

Effect of water absorption in polymers at low and high temperatures

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Abstract

Water is absorbed by most polymers, but a change of properties is induced only in specific types of polymers. Water is considered to be present in the free volume and active only when attached to polymer chains by hydrogen bonds. The materials considered are PEI, PEEK, PES, PC, PA 12, and PA 6. The changes in damping spectra, moduli, and thermal expansion due to the moisture absorption have been investigated in the broad temperature range of 4.2–320 K. It is surprising that properties are changed by water in a different or opposite ways at low and high temperatures. Even at very low temperatures, absorbed water influences the mechanical performance in an unexpected way. The results at low temperatures might be a tool for a better understanding of the features of the hydrogen bonded water, which itself could be a sensor for analysing molecular mobilities. The interpretation of results is generally not yet clear and some cryogenic results are in contradiction to well established correlations for dry polymers. Ideas for solving these problems are given in the conclusions of this study. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymers; Water absorption; Cryogenic properties

1. Introduction

It is well known that moisture induces property changes in polymers. At RT and above, water is considered to act as a softening agent (spacer between chains). At cryogenic temperatures, however, the contrary is true: wet specimens are stiffer than dry ones. Most polymers absorb more or less water, but not all of them exhibit a change in properties. i.r.- and MRS-analyses by several authors [1,2] indicated that only water connected to macromolecules by hydrogen bonds causes property changes. Polymer chains with strong polar groups are able to bind water by hydrogen bridges. Some examples are the ketone group (C = O) or the sulphone group (O = S = O) and nitrogen. There are, however, restrictions. Oxygen on both sides of a ketone group is considered to hinder the formation of hydrogen bonds [2]. An example is PC which contains ketone groups framed by oxygen.

The phenomenon of moisture absorption has been studied by several authors in polymers [3,4] and polymer-based composites [5] mainly at room temperature and above. In that temperature range, absorbed water reduces moduli and the main glass transition temperature [6] enlarges fracture strain and impact strength [7,8] (softening or plasticizing effect). These features may be explained by assuming that

water acts as a spacer between chains. However, cryogenic measurements and the behaviour of thermal expansion makes the spacer model doubtful.

Fewer measurements have been performed at low temperatures and nearly none at very low temperatures. In the temperature range between 160 and 200 K, for all polymers considered, a strong damping peak ('water peak') is induced or superimposed upon existing ones by water absorption. The temperature–frequency position of the 'water peak' depends on the type of polar groups to which water is bonded. The nature of the 'water peak' has been a topic of many theoretical and experimental investigations [9,10]. A consistent solution is not yet available. Most interpretations concentrate on two lines.

1.1. Side group motion of hydrogen bonded water

The 'water peak' is caused by the mobility of water which acts as a side group [11]. Some authors conducted test series of experiments on PEEK; absorbing water or alcoholic groups of increasing length resulted in the correlated damping peaks being shifted to higher temperatures [9]. The calculated activation energy of approx. 60 kJ/mol is rather high for side group motions. At similar configurations (e.g. PEMA, PPMA, PS) even longer side groups, which are covalently bonded, are correlated to an activation energy

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of approx. 10 kJ/mol, and damping peaks occur at approx. 30 K at 10 Hz [12]. For PEEK, another suggestion is a collective motion of the ketone group (with water) and both aromatic rings, which are linked.

1.2. Bonded water as a spacer which enhances preformed mobilities of chain segments

The range of activation energies of 'water peaks' is similar to that found for collective motions (e.g. crankshaft). It ranges from 40 to 70 kJ/mol and the damping peaks occur in the range of 150–200 K, and at 10 Hz [13]. The idea of providing space for collective segment motions by water could be realistic from the energetic point of view. However, results on thermal expansion contradict this idea. When crankshaft motions start, thermal expansion should be increased because more free volume is formed. But this has not been observed. There is no clear evidence in favour of any of the present explanations.

