Quantification of Response Time in Poly(Vinyl Alcohol)–Metal Complex Thermochromic Polymeric Systems

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ABSTRACT: Thermochromic poly(vinyl alcohol) (PVA)-based material was synthesized and an extensive study of its thermochromic behavior with respect to response time was carried out. It was observed that it is possible to manipulate the response time by keeping control over chemical and physical parameters. The response time, which is the most important property of a smart material, has in this case been found to be very much influenced by rate of heat transfer into the material. Different compositions of the thermochromic material and their corresponding response time with respect to rate of heat transfer were studied and correlated. First, a theoretical equation was derived and later on it was experimentally verified to quantify the response time in PVA–metal complex-based thermochromic systems. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4832–4834, 2006

Key words: poly(vinyl alcohol)–metal complex; response time; thermal diffusivity; thermochromism

INTRODUCTION

Stimuli-sensitive polymers have recently been attracting a great deal of attention due to their ability to undergo changes in response to small variation in environmental conditions. The polymer can show change in its physical or chemical properties by changing temperature, pH, concentration, magnetic field, electric field, etc.

Several types of polymers are reported in literature for this purpose. Thermosensitive polymer gels based on *N*-isopropyl acrylamide show reversible swelling–deswelling phenomena when isothermally heated or cooled.[1] However, the response time of these types of polymers is slow (in minutes). This disadvantage restricts their application to various fields, especially sensors. To overcome this problem, thermosensitive complexes based on poly(vinyl alcohol) (PVA) with variable-valence metals and orthophosphoric acid were synthesized.[2]

The main parameters in the chemistry of the material that play an important role in manipulating the response time are type of metal ions, concentration of metal ions, and concentration of orthophosphoric acid. Such type of material could give a response time in the range of 2 s to 10 min, depending on thickness, rate of heat input, and composition of the film. While conducting the experiments, it was observed that the rate of heat transfer into the polymeric system received significant influence on the thermochromic response time. Theoretical analysis revealed that thermal diffusivity of the film, which is an intrinsic property of the material, is inversely proportional to the response time. Extrinsic properties such as thickness of the polymeric film and rate of heat input also have an impact on response time.

EXPERIMENTAL

The polymer was synthesized by the method reported by Lazareva et al.[2] For synthesis of thermochromic polymer PVA (63% solution), $CoCl_2 \cdot 6H_2O$ and orthophosphoric acid were used. PVA from Aldrich 99% hydrolyzed powder with average molecular weight 85000 to 146000, $CoCl_2$ $6H_2O$ from Acros Organics (98%) and orthophosphoric acid from Acros Organics 85 wt% solution in water was used. Cobalt chloride was made anhydrous before using it in synthesis of PVA–metal complex. The polymer compositions were prepared by dissolving an appropriate amount of $CoCl_2$ in PVA solution and then adding the desired quantity of orthophosphoric acid in the solution. Polymeric films were prepared after drying the solution and then pressing the polymer in a hydraulic press. Films of different thicknesses and compositions were prepared in the same manner. Measurement of the film thickness was done by a thickness gauge with an accuracy of 0.01 mm. The response time for color change was measured with the help of a hot-stage microscope and a stopwatch. PVA films of known thickness were studied for their thermochromic response and correlated with the thermal diffu-

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TABLE I
Practical Data on Thermochromic Response of PVA-$CoCl_2$ Complexes

