Dynamics of absorbed water in model composites of polyamide 6 and carbon fibre evaluated by differential scanning calorimetry

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Abstract The crystallization and subsequent melting behaviour of absorbed water in the model composites of polyamide 6 (PA6) and carbon fibre were investigated by differential scanning calorimetry (DSC) in comparison with those in neat PA6, using the small rectangular specimens exposed to water at 90 °C. In the DSC curves of PA6 any exothermic peaks of crystallization and endothermic ones of melting were not observed, but a step corresponding to glass transition was observed at about −30 °C during the heating process. Thus water absorbed by neat PA6 was recognized as non-freezing bound water which does not crystallize, probably due to the strong interaction with the polyamide chains. On the other hand, for the model composite several exothermic peaks were clearly observed at temperatures ranging from −10 to −20 °C, and their intensity was increased with increasing the fibre content. The distinct endothermic peaks were detected around at 0 °C during the reversed heating process. The glass transition temperature was not affected by adding the carbon fibre. Comparing with the result of neat PA6 indicates that in the model composite water exists in a state near free water, besides the non-freezing bound water dispersed in the matrix polyamide. It is further implied that water is mainly accumulated in the matrix/fibre interfacial region with some microstructural heterogeneties or defects, in which the water molecules can easily move under much weaker interaction with the polyamide chains.

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Introduction

The mechanical strength and durability of fibre reinforced polymers (FRPs) are generally lowered by absorbed water, which gradually penetrates and is accumulated in FRPs during applications in wet environments [1, 2]. Many past studies have supposed that such a mechanical degradation is mainly caused by a reduction in the load-bearing ability of interfacial region between the matrix polymer and the embedded fibre upon water absorption [3–8]. Therefore it may be of great importance to elucidate the behaviour and action of absorbed water in the interfacial region. Analysing the existing state, i.e. the structure and mobility of water in the matrix/fibre interfacial region will be beneficial for replying to this subject. The above studies, however, are based on the macroscopic fracture tests, which entirely evaluate the variations of the fracture resistance and the fracture surface of bulk specimen with immersion in water. Since the interfacial region will be spaced in a microscopic scale (μm or less), it may be very difficult for the above studies to obtain precise information on the existing state, and further on the behaviour and action of absorbed water leading to the reduction in the load-bearing ability of matrix/fibre interfacial region.

Recently the Fourier transform infra-red (FT-IR) microspectroscopy has been developed for studying the molecular structure of accumulated water in such a microscopic region of interface. Kawagoe et al. [9, 10] have analysed the shape and the frequency range (wavenumber) of IR spectrum of water absorbed in a model composite of unsaturated polyester and aramid fibre (Kevlar 49), and revealed that two types of water, i.e. the isolated (gaseous) and the clustered (liquid-like) waters exist in the interfacial region, and the content of clustered water increases with increasing the soaking time in water. Their micro-IR analysis is based on the study of Kusanagi and Yukawa [11] on water contained in solid polymers, and, so to speak, may be featured by providing a static view of accumulated water.

Investigating a dynamic behaviour (mobility) of water molecules may also be of interest in relation to its existing state, which may strongly reflect the degree of interaction with the surrounding matter in the interfacial region. Differential scanning calorimetry (DSC) [12–15], nuclear magnetic resonance (NMR) [16, 17] and dielectric spectroscopy [18, 19] appear as useful techniques for this purpose, because they have already achieved satisfactory results for evaluating the dynamics of absorbed water in neat solid polymers. The DSC analysis is usually conducted for its generality and convenience, although it can give only indirect or rather qualitative information on the behaviour of water molecules in response to the cooling and heating processes. According to the DSC study of Nakamura et al. [12], there in general exist three types of absorbed water in solid polymers: ''free water'' showing the same freezing behaviour as pure bulk water, ''freezable bound water'' being frozen at lower temperature than free water, and ''non-freezing bound water'' with no exothermic peak due to crystallization in the DSC curve measured under cooling process. In addition the content of bound water was revealed to clearly correlate with the degree of hydrogen bonding of polymers (e.g. polyhydroxystyrene derivatives). Ping et al. [14] recently have conducted the DSC analyses of absorbed water in poly(vinyl alcohol) (PVA), and also indicated that water molecules are directly bound to the hydrophilic site of PVA to form non-freezing water. By making reference to these studies, it is expected that the DSC analyses provide valuable information on the mobility of water molecules in the interfacial region between the matrix polymer and the embedded fibre. In addition this may suggest a new approach to the structural analysis of interfacial region using water molecules, which act as a probe to detect the micro-

