

WATER STATES IN SBR BASED WATER SWELLING RUBBER

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Abstract Water swelling rubber (WSR) was prepared by reaction blending SBR and sodium polyacrylate (PAANa). The existing states of water in the WSR was studied by means of DSC and TG. It was found that water exists in three states: nonfreezing water, bound freezable water and free water. The relationships between water states and structure of PAANa were investigated. The results showed that the amount of non-freezing water was related to total water content, and the ratio of non-freezing water versus $-\text{COONa}$ groups on PAANa (mol/mol) was about 4. However, total water content slightly affected the content of bound freezable water and remarkably affected the amount of free waer.

Keywords Water swelling rubber; Water states; DSC

INTRODUCTION

Rubber and high absorptive resin (HAR) and other additives could be blended and crosslinked to form rubber-like vulcanite with HAR as the dispersed phase. The vulcanite has elasticity and is able to get swollen in water^[1], therefore, it is usually called water swelling rubber (WSR), and has been widely used as water-resisting sealing materials for dams, culverts, basements, etc.^[2~4]. HAR has strong affinity with water and is inclined to absorb water rapidly to form hydrogel, which results in the swelling of the rubber networks. The freezing temperature of the absorbed water would change because of the strong interaction between water and the hydrophilic groups of HAR. Child^[5], Zhang^[6] et al., have investigated the states of water in acetate cellulose and polyvinyl alcohol by differential scanning calorimetry (DSC)

* Project supported by the National Natural Science Foundation of China.

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Received March 13, 1998

and nuclear magnetic resonance (NMR), respectively. They have pointed out that the absorbed water in these hydrophilic polymers exist in three states: non-freezing water, bound freezable water and free water. In this paper, we will investigate the states of the absorbed water in the WSR prepared by reaction blending SBR and sodium polyacrylate (PAANa) in which the hydrophilic components cannot be extracted by the surrounding water.

EXPERIMENTAL

Preparation of the WSR

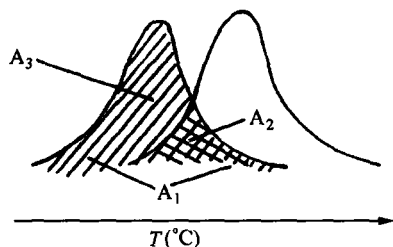
Compounding: SBR-1502 (produced by Qilu Petrochemical Co., Ltd.) 100 phr, zinc oxide 5.0 phr, stearic acid 2.0 phr, accelerator D 0.9 phr, accelerator DM 0.8 phr, white carbon black 50 phr, s 2.0 phr, PAANa 60 phr, compatibilizer 20 phr, prepared by reaction blending, and vulcanized at 150°C for 20 min.

Mechanical properties of the WSR

Tensile strength: 8MPa, elongation at break: 400%, hardness 75 (Shore A), maximum water content after water absorbing: 51.1 wt%.

DSC measurement

The principles of determining the states of water in the WSR are^[7]: in the DSC thermogram of WSR (or polymer hydrogels), the onset point of the thermal-effect peaks of phase transition corresponds to the melting temperature of the freezable water, and the area of the peaks represents the heat absorbed or released. In hydrogels, a part of water interacts with the hydrophilic polymer strongly and its phase transition does not occur within the range of $-60 \sim 30^{\circ}\text{C}$. Therefore the phase transition heat observed is smaller than that theoretically calculated, and based on



this discrepancy, the amount of non-freezing water could be determined. By comparing the area of the endothermic peak produced by the WSR sample (A_1) with that by bulk water and work out the area of the overlapping part (A_2), the thermal effect of the bound freezable water (A_3) can be calculated by $A_3 = A_1 - A_2$.

By A_3 and the phase transition heat of bulk water, the content of bound freezable water is determined. Finally, based on the content of different states of water and the content of PAANa in the WSR, the mole ratio of the hydrophilic groups of PAANa versus the different states of water in the WSR can be obtained.