The investigations presented in this paper cover a very broad temperature range from 4.2 to approx. 320 K. In particular, results at very low temperatures exhibit unexpected features which might help to better understand molecular motions when water is bonded. Furthermore, not only the damping behaviour has been studied but also the moduli and thermal expansion over the whole temperature range. Damping spectra, moduli and thermal expansion of polymers are compared in the dry and nearly water-saturated conditions. It is surprising that property changes are very different at low and high temperatures. For example, at low and very low temperatures the Young's and shear moduli are increased and the damping spectra are drastically changed by the incorporation of water. It is also surprising that, at very low temperatures, the damping behaviour is changed in the opposite way. Peaks existing for dry polymers between 30 and 100 K are suppressed in the wet state. It will be pointed out that there are some discrepancies concerning the influence of water on the modulus and on thermal expansion, especially at cryogenic temperatures. It is surprising that all polymers investigated exhibit nearly the same thermal expansion in the dry and wet states. A damping peak is usually considered an indicator for the onset of molecular mobilities, which increase the free volume and thus thermal expansion. It is surprising that thermal expansion is nearly uncorrelated to the 'water peak'. In fact, a tendency towards the opposite behaviour has been observed. Some polymers (e.g. PA12) exhibit a small decrease of thermal expansion above the 'water peak' in the wet state. Studying moisture in polymers could be a tool for better understanding the features of the free volume (see also ref. [10]).

2. Hydrogen bridges and bonding of water

This kind of weak bonds result from the ability of the hydrogen atom to act as a link between two other atoms.

These bonds occur in general between hydrogen and the electronegative elements nitrogen, oxygen, and fluorine, termed proton acceptors, where the electron density of the hydrogen atom will decrease by interaction with unbonded electron pairs of these proton acceptors. Typical hydrogen bond strengths between low-molecular weight molecules in general are between 1 and 50 kJ/mol.

This paper covers investigations of four aromatic polyethers and two polyamides. Only aromatic polymers are considered below. Besides aromatic rings and ether bridges these polymers contain polar groups, like imide (-CO-NH-CO-) moieties in poly(ether imide), sulfone (-SO₂-) groups in poly(ether sulfone), ketone (-CO-) groups in poly(ether ether ketone), and carbonate (-O-CO-O-) groups in polycarbonate. These characteristic polar groups contain nitrogen and/or oxygen as potential proton acceptors to form hydrogen complexes.

Water molecules close to polar groups should be able to form hydrogen-bonded complexes with nitrogen and oxygen. As indicated above, this interaction between hydrogen in water molecules and the corresponding proton acceptor results in a shorter distance and higher bond strength than in physisorption.

In contrast to physisorption and hydrogen bonding, chemisorption is the result of much stronger bonding forces, comparable with those leading to the formation of chemical compounds, i.e. the formation of covalent bonds. The energies of chemisorption are of the order of 40–400 kJ/mol.

3. Materials

Test polymers were selected according to their content of strong polar groups and their ability to absorb water. The PEI, PEEK, PES, PA 12, and PA 6 polymers contain strong polar groups which favour the bonding of water molecules by hydrogen bridges. PC also contains strong polar groups (C = O), but there are oxygen atoms on both sides which suppress the ability to bind water molecules. The aromatic polymers considered exhibit damping peaks or shoulders at very low temperatures (30–80 K), which are a special topic of these investigations. They are assumed to occur by intrachain rotation of rings which are in the right chemical position to establish potential barriers. Polyamides are known for their high water absorption capability.

3.1. Conditioning of specimens

Water absorption depends on temperature, time, thickness of specimen, and the amorphous content in a polymer. The latter is not well known for semi-crystalline polymers (PA 12, PA 6, PEEK) used for this investigation. Their maximum water content thus is not a well defined quantity. It is intended to study the property changes only qualitatively when more and more water is absorbed. For this purpose it is sufficient to end at a nearly saturated state.

Table 1
Conditioning parameters

| Material | Morphology or degree of crystallinity | Initial ^a max. water content [wt.%] | Water content after the experiment [wt.%] |
|-----------------------------|---------------------------------------|--|---|
| Polyetherimide (PEI) | amorphous | 1.1 | 0.8 |
| Polyetheretherketone (PEEK) | semi-crystalline | 0.4 | — |
| Polyethersulphone (PES) | amorphous | 1.7 | 1.1 |
| Polycarbonate (PC) | amorphous | 0.3 | — |
| Polyamide (PA 12) | semi-crystalline | 0.8 | 0.7 |
| Polyamide (PA 6) | semi-crystalline | 10.5 | 9.5 |

^a The initial max. water content is nearly that of the saturated state and published by the producers.

