

Polymer Latex Containing Carboxylic Acid Functional Groups. II. Humidity-Sensitive Properties of Rigid Films Made From MMA and AA

SHIH-CHANG HSU, YUAN-LING LIAO, WEN-YEN CHIU

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Received 13 October 1998; accepted 5 March 1999

ABSTRACT: The polymer latexes of poly(MMA-AA) were synthesized using two techniques: soapless seeded emulsion polymerization, and soapless emulsion copolymerization. Then a series of rigid polymer films containing a COOH group were prepared from the synthesized latex. The humidity-sensitive properties of the polymer films were investigated. Our studies confirmed that there exists both an optimum ratio of hydrophilic to hydrophobic monomers and initial structure of the latex particle that provides the humidity-sensitive polymer film with excellent water resistivity and sensitivity to humidity. In addition, little hysteresis and quick response were observed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3121–3129, 1999

Key words: polymer latex; MMA/AA; rigid film; humidity-sensitive property

INTRODUCTION

It is well known that humidity sensor technologies amenable to widespread application in electronic control systems have become increasingly important. Many kinds of humidity sensors have been investigated and placed on the market. The humidity sensitive materials used are classified into three groups: electrolytes, organic polymers, and porous ceramics.^{1,2} Despite the differences in materials, most sensors utilize physical adsorption (or absorption) of water molecules. Because high-temperature processing and heat cleaning are not required, this easily formed, low-cost, and stable polymer material attract many interests and researches.^{3–14} There are two main types of polymeric sensors: impedance and capacitance. The impedance type can be further subdivided

into ionic and electronic conduction types. A hydrophilic polymer is an adequate material for conventional humidity-sensitive sensors that require fast response, reproducibility, and durability. However, one of the problems to be solved is how the hydrophilic polymers can be made insoluble in water.

In 1986, Sakai et al.¹² proposed that three methods should be used to give a hydrophilic polymer water resistivity. The first method is crosslinking the polyelectrolyte by using an appropriate crosslinking reagent. For example, Sakai et al.¹⁵ reported that crosslinked with dibromobutane simultaneously quaternized poly-4-vinylpyridine showed excellent water resistivity as well as sensitivity to humidity. The second and the third methods are copolymerization with a hydrophobic polymer and graft copolymerization, respectively.

In 1993, Sakai et al.¹⁶ reported another method. They showed that an interpenetrating polymer network (IPN) film can be used effectively as a humidity sensor, with its durability against water and sharp sensitivity to humidity.

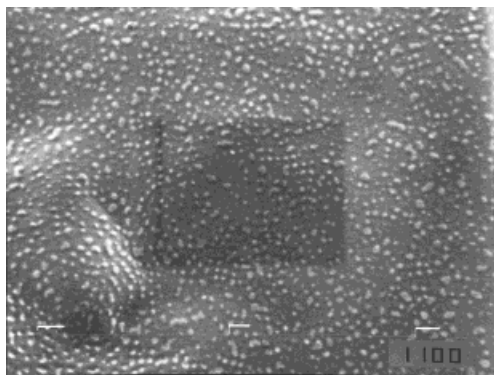
Correspondence to: W.-Y. Chiu.

Contract grant sponsor: National Science Council, Taiwan; contract grant number: NSC-85-2216-E-002-003.

Journal of Applied Polymer Science, Vol. 74, 3121–3129 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/133121-09

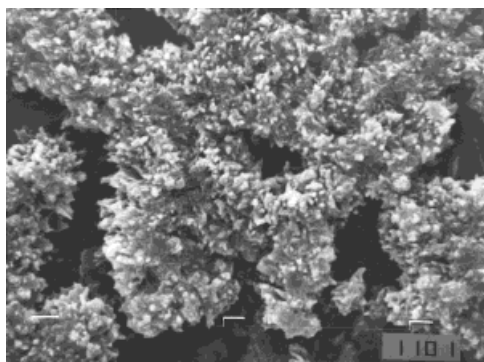


5 μm

Figure 1 SEM photograph of the polymer film melted from latex polymers at 200°C for 3 h.

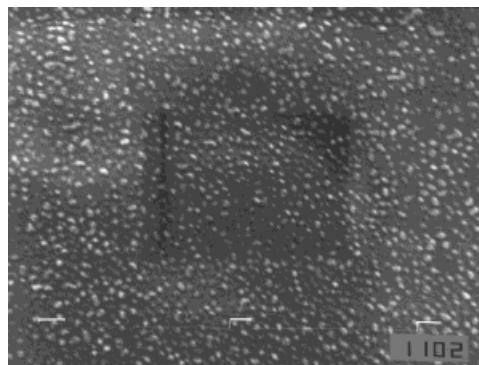
In 1988, Sakai et al.¹⁵ produced partially quaternized polyvinylpyridine homopolymer, and found that as the degree of quaternization increased, the sensitivity also increased.