Sample no.	$CoCl_2$ (wt %)	H_3PO_4 (wt %)	ρ	C_p	k	T_s (°C)	T_a (°C)	T_b (°C)	s (mm)	t (s)	Remarks
1	3.5	3	0.85	1.71	0.134	85	30	81	3.96	82	Response time responds very-well to eq. (2).
2	4		1.11	1.92	0.116	85	31	79	2.96	64	do
3	4.5		1.42	2.43	0.107	85	30	78	1.87	42	do
4	4	7	1.28	1.98	0.121	85	29	74	1.87	20	do
5	5		1.61	2.53	0.103	85	30	72	1.11	12	do
6	8		1.92	2.71	0.098	85	28	71	0.74	7	do
7	3.5	9	1.33	1.99	0.128	80	32	75	0.74	4	do
8	5		1.72	2.61	0.101	80	31	71	0.39	2	do
9	10		2.01	2.87	0.089	80	32	69	0.25	1	do
10	8	12	2.09	2.85	0.111	80	29	69	0.26	1	do
11	11		2.18	2.98	0.088	80	28	66	0.18	0.5	do
12	14		2.31	3.11	0.079	80	28	58	0.18	0.4	do
13	6	13	2.09	2.69	0.136	80	31	75	0.41	22	Not responding to eq. (2).
14	6	14	2.14	2.71	0.138	80	30	78	0.42	30	do

sivity of the material, which is a key property for heat transfer by conduction. Bulk density (ρ), thermal conductivity (k), and specific heat (C_P) were measured for individual films to evaluate thermal diffusivity. A differential volume density meter was used to find out bulk density, whereas a modulated differential scanning calorimeter (MDSC; make RCS-2920 TA Instruments) was used to measure thermal conductivity and specific heat of the material. All the data thus obtained were systematically tabulated to study and correlate the thermochromic behavior of the material. Mainly cobalt, copper, and iron complexes were used to observe thermochromic behavior. Of these metal complexes, cobalt was given the best results with respect to response time as well as reproducibility of the results. In this article, only cobalt complex–PVA thermochromic behavior is discussed in detail; however, a similar approach can be applied for any such system to quantify the response time.

RESULTS AND DISCUSSION

The results tabulated in Table I are highly informative of the variation in response time with respect to different chemical and physical parameters. The chemistry of the thermochromic system varies with the change in type of metal complexes (e.g., Co, Cu, Fe, and Ni, etc.). Concentration of these metal complexes in the polymer matrix and also that of orthophosphoric acid have a great impact on PVA–metal complex bonding and thus properties such as density, thermal conductivity, and specific heat of the system vary according to the chemical composition of the system. Results obtained by changing cobalt complex and H_3PO_4 concentrations are presented in Table I. Similar results can be obtained by carrying out experiments using other metal complexes such as Cu, Fe, and Ni, etc.

Heating of the polymeric layer at a constant temperature hot surface gradually increases the temperature and, when average temperature of the film reaches a certain value, thermochromic response of the system is manifested. Initially, polymer is at room temperature and its sudden contact with a constant temperature hot surface starts an unsteady-state heat transfer. Conduction of heat through the polymeric layer is driven by the temperature difference between the hot surfaces of the heater and the cold surface of the polymer.

Heat transfer equations for an unsteady state heat flow can be described as follows.[3]

If response time of the material is t, then heat taken by the material after time t is given as

$$Q = mC_p.\Delta T$$

$$= mC\hat{p}.(T_b - T_a)$$

where T_a is initial temperature of the film and T_b is average temperature of the film at time t.

Unsteady-state heat transfer by conduction in solids is given by[4]

$$(T_s - T_b)/(T_s - T_a) = 8/\pi^2(e^{-a_1 N_{Fo}} + 1/9e^{-9a_1 N_{Fo}} + 1/25e^{-25a_1 N_{Fo}} + \text{—})$$

where N_{Fo} is the Fourier number, defined as $\alpha t/s^2$, α is the thermal diffusivity of the material, s is the thickness of the film, and T_s is the hot surface temperature of the film.