The maximum thickness of specimens was 3 mm; most specimens had a thickness of 1 mm. Immersion in water for more than 6 days at ambient temperatures was sufficient to establish a nearly saturated state. Dry specimens were conditioned under vacuum in an oven for 24 h at 100°C. The relative water content, W , was determined as the percentage increase in weight, m , at different times, t .

$$W = 100 \frac{m_{\text{wet}}(t) - m_{\text{dry}}}{m_{\text{dry}}}$$

The saturated water contents of test specimens are compiled in Table 1. There is a broad range of W . The highest value in this series applies to PA 6 (ca. 10 wt.%), the lowest to PC (0.3 wt.%). It should be mentioned that the different water contents of polymers are not reflected directly in the extent of property changes; even a low water content might induce a large effect.

All measurements were performed on dry and nearly saturated specimens. Tests in the intermediate state are added for some polymers. After conditioning, the samples were immediately installed in the measuring devices. The water content unavoidably changes over the time of measurement. A change by -0.3 wt.% was detected after cryogenic measurements for polymers which contained more than 1 wt.% at the beginning. Some values are listed in Table 1. The spatial distribution in the specimens is probably not homogeneous and will be changed somewhat during the time of the experiments. It is not the goal of this study to find a quantitative correlation of water absorption and property changes. It has been verified by i.r.-spectroscopy that water is incorporated only in the bonded state and not as a free deposit in holes or microcracks [14]. The spectrum of free water is clearly different from that in the bonded state (small amount of free water was detected for PES).

3.2. Apparatus

Damping spectra and shear moduli were measured in a torsion pendulum at approx. 10 Hz. The loss factor, $\tan \delta$, can be determined from the logarithmic decrement, and the shear modulus from the frequency of the free torsional

vibrations. Young's modulus was determined in a tensile-test machine by stress–strain diagrams. For measuring thermal expansion, an inductive dilatometer was applied. For low-temperature measurements down to 4.2 K, the equipment was modified for cryogenic use. More details of the cryogenic measuring devices are given in ref. [15]. The accuracy of these devices was better than 3%.

4. Results

The measurements comprise a very wide temperature range between 4.2 and 320 K. As already mentioned, the influence of water absorption is different, even opposite, at high, low, and very low temperatures. For easier understanding of the complex situation, schematic diagrams of the damping spectra (loss factor, $\tan \delta$) and the shear moduli (G) of dry and wet specimens over the whole temperature range are shown in Fig. 1. They reflect the typical response to water absorption. The figures apply to the aromatic-based polymers which exhibit damping peaks at very low temperatures; this is not the case for polyamides. The general tendencies of property changes by water absorption are these.

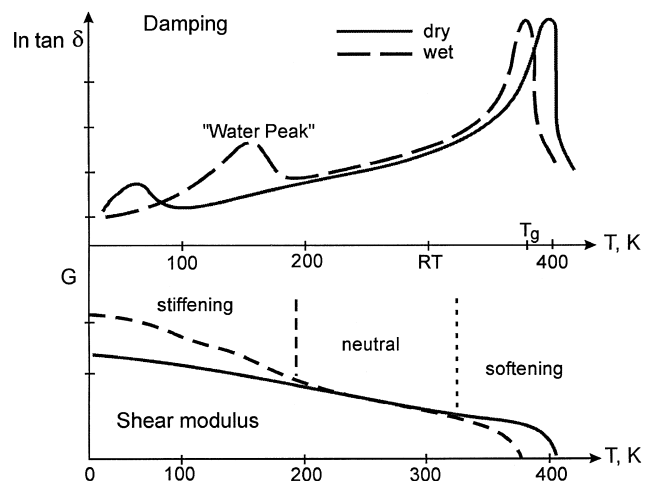


Fig. 1. Schematic presentation of loss factor and shear modulus for dry and wet specimens.