In our previous study,¹⁷ we used MAA as the hydrophilic monomer to copolymerize with a hydrophobic polymer via soapless emulsion polymerization. However, from our analysis of acid in water solution and the content analysis of water-soluble and water-insoluble polymers, we found



5 μm

Figure 2 SEM photograph of the polymer film melted from latex polymers at 200°C for 3 h, and then chemically modified for 5 min.



5 μm

Figure 3 SEM photograph of the polymer film melted from latex polymers at 200°C for 3 h, chemically modified for 5 min, then rinsed repeatedly with water.

that the MAA monomer reacted mostly on or in the polymer latex. A negligible amount of PMAA was formed in water phase.

Moreover, by using AA as the hydrophilic monomer, in the process of the soapless emulsion polymerization, the AA monomer reacted on the polymer latex and in the aqueous phase as well. The small and uniform polymer latex dispersed all over the PAA continuous phase. In a sense, the hydrophobic polymer phase mixed very well with the hydrophilic polymer phase. Thus, the polymer film exhibited both humidity sensitive and water resistivity. On the contrary, if bulk or solution polymerization was used, polymers formed would be sequences of PMMA and PAA; namely, purely copolymers. According to related researches,^{16,18} in films with a IPN structure their impedance decreased exponentially of the order of 10^3 to 10^2 , with increasing humidity from 50 to 90% RH. These sensors had the best humidity-sensitive properties, such as sharper humidity sensitivity and lower impedance. So the copolymers do not exhibit better humidity-sensitive character than that of the IPN polymer films. Thus, the emulsion polymerization method would be preferred and adopted in the present study.

In the present report, we will investigate the humidity-related characteristics of the polymer film melted from latex polymers prepared using the methods of soapless seeded emulsion polymerization and soapless emulsion copolymerization from Part I of our work.¹⁹

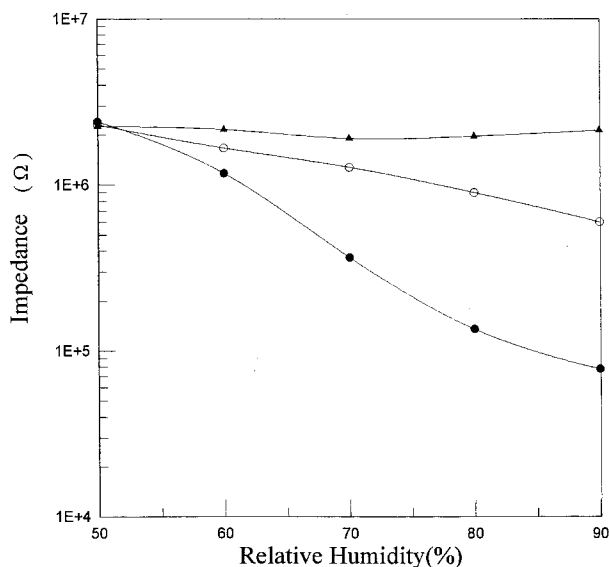


Figure 4 Comparison of response curves with different modification time lengths. (●: modified for 5 min; ○: modified for 1 min; ▲: unmodified).

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and acrylic acid (AA) were distilled under nitrogen atmosphere and reduced pressure prior to polymerization. The other materials were analytical grade and used without further purification.

Ingredients and Conditions for Polymerization

Seeded emulsion polymerization and emulsion copolymerization reactions were carried out with the detailed procedures mentioned in Part I of our work.¹⁹

Morphology

The morphology of the polymer films melted from latex polymers was observed under scanning electron microscopy (SEM).

Coating and Chemical Modification

The latex was dip coated on the sintered alumina substrate with a pair of interdigitated silver-palladium (Ag-Pd) electrodes. The latex was then melted at 200°C for 3 h, cooled at 50°C for 1 h, chemically modified with 1 N NaOH, rinsed repeatedly with water, and finally dried at 50°C for 24 h.

Measurement of Impedance under Various Relative Humidity

The fabricated humidity sensor was placed in a chamber where the temperature and the relative humidity were controlled. The impedance of the sensor at various humidities was measured with an LCZ meter (GenRad 1689M) at a frequency of 1 kHz.

Hysteresis

The impedance of the sensor was measured at various humidities, ranging from 90% RH to 50% RH and then back to 90% RH.

Temperature Effect

The impedance of the sensor at various humidities (90% RH to 50% RH) was measured under different temperatures (i.e., 28°C, 40°C, and 60°C).

Response Time

The response rate was evaluated by recording the humidity and the corresponding impedance every 10 s for the first 10 min, and every 30 s for the remaining 10 min. The humidity was changed from 90 to 50% within 4 min and 50 to 90% within 7 min.

RESULTS AND DISCUSSION

In this work, the polymer latexes of poly (MMA-AA) were synthesized using the techniques of

Table I Effect of Modification Time Length on Impedance Change

Time Length for Chemical Modification	Range of Impedance Change ^a (Low Humidity ~ High Humidity)		Degree of Impedance Change (Low Humidity/High Humidity)
5 minutes	2.4 MΩ	77.4 kΩ	31.00 times
1 minute	2.3 MΩ	592 kΩ	3.90 times
Unmodified	2.3 MΩ	1.9 MΩ	1.20 times

^a The relative humidity range: 50 to 90%.