The detailed procedures in DSC measurement are: Soak the WSR samples in deionized water to let it swell to have different water content. Take out the samples and wipe off the surface water quickly, and get about 5 mg piece from each sample to put into aluminum box for DSC (U.S. Perkin Elmer, standardized by In) use. The temperature was lowered to -60°C first, kept there for 15 min, then raised the temperature to about 20°C at the rate of $10^{\circ}\text{C}/\text{min}$. The DSC curve for each sample obtained in the heating run represented the transition of water in the WSR.

Thermogravimetry (TG) measurement

The weight loss curve of water-bearing WSR sample was obtained from Perkin-Elmer TGA7.

RESULTS AND DISCUSSION

Water states in WSR as studied by DSC

Fig. 1 is the DSC thermograms for WSR with different water contents.

In Fig. 1 curve 1 illustrates the transition of pure bulk water, which forms an endothermic peak in the vicinity of 0°C with about the same endothermic heat value calculated by the area of the peak as its theoretical value. This shows that bulk water freezes at 0°C . Curve 2 stands for the dried sample of WSR, which gives no indication of heat release or absorption. So it could be deduced that no phase transition takes place during the heating run. Curve 3 shows that WSR sample with 15% water content does not absorb heat in the heating process, thus no phase transition occurs. Curve 4 is that of the WSR sample with 24.2% water content, in which a small and broad endothermic peak appears in the range of $-33 \sim -4^{\circ}\text{C}$ with a calculated endothermic heat value of 20.1 J/g . Based on this value and the melting heat of bulk water (333.5 J/g)^[8], the amount of water whose phase state has changed could be calculated. The result shows that only 0.0603g water has changed its phase, corresponding to a small fraction of the total water of 0.242g. After DSC measurement, this sample was treated in the procedure of weight loss (by TG measurement, Fig. 2).

Fig. 2 shows that the weight loss of the sample reaches 23.15% after being heated at 100°C for 35 min, indicating the content of water in this WSR sample is about the same as its initial value after DSC measurement. Based on these data, a conclusion can be drawn that a certain amount of water (75%) does not freeze in the heating run, and this part of water which is undetectable within the scanning range (as low as -60°C) of DSC is called the non-freezing water. In addition, it could be found

that in curve 4 (Fig. 1), the melting point of the freezable water (-33°C) is much lower than that of the bulk water. This part of water is called the bound freezable water.

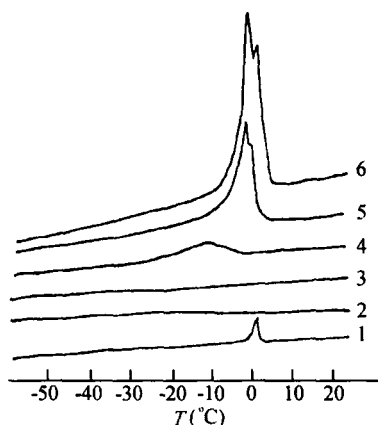


Fig. 1 DSC thermograms for the PAANa-WSR with different water contents
1. bulk water; 2. dried sample;
Water contents in WSR (wt%):
3. 15.0%; 4. 24.2%; 5. 39.0%; 6. 47.1%

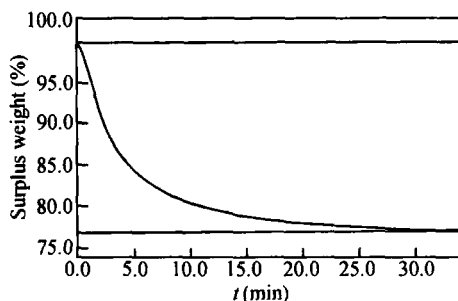


Fig. 2 TG curve of PAANa-WSR with 24.2% content of H_2O in the WSR

As the water content of WSR became higher (curve 5, 6), the phase transition temperature of freezable water also increased. For example, WSR sample containing 47.1% water (curve 6) began to melt at -15°C , which was 18°C higher than that of the WSR sample containing 24.2% water. Its endothermic range was $-15 \sim 4.5^{\circ}\text{C}$, which meant that a part of water melted above the melting point of bulk water. The appeared double peaks indicated that besides the bound freezable water, there is some free water present whose melting point is the same as that of the pure bulk water.

