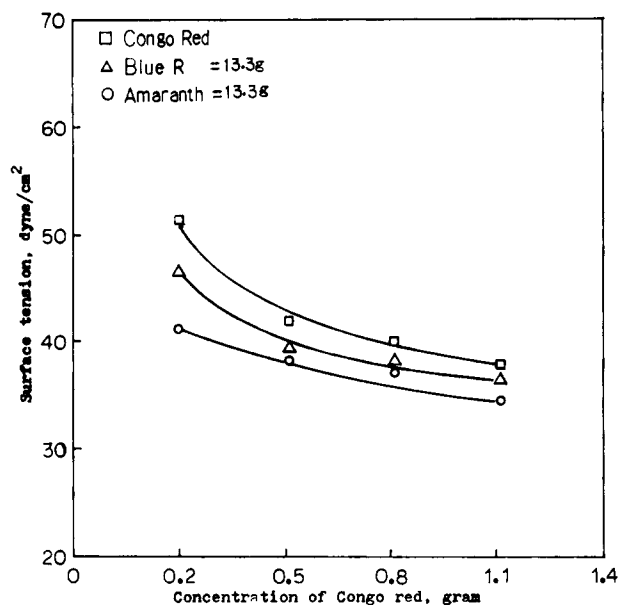


Figure 4 Plot of the surface tension vs. the concentration of Congo Red in the presence and absence of a fixed concentration of Remajol Brilliant Blue R and Amaranth, respectively, used to prepare Congo Red-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

Red-based PU ionomer prepared in the absence of Remajol Brilliant Blue R or Amaranth. This is the result of the higher hydrophobicity of Congo Red mixed Blue R or Congo Red mixed Amaranth-based PU ionomers. These results suggest that since Congo Red-based PU ionomer can substantially lower the air-water interfacial tension it may be considered as a surface-active agent.

The plot of the number-average particle sizes vs. the concentration of dye (i.e., Congo Red or Remajol Brilliant Blue R or Amaranth) alone and the concentration of Congo Red in the presence of a fixed concentration (2.2×10^{-2} mol/L) of, respectively, Remajol Brilliant Blue R and Amaranth, are given in Figures 5 and 6. Figure 5 clearly indicates that the number-average particle size, increasing with increasing concentration of dye, is the result of increased interaction between dye molecules themselves and between dye molecules and carboxyl anions or water molecules (i.e., hydrogen-bond formation). This increased repulsive interaction, resulting from anionic dye molecules and/or carboxyl anions of dye-based PU ionomer molecules, may make the conformation of these PU ionomer molecule become a less compact structure. This is the reason why the number-average particle sizes of these PU ionomer molecules increase with increasing concentration of dye used to prepare dye-based PU ionomer molecules.

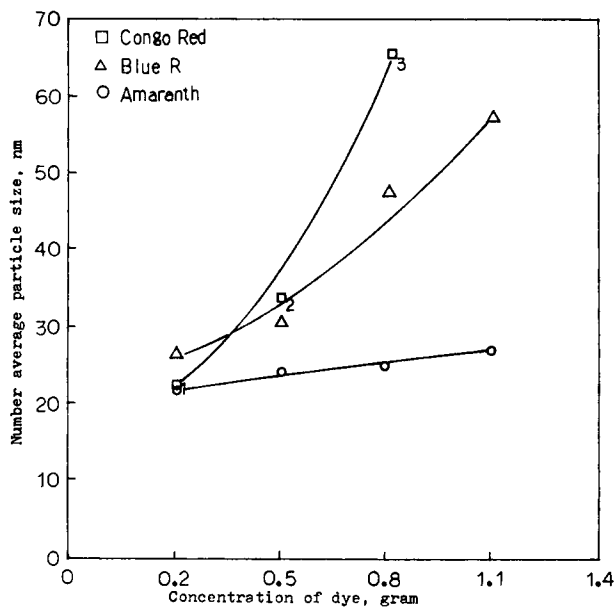


Figure 5 Plot of the number-average particle size vs. the concentration of Congo Red, Remajol Brilliant Blue R, and Amaranth, respectively, used to prepare dye-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

More interestingly, the number-average particle sizes of these ionomer molecules are seen to decrease with increasing concentration of Congo Red in the presence of a fixed concentration of Remajol Brill-