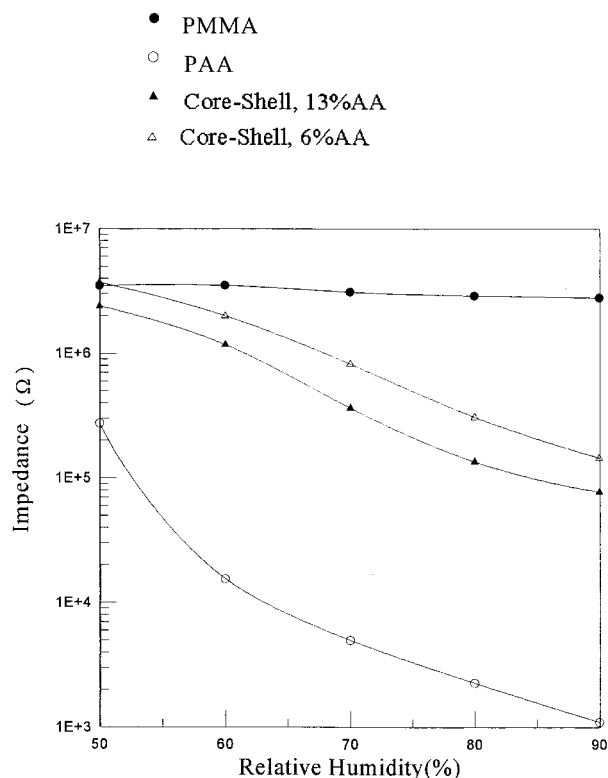


Figure 5 Influence of hydrophilic monomer concentration on the response curve.

soapless seeded emulsion polymerization or soapless emulsion copolymerization. The latex particles carried carboxyl groups on their surfaces. In addition, the latex particles synthesized through seeded emulsion polymerization had a core-shell structure.

When the latex with functional group $-\text{COOH}$ reacted with NaOH solution, an acid-base neutralization reaction occurred. In this reaction, Na^+ replaced H^+ on the original COOH group to make the polymer into a much more dissociable alkali form.

Through this chemical modification process, the Na^+ ion, serving as the charge transport car-

rier, equipped the polymer with highly humidity-sensitive property. Using the fact that their ionic conductivity increased with an increase in water absorption, we evaluated their response characteristics through interpreting the impedance vs. the relative humidity plot.

Morphology

Figures 1, 2, and 3 show SEM photos of latex film under three conditions, respectively: melted under 200°C for 3 h before chemical modification, without water rinsing after chemical modification, and with repeated water rinsing after chemical modification. These figures show that repeated water rinsing completely eliminated NaOH crystals from polymer films. All the films are rigid with T_g around 120°C .¹⁹

Length of Time for Chemical Modification

It was certain that with sufficient chemical modification, the Na^+ extensively replaced the H^+ of the $-\text{COOH}$ functional group to make the alkali ion Na^+ in the polymer film the charge carrier. Figure 4 showed different response curves for various chemical modification time lengths. For the film modified for 1 min, its impedance changed from $592\text{ k}\Omega$ to $2.3\text{ M}\Omega$ as the humidity changed from 90 to 50%. The degree of impedance change was only 3.9 times, less than one order. However, those films modified for 5 min displayed high sensitivity, with a degree of impedance change up to 31 times. To avoid structural damage of the film due to long-term reaction with a strong base solution of NaOH , 5 min was selected as the time length for modification in our experiments. The above analysis is shown in Table I.

Ratio of Hydrophilic to Hydrophobic Monomers

The polymer without a hydrophilic functional group, such as pure PMMA, was not capable of

Table II Effect of Hydrophilic Functional Group Content on Impedance Change

Structure of Latex Particles, Weight Fraction of AA in Total Monomers	Range of Impedance Change ^a (Low Humidity ~ High Humidity)		Degree of Impedance Change (Low Humidity/High Humidity)
PMMA	$3.5\text{ M}\Omega$	$2.8\text{ M}\Omega$	1.25 times
Core-Shell, 6%AA	$3.7\text{ M}\Omega$	$145\text{ k}\Omega$	25.50 times
Core-Shell, 6%AA	$2.4\text{ M}\Omega$	$77.4\text{ k}\Omega$	31.00 times
PAA	$275\text{ k}\Omega$	$1.1\text{ k}\Omega$	250.00 times

^a The relative humidity range: 50–90%.