structure, reflecting the power of interaction with the surrounding.

In view of the above, we have conducted the DSC measurements for the model composites of polyamide 6 (PA6) and carbon fibre with different contents, which were soaked in water at 90 °C until the saturation in weight. PA6 chosen as a matrix polymer is one of the typical hydrophilic polymers with the strong attractive sites for water molecules. Therefore by comparing the behaviour of water molecules absorbed in the model composite with that in neat PA6 under the cooling and reversed heating processes we characterized the existing states of water molecules in the matrix/fibre interfacial region. Based on these analyses the microstructural features of this region were inversely explored by examining the degree of attractive tendency of PA6 for water molecules.

Experimental

Materials and sample preparation

The materials used were commercially available pellets of polyamide 6 (PA 6), Ube Nylon 6, S1013NW8 (Ube Kosan Co. Ltd.) and PAN-based carbon fibre, Besfight HTA–6K (Toho Rayon Co. Ltd.), which was obtained in strand of 6,000 filaments of 7 μm in diameter.

The PA pellets were preliminarily dried at 80 °C for 3 h in a vacuum chamber, VOR-300 (Shibata Kagaku Kikai, Co. Ltd.), and then uniformly dispersed in a rectangular mould of stainless steel. A great number of carbon fibres were set to align in one direction on a median plane of the mould so as to be completely covered with the PA pellets. The volume fraction of fibre was roughly estimated from the volumes of fibre and matrix, which were calculated by dividing each added mass by density. Two volume fractions of fibre of about 8 and 18% were prepared.

The pellets and fibres in the mould were pre-heated at 225 °C for 5 min, and then compressed under about 15 MPa for 5 min by means of a hot-pressing equipment, TF1 (Imoto Co. Ltd.) to impregnate the fibres with molten PA. The mould and all were taken out from the equipment, and immediately thrown into ice water at 0 °C. The sheet was removed from the mould, and then cut into small rectangles by a low-speed disc cutter, Minitom (Struers Co. Ltd.). Finally the rectangular specimens with dimensions of about $3 \times 3 \times 0.5$ mm were finished by polishing the cut surfaces with an abrasive paper of No. 1000. The neat PA specimens were also prepared in almost the same

way, excluding the procedure to set the carbon fibres in the mould.

The degree of crystallinity of PA phase was roughly estimated to 23.1% from the measured density of neat PA specimen by referring to the literature [20] on the densities of crystalline and amorphous phases of PA6. The specific gravity for calculating the density of PA was measured on the basis of JIS K7112 [21] by an electronic densimeter, SD-200 L (Mirage Trading Co. Ltd.) using the rectangular specimen with size of $50 \times 10 \times 1$ mm, cut from the PA sheet moulded and heat-treated in the above way.

Treatment of water absorption

The neat PA and the model composite specimens were preliminarily dried at 80 °C for 5 h in the above-mentioned vacuum chamber, and subsequently immersed in distilled water at 90 °C until the saturation in weight. According to the weight gain measurements with an electronic balance, AE240 (Mettler-Toledo AG), the weight gains at saturation by the neat PA specimen and the composite specimens with fiber volume fractions of about 8 and 18% were 9.7, 8.2 and 9.1 wt%, respectively. Assuming water to be absorbed only by the PA phase in the composite, the latter two values are converted to 9.4 and 12.2 wt%, respectively. The amount of absorbed water on the model composite is almost equal to or larger than that by the neat PA specimen in terms of PA content. This implies that water is stored not only in PA matrix but also in other sites like the interfacial regions.