4.1. Damping spectra (loss factor, $\tan \delta$)

- Reduction of the main glass transition temperatures without change in the damping peak height.
- Formation of a ‘water peak’ or enhanced damping behaviour in the range 1600–200 K.
- Suppression of peaks at very low temperatures (for aromatic polymers).

4.2. Moduli

- Reduction of shear (and Young’s) moduli especially in the vicinity of the main glass transition (softening effect).
- Increase in the moduli especially below the temperature of the ‘water peak’ (stiffening effect).
- No water influence on moduli in the temperature range between the ‘water peak’ and the main glass transition temperature (neutral range).

Another result is that the thermal expansion well below the main glass transitions is nearly unaffected by water.

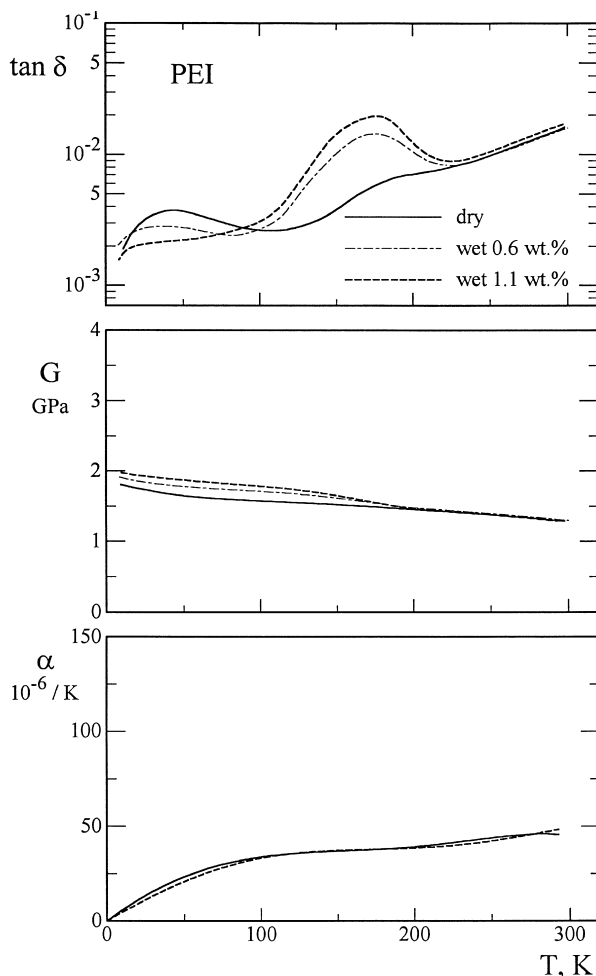


Fig. 2. Loss factor, shear modulus, and thermal expansion of dry and wet PEI.

The experimental results on the loss factor, $\tan \delta$, the shear modulus, G , and the coefficient of thermal expansion, α , are presented in Figs. 2–8. They display properties of polymers in the dry and nearly water-saturated state. An intermediate state is added in some figures.

It can be seen from Fig. 2 that the results on PEI reflect directly the features summarized in the schematic diagrams. Below the ‘water peak’, the shear modulus, G_{wet} , is increased, the damping peak at very low temperatures is suppressed by water absorption, and nearly no influence on the thermal expansion has been observed below 320 K. It should be mentioned that the ‘water peak’ is increased by more water absorption, but the temperature position is almost unchanged. A similar behaviour has been observed for PEEK, but to a lesser degree as less water (0.4 wt.%) is absorbed, and PEEK is semi-crystalline. As seen from Fig. 3, a ‘water peak’ at 170 K is superimposed upon a small existing one at 190 K, while a peak (or shoulder) below 100 K is suppressed in the wet state. In the temperature range 180 to at least 320 K water does not influence the modulus. Thermal expansion again is not influenced in the whole temperature range considered.