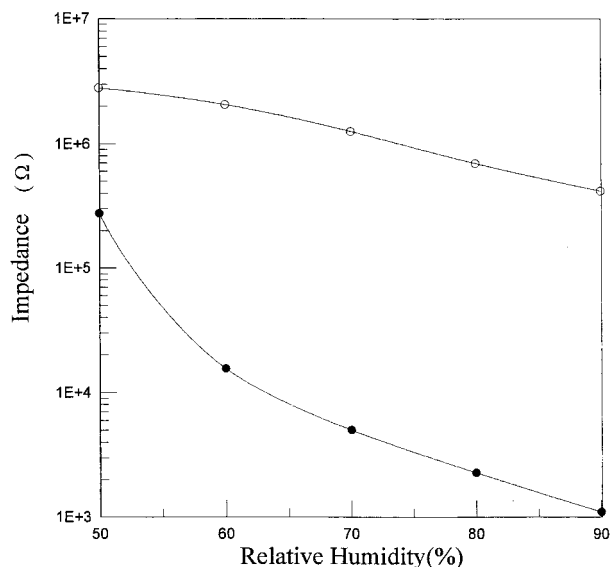


Figure 6 Comparison of the response curves after multiple uses of PAA film. (●: first use; ○: second use).

absorbing water molecules, and could not acquire strong alkali ion through chemical modification process. Therefore, it had no sensitivity to humidity changes. Judging from the above, it was certain that undesirable NaOH crystals could be completely removed by repeated water rinsing. Therefore, the possibility that undesirable NaOH could interact with the conductivity mechanism was eliminated. These cases are shown in Figure 5, which indicates that the higher the concentration of the hydrophilic functional group, the lower the impedance. This result suggests that with the higher hydrophilic functional group ratio, ions were better able to dissociate. The ionic mobility (e.g., Na⁺) increased due to the absorption of significantly more water vapor molecules at higher relative humidity. The degree of impedance changes is shown in Table II.

However, Figure 6 showed that after multiple uses, the humidity sensitivity of PAA film worsened, while the impedance soared. This was because without the protection of a hydrophobic structure, the PAA film is destroyed due to its hydrophilic property. Hence, its sensitivity to humidity decreased.

Figure 7 showed that with a certain degree of hydrophobic structure water resistivity could be increased; therefore, there was no obvious change in sensitivity. However, a downward shift of the characteristic curve was observed after second-time use. As for films with crosslinking structures, the characteristic curves expressed strong

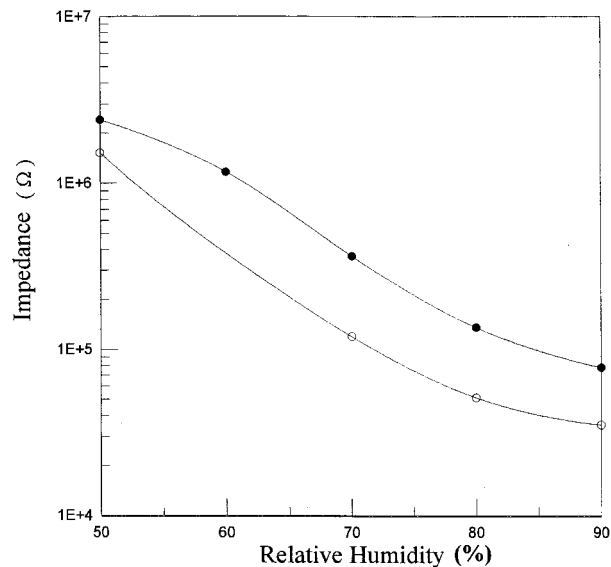


Figure 7 Comparison of the response curves after multiple uses of the humidity-sensitive polymer film formed from melted latex polymers synthesized through seeded emulsion polymerization (●: first use; ○: second use).

correspondence after second-time use, as shown in Figure 8.

The above results indicate that there exists an optimum ratio of hydrophilic to hydrophobic

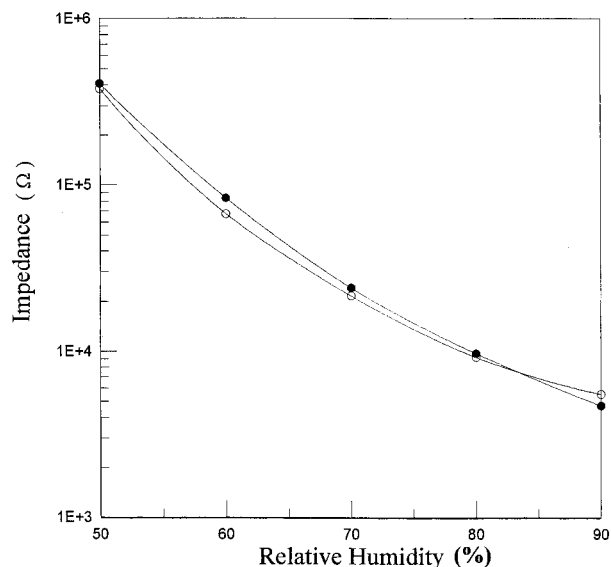


Figure 8 Comparison of the response curves after multiple uses of the humidity-sensitive polymer film formed from melted latex polymers with a crosslinking shell synthesized through seeded emulsion polymerization (●: first use; ○: second use).