DSC measurements

After removing the external surface water, the water-soaked neat PA and composite specimens were immediately sealed in aluminium pans. The DSC measurements of sealed samples were conducted by means of a heat-flow type differential scanning calorimeter, DSC 6100 (Seiko Instruments Co. Ltd.) with a cooling device. The DSC curves were obtained by cooling the specimen from 25 to −70 °C at the scanning rate of 2 °C min^{-1}, and subsequently heating it to 25 °C at the same rate. The alumina (Al_2O_3) powder of about 10 mg was used as a reference matter.

Results and discussion

The DSC curves for the neat PA6 specimen subjected to water absorption treatment at 90 °C showed no exothermic peaks of crystallization and endothermic ones of melting during the cooling and the reversed heating processes, respectively, despite a considerable absorbed water of about 9.7 wt% in the specimen. In an extended scale of DSC on the ordinate for the heating process, however, a step of base line corresponding to the glass transition in the polymer is clearly found at about −30 °C, as shown in Fig. 1. Since the glass transition temperature, Tg, of dried PA6 specimen is observed at about 40 °C, as indicated in Fig. 2, the Tg of PA6 is greatly lowered by about 70 °C by absorbing water of above content. These results suppose that the water molecules absorbed by the neat PA6 specimen are strongly restricted to the hydrophilic site of amide group, and are in a state of non-freezing bound water which cannot be crystallized at all. However, they may form a cluster [11] to expand the spaces among the molecular chains, and as a result may enhance the mobility of chains leading to reduction in Tg of PA, called a plasticization effect.

Figure 3 shows the DSC curves for a model composite with a fibre volume fraction of 8%. The apparent water content of 8.2 wt% is stored in the specimen
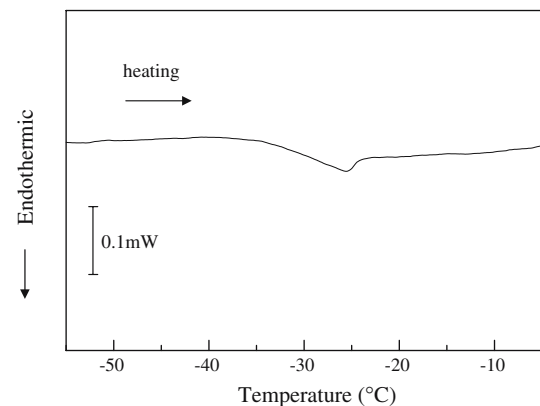

Fig. 1 DSC curves under subsequent heating process for the neat PA6 specimen absorbing water of about 9.7 wt% by exposure to water at 90 °C
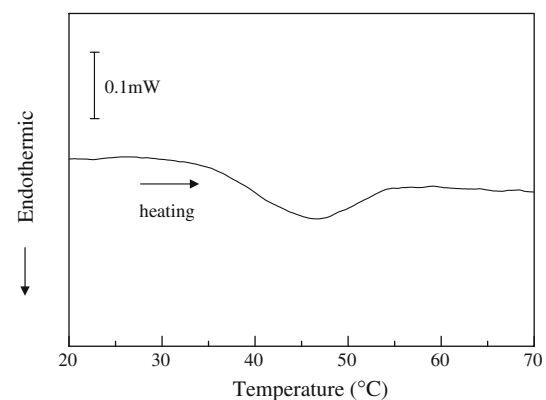