The above results show that three states of water would appear when the water content in the WSR reaches a certain value, i.e., non-freezing water, bound freezable water and free water. As the water content in the WSR increased, the non-freezing water formed first, then the bound freezable water, finally the free water. The calculated results of WSR samples with different content of water (1[#] ~ 7[#]) were presented in Table 1.

As it could be seen from Table 1, when the water content in WSR increases, the melting point of bound freezable water becomes higher. e.g., when the water content reaches 47%, it increases to as -15°C . It will not increase any more as the water content increases to 51%.

Table 1 Distribution of water in the WSR with different water content

Sample No.	Total water content (g/g wet WSR)	Nonfreezing water content (wt%)	Freezable water content (wt%)	
			Bound	Free water
1 [#]	—	—	—	100, (0°C)
2 [#]	—	—	—	—
3 [#]	0.15	100.0	0.0	0.0
4 [#]	0.24	73.6	2.64 (−35°C)*	0.0
5 [#]	0.39	43.0	57.0 (−18°C)	0.0
6 [#]	0.47	25.3	42.0 (−15°C)	32.7 (0°C)
7 [#]	0.51	21.7	36.8 (−15°C)	41.5 (0°C)

* Melting point of water in the WSR

Relationships between water states in the WSR and the amount of PAANa

Based on the relative content of water and monomer unit mass of PAANa in the WSR, the mole ratio of different states of water in WSR samples (3[#] ~ 7[#]) versus structural unit of PAANa was calculated, and the results were presented in Table 2. It could be seen from Table 2 that as the water content in WSR increases, the mole ratio of non-freezing water and bound freezable water versus monomer unit of PAANa is about 4 and 7, respectively. This shows that there should be saturation between the non-freezing water, bound freezable water and the hydrophilic groups of PAANa, but the content of free water keep rising as the total water content becomes higher. This phenomenon is dictated by the micro structure of the high absorptive resin in the WSR.

Table 2 Mole ratio of different states of water versus PAANa monomer unit in the PAANa-WSR

Sample No.	Total water content (g/g wet WSR)	NFW ^a content (mol/mol monomer unit)	BFW ^b content (mol per mol of monomer unit)	FW ^c content (mol per mol of monomer unit)
3 [#]	0.15	3.8	3.8	0.0
4 [#]	0.24	6.0	4.3	0.0
5 [#]	0.39	12.1	4.4	6.9
6 [#]	0.47	17.0	4.4	7.1
7 [#]	0.51	20.0	4.4	7.3

a: Non-freezing water; b: Bound freezable water; c: Free water

The saturation of non-freezing water and bound freezable water indicated that water molecules interacted with PAANa with some saturation at different structural level. The first structural level is the layer formed by first entered non-freezing water, in which about 4 molecules of water are bound closely to 1 carboxyl group of PAANa, so this part of water does not freeze in the freezing process. The second level

is bound freezable water layer that formed after the first layer of non-freezing water has saturated and stay beyond the first level whose freezing point is lower than that of the bulk water because of the weak interaction between water and PAANa that it which hindered its crystallization. As the water content increases, the freezing point of this part of water become higher, reaching -5°C when saturated, and at this moment, every mole of monomer unit of PAANa bound 7 moles of bound freezable water. When the water content of the WSR increases further, the water absorbed would belongs to the category of free water with normal freezing point and phase transition heat.

REFERENCES

- [1] Yamaji, I., *Polymer Digest (in Japanese)*, **1984**, (10), 17
- [2] Xue, S.J., Hua, X.J., *Chinese Building Sealing Materials (in Chinese)*, **1994**, (3), 27
- [3] Zhang, Boxian, *Chinese Building Sealing Materials (in Chinese)*, **1995**, (2), 29
- [4] Motohashi Tadaichi. *Processing of Polymers (in Japanese)*, **1984**, 33 (9), 453
- [5] Child, T.F., *Polymer*, **1972**, 13, 259
- [6] Zhang, W.Z., Jiro Komiyama, *Journal of Membrane Science*, **1989**, 42 (3), 303
- [7] Akon Higuchi, Toshiro Lijima, *Polymer*, **1985**, 26, 1207
- [8] Hatakeyema, T., Yamanchi, A., *Eur. Polym. J.*, **1984**, 20, 61