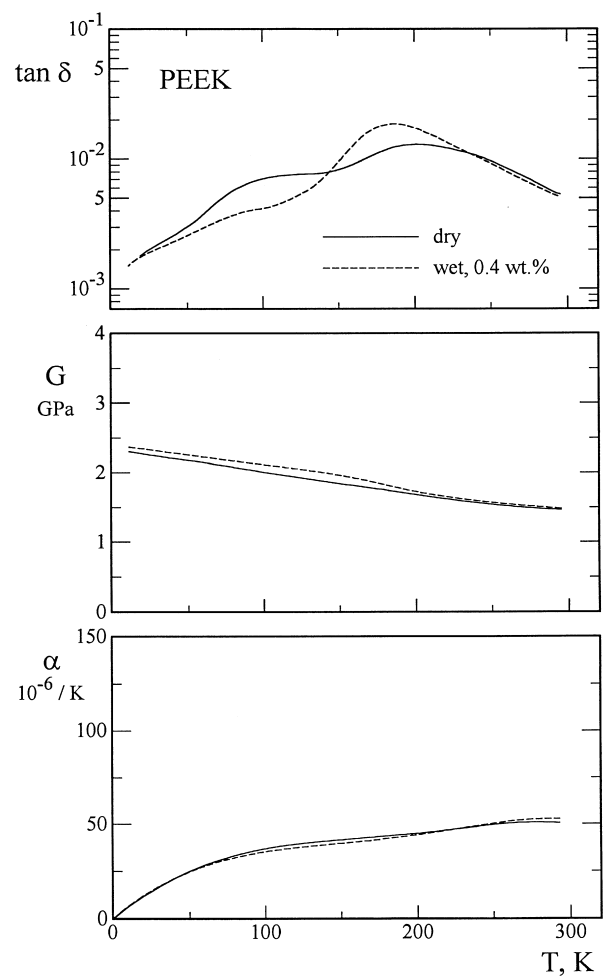


Fig. 3. Loss factor, shear modulus, and thermal expansion of dry and wet PEEK.

Table 2
Young's modulus of dry and wet specimens

| T | PES | | PA 12 | | |
|-------|------------------|---|------------------|---|---|
| | E_{dry} | E_{wet} (1.4 wt.% H ₂ O) | E_{dry} | E_{wet} (0.4 wt.% H ₂ O) | E_{wet} (1.0 wt.% H ₂ O) |
| 77 K | 4580 MPa | 5660 MPa | 6650 MPa | 6700 MPa | 6700 MPa |
| 293 K | 2830 MPa | 2700 MPa | 2050 MPa | 1830 MPa | 1290 MPa |

The influence of water on PES is similar, but again less pronounced on the damping behaviour, although PES is amorphous and much more water (≈ 1.7 wt.%) is incorporated. One reason might be that water is attached to a different polar group (sulphone group). As is seen from Fig. 4, the existing damping peak at 175 K is increased only slightly while the shear modulus is increased remarkably below 170 K. This is also true of the Young's modulus. In Table 2, some results on the Young's modulus, E , are given. A slight reduction of E_{wet} has been observed at RT. However, the shear modulus is almost uninfluenced by water between 180 and at least 320 K. In the series of aromatic

polymers, the results on PC are given in Fig. 5. For the reasons mentioned above there is indeed no influence of water.

The situation is somewhat different for polyamides, which are non-aromatic and have a low main glass transition temperature. No damping peaks exist at very low temperatures and no influence of water has been observed below 140 K at low water concentrations. For PA 12, as seen in Fig. 6, water absorption causes an existing peak at $T \approx 140$ K (probably crankshaft motion) to be reduced slightly at one end and a small 'water peak' at 200 K to be induced. A small increase in modulus due to water has only been observed in the small temperature region of the 'water