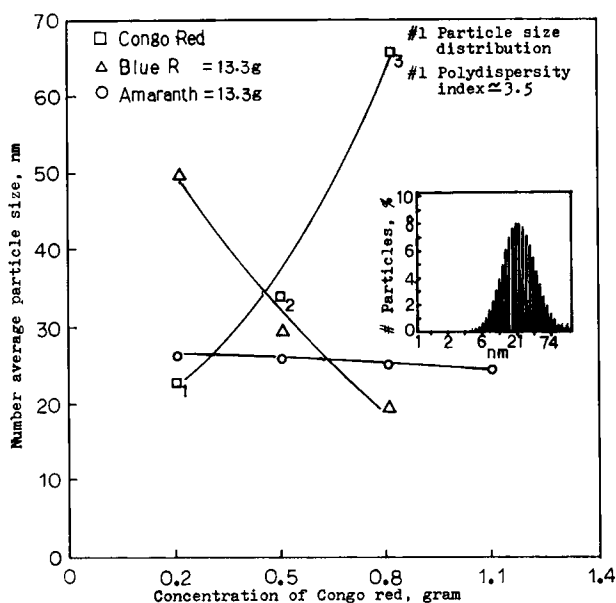


Figure 6 Plot of the number-average particle size vs. the concentration of Congo Red in the presence and absence of a fixed concentration of Remajol Brilliant Blue R and Amaranth, respectively, used to prepare Congo Red-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

liant Blue R (2.13×10^{-2} mol/L = 13.3 g) and Amaranth (2.2×10^{-2} mol/L = 13.3 g), respectively, as shown in Figure 6. This may be due to the intramolecular interaction being significantly greater than is the intermolecular interaction. The intramolecular interaction, arising from the formation of hydrogen bonding between functional groups (i.e., $-\text{NHCO}-$, $-\text{OH}$, $-\text{NH}-$, $-\text{SO}_3-$, etc.) of dye-based PU ionomer molecules, is likely to force these ionomer molecules to form a compact conformation with relatively smaller free volume than that of the ionomer molecules given in Figure 5. Thus, the number-average particle size of the Congo Red-based PU ionomer molecule with a fixed concentration of Remajol Brilliant Blue R or Amaranth decreases. It is also interesting to point out that at a high concentration of Congo Red used to prepare this ionomer molecule, the average particle size is seen to be smaller for the Congo Red-based PU ionomer molecule with Remajol Brilliant Blue R than for the Congo Red-based PU ionomer with Amaranth, as a result of strong intramolecular interaction.

Both tensile and elongation properties of self-cured films of Congo Red-based PU ionomers are shown in Figures 7 and 8. Figure 7 clearly illustrates that the tensile strength of dry film at break appears to increase steadily with increasing concentration

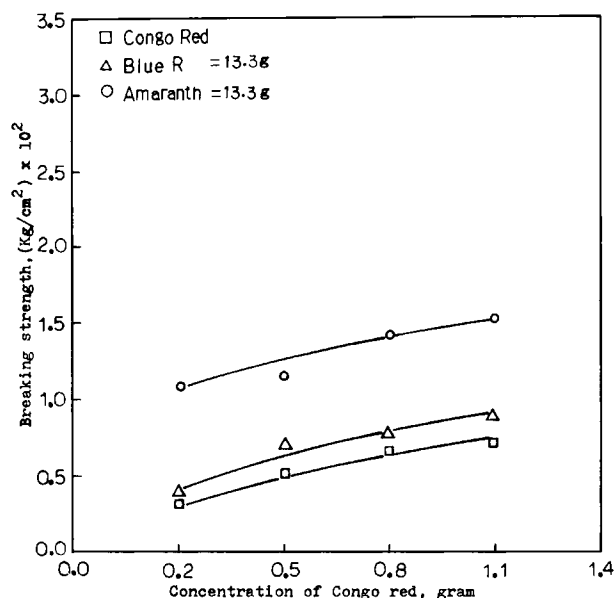


Figure 7 Plot of the breaking strength of dry film vs. the concentration of Congo Red in the presence and absence of a fixed concentration of Remajol Brilliant Blue R and Amaranth, respectively, used to prepare Congo Red-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