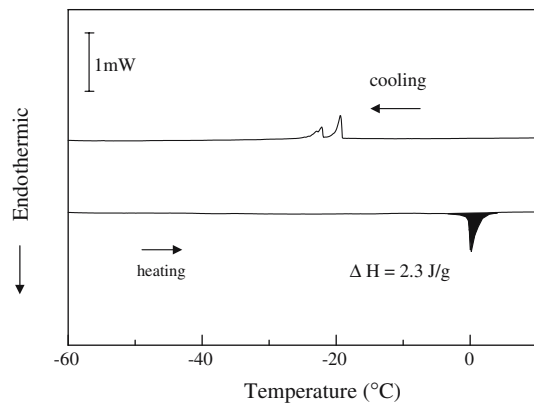**Fig. 2** DSC curve of the dried PA6 specimen under heating

Fig. 3 DSC cooling and subsequent heating curves for the model composite with a fibre volume fraction of 8%, containing the apparent water of 8.2 wt% by immersion in water at 90 °C

by the immersion in water at 90 °C. Two exothermic peaks are distinctly observed near about −20 °C under the cooling process, being in a marked contrast to the result of neat PA6. In a reversed heating process a clear endothermic peak is detected at about 0 °C, as well as bulk water. Extending the scale of DSC on the ordinate, particularly for the behaviour under the heating process, a weak step of DSC base line due to the glass transition was faintly measured at about −38 °C, which is near the Tg of neat PA6 specimen containing 9.7 wt% water (Fig. 1). In comparison with neat PA6 it may be interpreted that such a glass transition phenomenon in the model composite is also caused by the plasticization effect of absorbed water on the matrix phase of PA6.

Figure 4 shows the result for a model composite, the fibre volume fraction of which is raised to 18%. The content of absorbed water is apparently 9.1 wt% by also soaking the specimen in water at 90 °C. One may
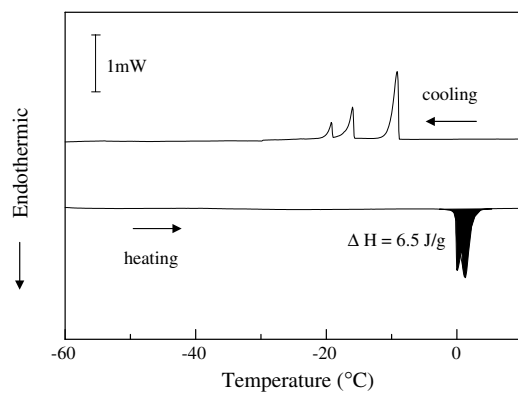

Fig. 4 DSC cooling and subsequent heating curves for the model composite with a fibre volume fraction of 18%, containing the apparent water of 9.1 wt% by exposure to water at 90 °C

easily find a greater exothermic peak at −10 °C, and also two peaks near −20 °C as well as the previous result for the composite with less fibre content (Fig. 3). In the heating process two endothermic peaks are observed at about 0 °C. Extending the ordinate scale of DSC indicated the glass transition to also take place at about −30 °C in the reversed heating process.

A series of DSC results mentioned above supposes that in the specimens of model composite there exists some water which shows a similar freezing behaviour to the distilled bulk water under the cooling process, and further suggests that water absorbed by the composites mainly exists in a state near free water, being very weakly interacted with the surrounding. Other contained water in the composite may be of a type of non-freezing bound water as well as in the neat specimen, showing no exothermic peak in the DSC curve during the cooling process. This type of water, however, may be uniformly dispersed in PA matrix phase in the composite, and clearly contributes to a reduction in Tg of PA phase, irrespective of little molecular mobility due to the strong attraction from the amide group through the hydrogen bonding. In the reversed heating process, on the other hand, the DSC results for the water-soaked composites with different fibre contents commonly show marked endothermic peaks at about 0 °C, as bulk water. It may be interpreted that these peaks arise from the melting of frozen water, which may behave as entire free water, being completely released from the interaction with the matrix polymer as the crystallization proceeds under the cooling process.