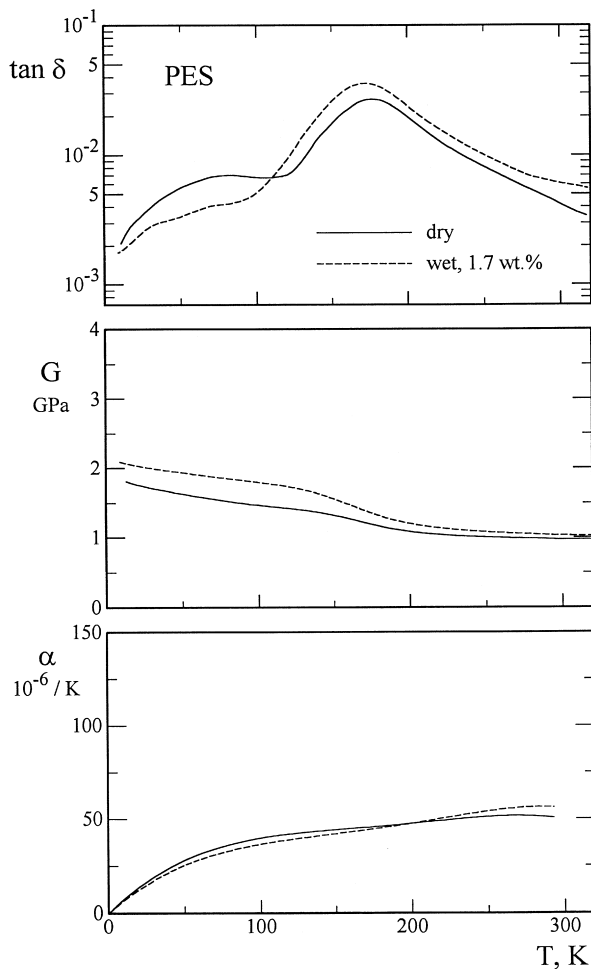


Fig. 4. Loss factor, shear modulus, and thermal expansion of dry and wet PES.

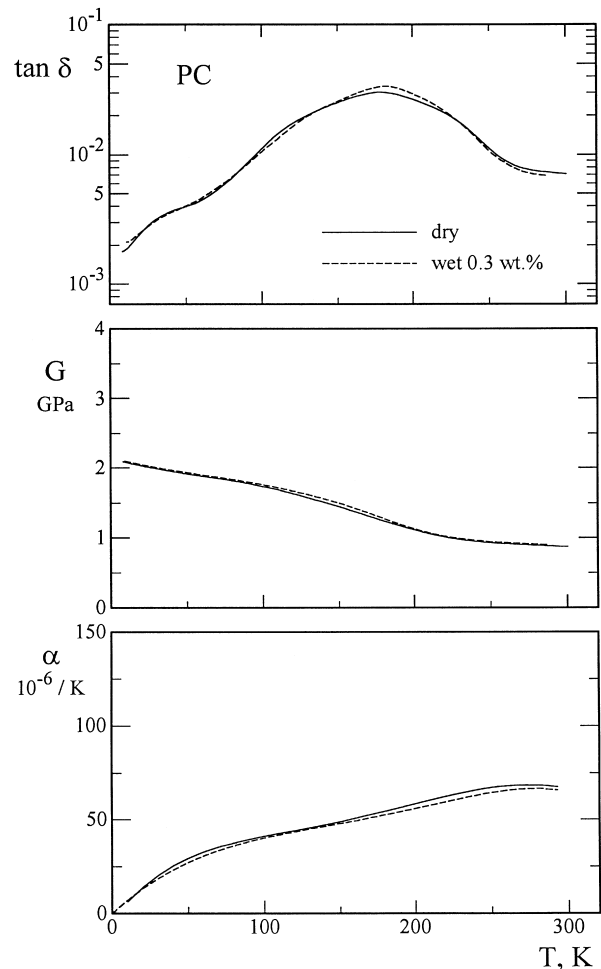


Fig. 5. Loss factor, shear modulus, and thermal expansion of dry and wet PC.

peak' down to the existing peak at 140 K. Below that temperature no modulus increase has been observed. A modulus decrease by water (softening effect), however, starts above 280 K. Probably this is already the influence of the main glass transition whose tail can be seen from the damping spectra above 300 K. In Table 2, the Young's modulus of PA 12 is plotted for the dry, intermediate, and nearly water-saturated state. The coefficient of thermal expansion is changed slightly by water absorption, but surprisingly in the opposite direction than expected. Wet PA 12 shows a lower expansion coefficient.