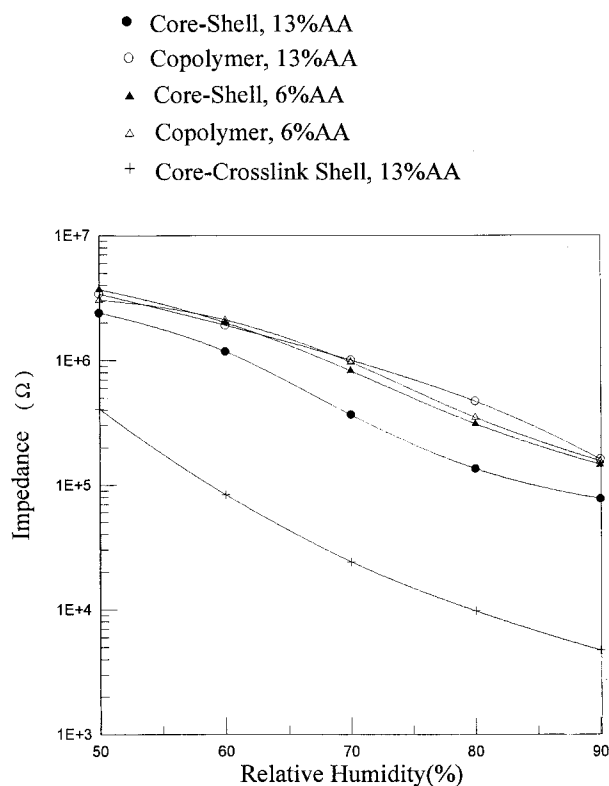


Figure 9 Influence of different synthesis techniques on the response curve.

monomers, where the polymer is given strong water resistivity as well as sharp humidity sensitivity. Y. Sakai and Y. Sadaoka et al.²⁰ did research on the best degree of the grafting ratio and came to a similar conclusion.

Effect of Method of Synthesis

As shown in Figure 9, polymer film melted from the core-shell structure latex had lower impedance than polymer film melted from copolymer latex, and also had better sensitivity to humidity.

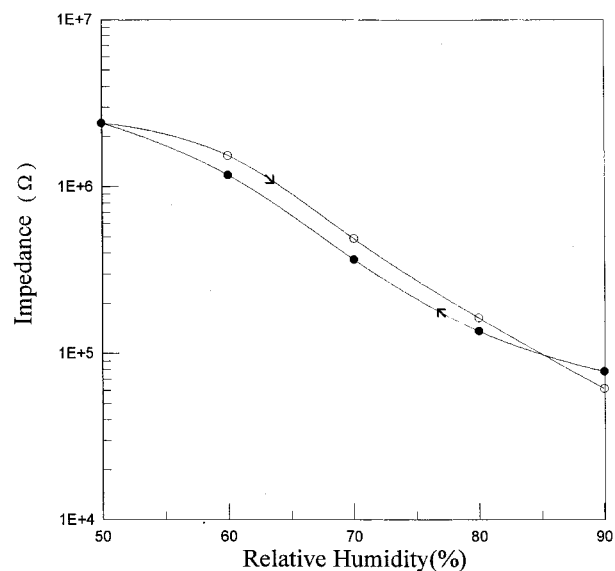


Figure 10 Hysteresis behavior of humidity-sensitive polymer film formed from melted latex polymers synthesized through seeded emulsion polymerization with 13% AA (●: desorption; ○: sorption).

Functional groups of the polymer produced by the copolymerization method were often merged inside the latex particle due to twisting and coiling of polymer chains. However, functional groups of the polymers by the seeded polymerization method were mostly located on the surface of latex particles. The above analysis is shown in Table III.

In addition, if the shell had the crosslinking structure, the degree of impedance change sharply increased up to 86.6 times. The reason is not well understood; it mostly likely relates to its IPN structure. That is, the latex particle domains uniformly distributed in a continuous PAA phase. In the crosslinked film, the PAA continuous phase was better protected during the NaOH chemical modification and water-rinsing process; hence,

Table III Effect of Synthetic Method on Impedance Change

Structure of Latex Particles, Weight Fraction of AA in Total Monomers	Range of Impedance Change ^a (Low Humidity ~ High Humidity)		Degree of Impedance Change (Low Humidity/High Humidity)
Core-shell, 6%AA	3.7 MΩ	145 kΩ	25.50 times
Core-shell, 13%AA	2.4 MΩ	77.4 kΩ	31.00 times
Copolymer, 6%AA	3.04 MΩ	155 kΩ	19.60 times
Copolymer, 13%AA	3.4 MΩ	160 kΩ	21.25 times
Core-crosslinked shell, 13%AA	407 kΩ	4.7 kΩ	86.60 times

^a The relative humidity range: 50–90%.