When the Fourier number is greater than about 0.1, only the first term of the series in the above equation is significant, and time required t can be found as[4]

$$t = 1/\alpha(s/\pi)^2 \ln[8/\pi^2(T_s - T_a)/(T_s - T_b)] \quad (1)$$

The above equation is a theoretically derived equation that shows little deviation with experimental data;

however, for practical application, a calibration constant has to be multiplied which caters for parameters such as heat losses, solvent evaporation, and many such trivial parameters that are not taken into consideration for calculation of response time. An equation based on practical results is developed as

$$t = 0.2s^2/\alpha \ln[0.81(T_s - T_a)/(T_s - T_b)] \qquad (2)$$

Equation (2) can be very useful in calculating the time for a solid material to attain a certain temperature when heat is being transferred to it by conduction. Experimentally, it was observed that different compositions of PVA–$CoCl_2$ complexes probably have a different degree of binding between polymer and metal chloride and thus they show color change at different bulk temperatures. Also, they take different times for attaining a certain temperature as their thermal diffusivity α changes according to the chemistry of the material. Thermal diffusivity α is the ratio of $\rho Cp/k$, which plays a key role in reaching the temperature of the PVA–metal complex at which thermochromic behavior is observed and thus it influences response time of the material at which thermochromism is manifested.

A change in concentration of cobalt chloride and orthophosphoric acid both show the change in response time, which corroborates very well with eq. (2). However, as shown in Table I, cobalt concentration $> 14\%$ by weight and orthophosphoric acid $> 12\%$ by weight does not follow eq. (2). Therefore, it is advisable to estimate response time with the help of the equation when cobalt concentration is in the range of 3.5–14% and phosphoric acid concentration is in the range of 3–12%. PVA–cobalt complex beyond the above-mentioned concentration probably no longer has an effect on the chemistry of the material and it is just a physical mixing beyond the aforesaid concentration of cobalt chloride and orthophosphoric acid.

This phenomenon indicates that it is the change in chemical composition that effects the response time of the material. The role of orthophosphoric acid is to develop linkage between the polymer chain and the metal ion as described in the structures displayed in Figures 1 and 2.[2]

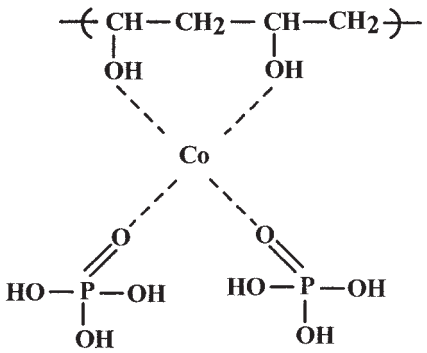

Figure 1 Linkage among orthophosphoric acid, metal ion and polymer chain.

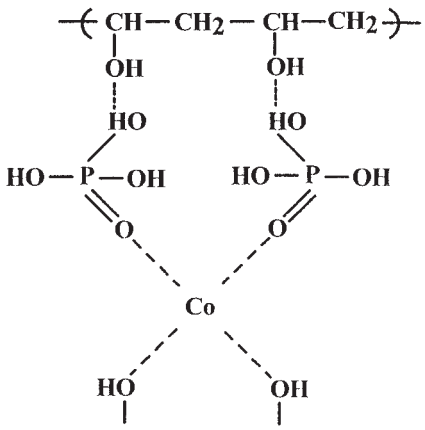

Figure 2 Orthophoshoric acid in middle forms linkage with metal ion as well as polymer chain.

It is experimentally observed that the excess amount of cobalt chloride ($\sim 100\%$ extra) is required to complete the bonding as compared to the amount of cobalt chloride required stoichiometrically for formation of structures shown in Figures 1 and 2.

CONCLUSIONS

Thermochromic response of PVA–cobalt complex makes it a useful material for many temperature-sensing applications. Quantification of its response time in different chemical compositions has made it a very useful material for the systems where thermochromic response with respect to time is important. The equation developed here is thought applicable for a specific PVA–metal complex but similar studies can be repeated for different types of thermochromic systems and a tailor-made specific thermochromic system can be designed.

An interesting application of the thermochromic smart material could be in the development of temperature-sensitive color-changing paints that would automatically indicate the skin temperature of a machine component without any instrumentation and electronic circuitry.

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