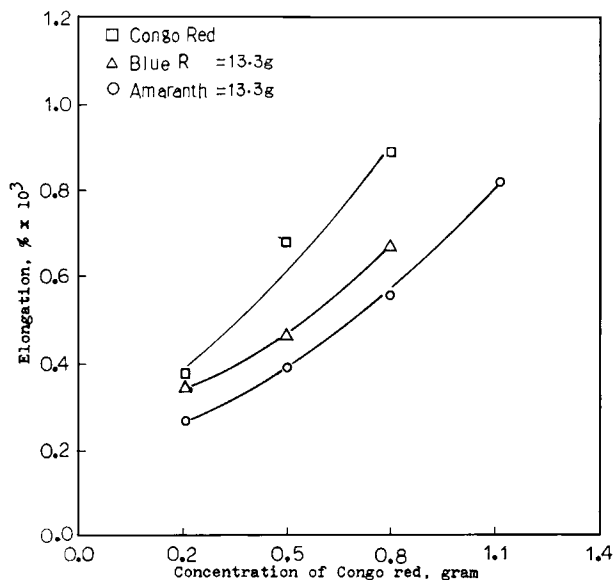


Figure 8 Plot of the elongation of dry film at the breaking point vs. the concentration of Congo Red in the presence and absence of a fixed concentration of Remajol Brilliant Blue R and Amaranth, respectively, used to prepare Congo Red-based PU ionomer, at $25 \pm 0.05^\circ\text{C}$.

of Congo Red in the absence and presence of fixed concentrations of Remajol Brilliant Blue R or Amaranth used to make Congo Red-based PU ionomers. This is the result of increased functional groups (i.e., $-\text{OH}$, $-\text{NH}-$, $-\text{SO}_3-$, $-\text{O}-$) of the backbone of PU ionomer molecules. These functional groups enable the Congo Red-based PU ionomer molecules to crosslink readily and possibly to form more hydrogen bonding, thus resulting in increasing the tensile strength of these ionomer molecules. Figure 7 also indicates that the tensile strength for dye-based PU ionomer molecules follows the order

Congo Red with $2.2 \times 10^{-2} M$ Amaranth >
 Congo Red with $2.13 \times 10^{-2} M$ Remajol Brilliant
 Blue R >
 Congo Red alone.

This behavior may be attributed to more crosslinking for strong tensile strength than for weak tensile strength, resulting from more functional groups built up on the backbone of PU ionomer molecules.

On the other hand, the elongation of dry film of dye-based PU ionomer molecules at the breaking point was found to maintain the following order:

Congo Red >

Congo Red with $2.13 \times 10^{-2} M$ Remajol Brilliant
Blue R >

Congo Red with $2.2 \times 10^{-2} M$ Amaranth.

The above result, shown in Figure 8, is exactly opposite to the result given in Figure 7. For PU ionomer molecules, the crosslinking was found to be weaker for the ionomer molecule with Congo Red alone than for the ionomer molecule with Congo Red containing the other dye, thus causing the elongation of the PU ionomer molecule with Congo Red alone to be higher.

CONCLUSION

The reaction of Congo Red with toluene diisocyanate and other additives to form the Congo Red-based PU ionomer has been proven to occur by infrared (IR) spectra. For PU ionomer molecule solutions, the surface tension was found to decrease with increasing concentration of Congo Red, in the absence and presence of Remajol Brilliant Blue R or Amaranth, but the number-average particle size was found to increase with increasing Congo Red, Remajol Brilliant Blue R, and Amaranth's concentration employed to prepare the PU ionomer, respectively. More interestingly, the number-average particle size of PU ionomer molecules is seen to decrease with increasing concentration of Congo Red in the presence of fixed concentrations of Remajol Brilliant

Blue R or Amaranth, as a result of intramolecular interaction resulting from the functional groups of the ionomer molecule. Our experimental results also indicate that the addition of a fixed concentration of Amaranth, to prepare Congo Red-based PU ionomer molecules, will substantially increase the tensile strength but relatively decrease the elongation of this ionomer. However, the acetone process is considered to be a good technique to prepare dye-based PU ionomer.

We are grateful to the National Science Council of the Republic of China for financial support of this research.

REFERENCES

1. O. Lorenz and G. Rose, *Angew. Makro. Chem.*, **45**, 85 (1975).
2. O. Lorenz and H. Hick, *Ang. Makro. Chem.*, **72**, 115 (1978).
3. R. Homback and W. Wenzel, U.S. Pat. 4,433,095 (1984).
4. O. Dieterich, *Adv. Org. Coat. Sci. Technol. Ser.*, **1**, 55 (1979).
5. O. Dieterich, *Adv. Org. Coat. Sci. Technol. Ser.*, **4**, 15 (1982).
6. Y. Chen, *J. Appl. Polym. Sci.*, **46**, 435 (1992).
7. J. F. Lee and D. Y. Chao, *Colloid Polym. Sci.*, **272**, 1508-1513 (1994).

Received October 24, 1994

Accepted February 5, 1995