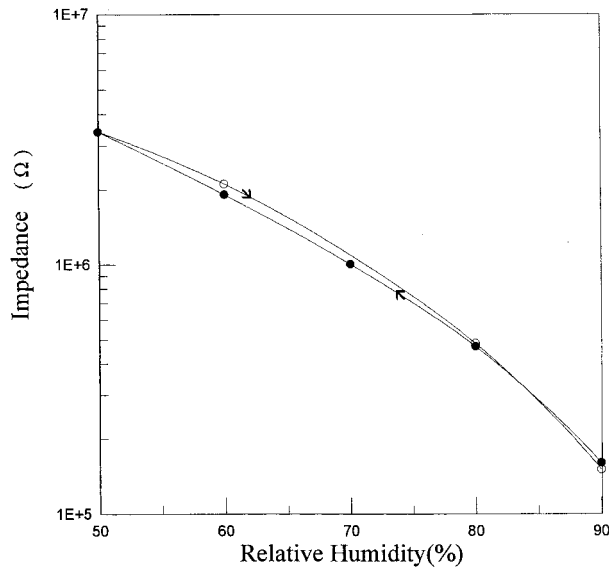


Figure 11 Hysteresis behavior of humidity-sensitive polymer film formed from melted latex polymers synthesized through emulsion copolymerization with 13% AA (●: desorption; ○: sorption).

the resulted film benefited from the hydrophilic property of the PAA phase and showed excellent humidity-sensitive properties.

According to the research by Y. Sakai et al.,¹⁸ Films with IPN structure had the best humidity-

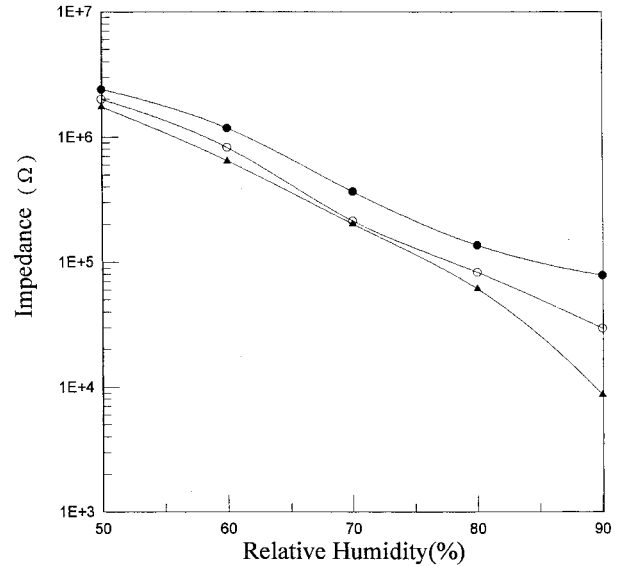


Figure 13 Temperature effect on the response curve of the humidity-sensitive polymer film formed from melted latex polymers synthesized through seeded emulsion polymerization with 13% AA (●: 28°C; ○: 40°C; ▲: 60°C).

sensitive properties, such as sharper humidity sensitivity and lower impedance, corresponding with our results.

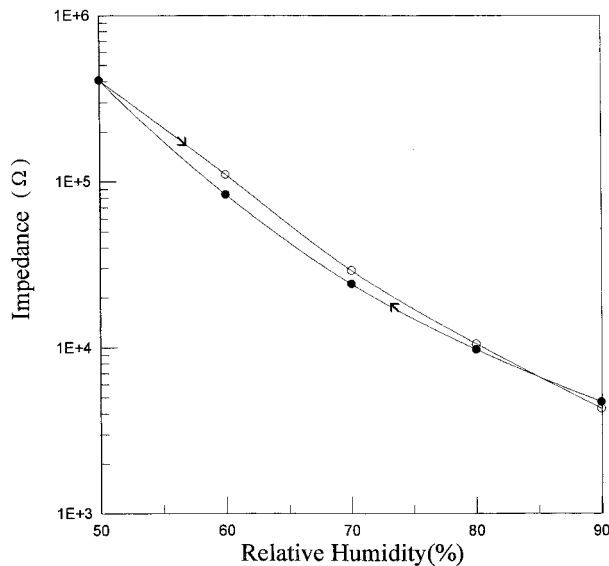


Figure 12 Hysteresis behavior of humidity-sensitive polymer film formed from melted latex polymers with a crosslinking shell synthesized through seeded emulsion polymerization with 13% AA (●: desorption; ○: sorption).

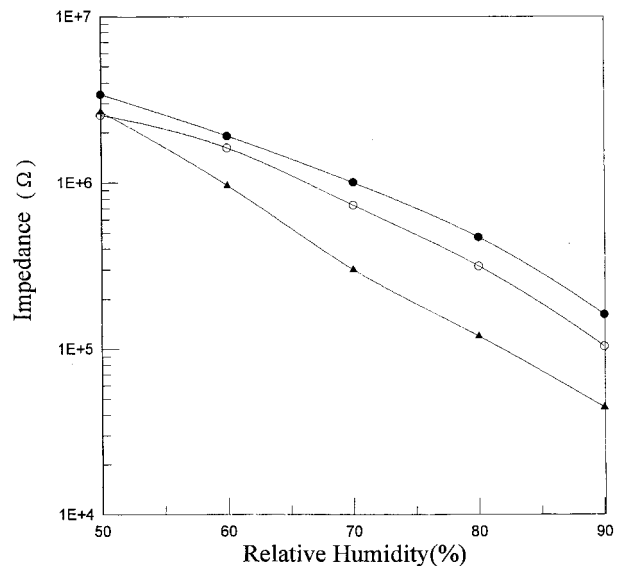


Figure 14 Temperature effect on the response curve of the humidity-sensitive polymer film formed from melted latex polymers synthesized through emulsion copolymerization with 13% AA (●: 28°C; ○: 40°C; ▲: 60°C).