Even more surprising are the results on PA 6. It absorbs a tremendous amount of water (about 10 wt.%) and properties are influenced greatly by water. As a first step, the effect of a low water content (0.7 wt.%) is considered in Fig. 7. The situation is similar to that found for PA 12. A 'water peak' is superimposed to an existing small one at approx. 210 K. However, PA 6 is capable of more water absorption. At a higher water content (≈ 10 wt.%), the situation has changed drastically, as is seen from Fig. 8. A large damping peak occurs at approx. 250 K for water-saturated specimens, and the 'water peak' and a peak

existing for dry specimens at 140 K are totally suppressed. The shear modulus, G_{wet} , is increased generally below 250 K (even below the suppressed peak), but drastically decreased above 250 K. This feature is surprising. There is a stiffening effect below 250 K directly followed by a softening effect above 250 K. Furthermore, the strong damping peak 'caused' by water at 250 K induces a drastic increase in thermal expansion. This is what is expected from a damping peak, but never has been observed for 'water peaks'. As will be demonstrated by Fig. 9, the peak at 250 K and 10 Hz is not a 'water peak'. It is the main glass transition peak of the amorphous phase of PA 6 which is shifted to such a low temperature by water absorption. The indication is obvious. First, the loss factor is high ($\tan \delta \approx 10^{-1}$) and secondly, the peak is shifted successively to lower temperatures by more water being absorbed. The peak height is relatively constant. At a main glass transition, thermal expansion is increased and the modulus is decreased as expected. From Fig. 9 it can be seen that already at some 4 wt.% of water a new category of property changes starts. An increase in absorbed water produces only minor changes.

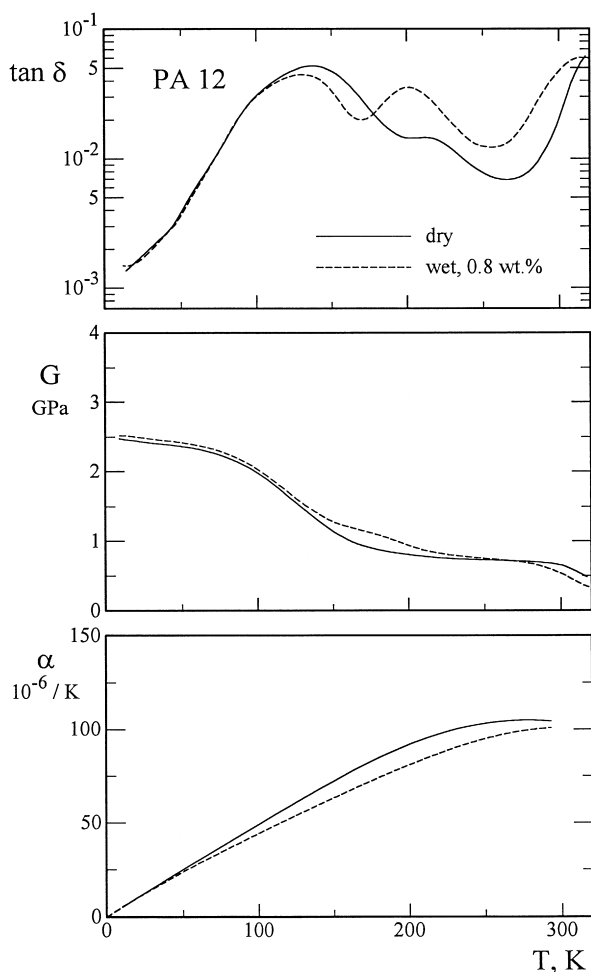


Fig. 6. Loss factor, shear modulus, and thermal expansion of dry and wet PA 12.