The quantity of free water in the composites thus may be properly evaluated from the endothermic peaks of DSC curves obtained during the heating process. Referring to the study of Ping et al. [14], the mass of free water is given by

$$W_f(g) = Q(J)/\Delta H_{dw}(J/g) \tag{1}$$

where ΔH_{dw} (J/g) is the melting enthalpy of distilled bulk water, estimated as 334 J/g from our DSC measurement. This estimated value of ΔH_{dw} (J/g) is almost the same as those in the literatures [12, 14]. $Q(J)$ is the heat absorbed during the melting (heating) process of frozen water in the composite specimen, and obtained by multiplying the melting enthalpy, ΔH(J/g), corresponding to the area of the endothermic peak (coloured black in Figs. 3, 4) by the mass of water-soaked specimen. The percentage content of free water included in the total absorbed water is given by

$$C_f = (W_f(g)/W_t(g)) \times 100 \tag{2}$$

where $W_t(g)$ is the total mass of absorbed water, which is given by the weight gain of specimen under the exposure to water. The values of $W_t(g)$, $W_f(g)$ and C_f are summarized in Table 1. The table shows that the fraction of free water included in the total absorbed water in the composite is generally low, as showing about 10 and 28% for the specimens with the fibre volume fractions of 8 and 18%, respectively. It is thus indicated that most of absorbed water in the model composite exists in a state of non-freezing bound water, which may not be crystallized, although the free water is partially contained.

As is demonstrated by the above examinations, the non-freezable bound water commonly exists both in the neat and in the model composite specimens, and clearly causes the plasticization effect leading to a reduction in the glass transition temperature of PA in both the specimens. However, the presence of water in a state of or near the free water is identified only in the composite specimens. These results suggest that the latter type of water is accumulated mainly in the matrix/fibre interfacial regions, which are peculiar to the composites. In such regions some water may behave as the free water, corresponding to very weak interaction with the surrounding with some structural heterogeneities or defects like microvoids. The plural exothermic peaks in the DSC curve observed under the cooling process (Figs. 3, 4) may express the intensity of this interaction to be at various degrees. The above suggestions are consistent with the experimental results that the exothermic peaks are much clearer in the specimen with higher fibre content (Fig. 3). That is, since an increase in the content of filled-up fibres, at the same time, brings about an increase in the interfacial region with heterogeneous structure, the quantity of water accumulated in such a site is also increased, and as a result a thermal behaviour of free water becomes much more remarkable. From the above discussions one may further expect that a microstructural analysis of composites, especially of interfacial region, is possible by examining the crystallization and/or the melting behaviour of absorbed water, which is in this case used as a probe to detect the microstructure in response to the power of interaction with the surrounding.

Conclusions

The DSC studies were conducted on the specimens of neat PA and PA/carbon fibre model composite, which were preliminarily immersed in water at 90 °C until the saturation in weight. In both the specimens the glass transition was commonly observed at about −30 °C, which was lower by about 70 °C than the dried PA specimen under the plasticization effect of absorbed water. Only in the composite specimens, on the other hand, the exothermic peaks of crystallization of water and the endothermic ones of melting of ice were observed in temperature range from −10 to −20 °C under the cooling process and at about 0 °C under the reversed heating one, respectively. Their intensity was enhanced with increasing the fibre content. These experimental results and the estimation of free water quantity suggest that in the composite specimens the absorbed water partially exists in a state of or near the free water with great molecular mobility, although most of water is type of non-freezing bound water, which may be uniformly dispersed in the specimen, and act as a plasticizer. The free type of water is supposed to be accumulated mainly in the matrix/fibre interfacial regions with inhomogeneous microstructure, in which the water molecules are almost released from the interaction with the amide group of matrix PA phase.

Table 1 Total mass of absorbed water, W_t, the mass of free water, W_f, and the percentage content of free water, C_f, in each specimen

Fibre volume fraction (%)	W_t (mg)	W_f (mg)	C_f (%)
0	0.85	0	0
8	0.71	0.07	10
18	0.76	0.21	28

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