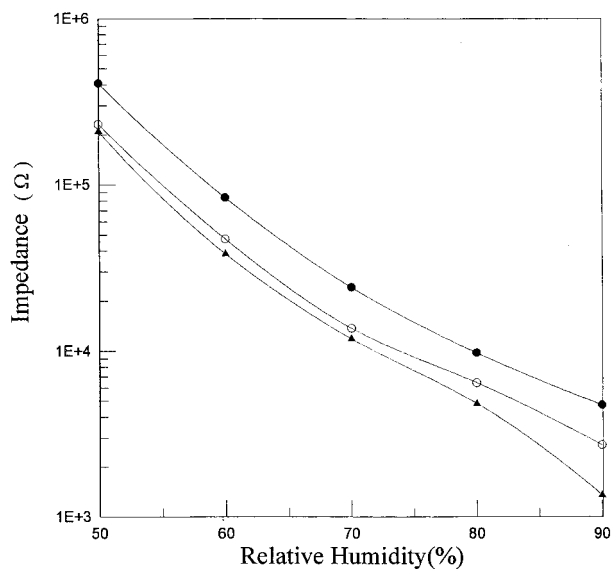


Figure 15 Temperature effect on the response curve of the humidity-sensitive polymer film formed from melted latex polymers with a crosslinking shell synthesized through seeded emulsion polymerization with 13% AA (●: 28°C; ○: 40°C; ▲: 60°C).

Hysteresis

The hysteresis behavior of the polymer films was shown in Figures 10–12. Little hysteresis was observed for each of the humidity-sensitive polymer films. During the sorption processes, water molecules permeated into the polymer film and accumulated inside the humidity-sensitive polymer film, so during the desorption processes they were not easily or quickly removed. It was expected that the impedance for desorption processes was always lower than that for sorption processes.

Temperature Effect

The temperature effect on the humidity-sensitive polymer films was shown in Figures 13–15 and

Table IV Effect of Temperature on Impedance Change

Structure of Latex Particles, Weight Fraction of AA in Total Monomers	Degree of Impedance Change at 28°C ^a	Degree of Impedance Change at 40°C ^a	Degree of Impedance Change at 60°C ^a
Core-shell, 6%AA	26 times	48 times	108 times
Core-shell, 13%AA	31 times	91 times	368 times
Copolymer, 6%AA	20 times	38 times	77 times
Copolymer, 13%AA	21 times	36 times	64 times
Core-crosslinking shell, 13%AA	87 times	410 times	874 times

^a The relative humidity range: 50–90%.

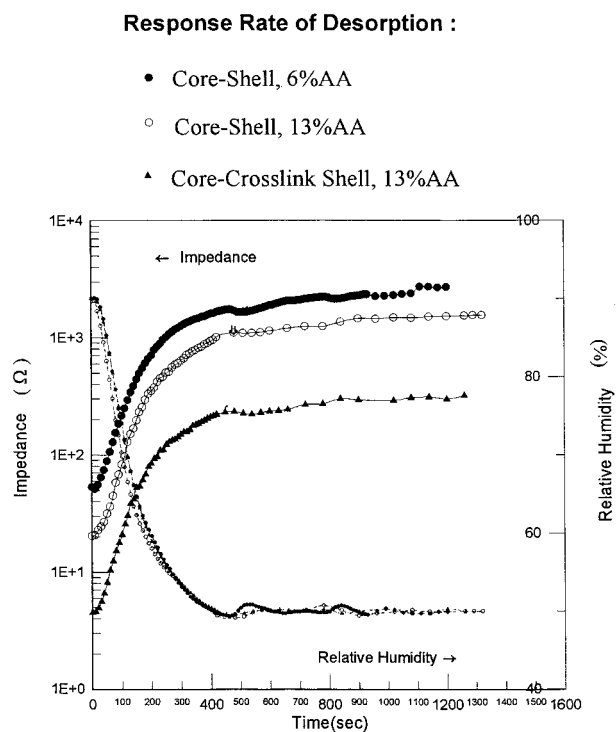


Figure 16 Impedance variation upon humidity change with time for different humidity-sensitive polymer films during the desorption process.

Table IV. These results showed that the impedance decreased with an increase in temperature. In addition, the degree of impedance change was increased; that is, the sensitivity to humidity was enhanced. This was due to higher mobility of charge carrier (e.g., Na⁺) at higher temperature. Our results corresponded with the research done by S. Tsuchitani.²⁰

Response Time

The variation of impedance with changes in humidity was plotted against time for both sorption

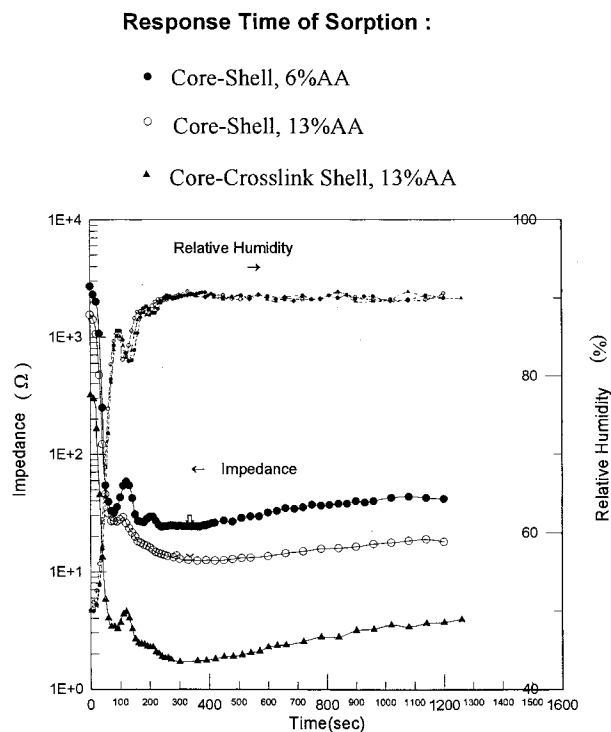


Figure 17 Impedance variation upon humidity change with time for different humidity-sensitive polymer films during the sorption process.

and desorption process, as shown in Figures 16 and 17, respectively. We found that the impedance changed immediately upon any slight variation of ambient humidity. It was remarkable that as the ambient humidity changed, polymer film responded to the change almost simultaneously.

CONCLUSION

Humidity-sensitive polymer films formed from melted latex particles with core-shell structure had lower impedance and better sensitivity than those having simply a copolymer particle structure. All of our humidity-sensitive polymer films showed a quick response to changes in humidity, high sensitivity, and little hysteresis. The impedance lowered and the sensitivity sharpened with increasing temperature. In addition, films with

better humidity-sensitive properties, having more functional groups or crosslinking structure, also responded more rapidly.

The authors gratefully acknowledge financial support from the National Science Council, Taiwan, R.O.C., through Grant No. NSC-85-2216-E-002-003. They are also grateful to Professor K. S. Chen of Tatung Institute of Technology, Taiwan, R.O.C., for his helpful comments.

REFERENCES

1. Yamazoe, N.; Shimizu, Y. *Sensors Actuators* 1986, 10, 379.
2. Kulwicki, B. M. *J Am Ceram Soc* 1991, 74, 697.
3. Hijikigawa, M.; Miyoshi, S.; Sugihara, T.; Jinda, A. *Sensors Actuators* 1983, 4, 307.
4. Kinjo, N.; Ohara, O.; Sugawara, T.; Tsuchitani, T. *Polym J* 1983, 15, 621.
5. Takaoka, Y.; Maebashi, Y.; Kobayashi, S.; Usui, T. *Jpn. Pat.* 58 (1983).
6. Sadaoka, Y.; Sakai, Y. *Denki Kagaku* 1984, 52, 132.
7. Sakai, Y.; Sadaoka, Y.; Omura, H.; Watanabe, N. *Kobunshi Ronbunshu* 1984, 41, 205.
8. Sakai, Y.; Sadaoka, Y.; Omura, H.; Watanabe, N. *Kobunshi Ronbunshu* 1984, 41, 209.
9. Sadaoka, Y.; Sakai, Y. *Denki Kagaku* 1985, 53, 150.
10. Sadaoka, Y.; Sakai, Y.; Akiyama, H. *J Mater Sci* 1986, 21, 235.
11. Sadaoka, Y.; Sakai, Y. *J Mater Sci Lett* 1986, 5, 772.
12. Sakai, Y.; Sadaoka, Y.; Ikeuchi, K. *Sensors Actuators* 1986, 9, 125.
13. Sakai, Y.; Sadaoka, Y.; Fukumoto, H. *Sensors Actuators* 1986, 13, 243.
14. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M. *J Electrochem Soc* 1989, 136, 171.
15. Sakai, Y.; Sadaoka, Y.; Fukumoto, H. *Sensors Actuators* 1988, 13, 243.
16. Sakai, Y.; Matuguchi, M.; Sadaoka, Y.; Hirayama, K. *J Electrochem Soc* 1993, 140, 432.
17. Hsu, S. C.; Lee, C. F.; Chiu, W. Y. *J Appl Polym Sci* 1999, 71, 47.
18. Sakai, Y.; Sadaoka, Y.; Matuguchi, M.; Rao, V. L.; Kamigaki, M. *Polymer* 1989, 30, 1068.
19. Hsu, S. C.; Liao, Y. L.; Lee, C. F.; Chiu, W. Y. *J Appl Polym Sci*, submitted.
20. Tsuchitani, S.; Sugawara, T.; Kinjo, N.; Ohara, S. *Sensors Actuators* 1988, 15, 375.