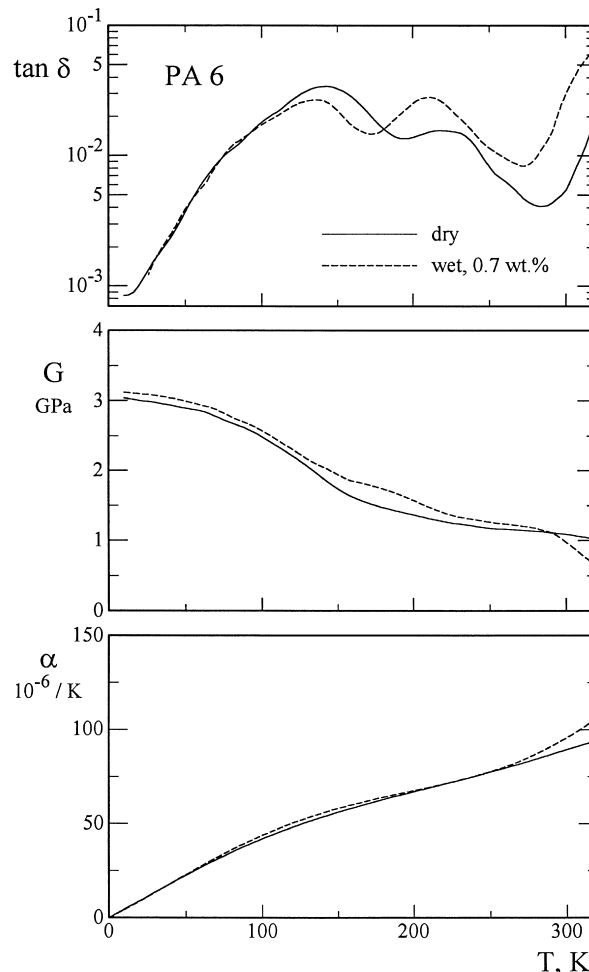


Fig. 7. Loss factor, shear modulus, and thermal expansion of dry and wet PA 6 (0.7 wt.%).

5. Discussion

5.1. Damping

For secondary glass transitions of amorphous polymers the statistical process of place changes in a double potential is assumed to cause damping. Two neighbouring potential minima are separated by a potential barrier whose height controls the temperature position of a damping peak at a given activation frequency. It is not clear whether or not a ‘water peak’ follows the same principle of molecular dynamics. There are, however, several general tendencies of how water absorption influences the damping spectra:

- The main glass transition is shifted to lower temperatures. The peak height remains relatively unchanged.
- A ‘water peak’ is formed whose height is increased by more water being attached; the temperature position, however, is nearly unchanged. The peak height is not proportional to the water content.
- A ‘water peak’ can be superimposed upon an existing peak at a similar temperature position.

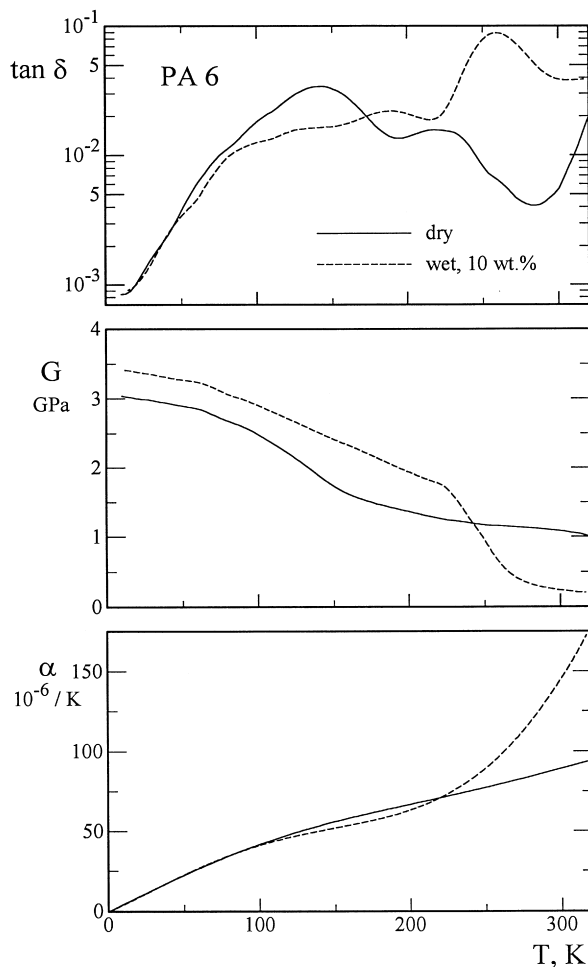


Fig. 8. Loss factor, shear modulus, and thermal expansion of dry and water-saturated PA 6 (10 wt.%).

- Neighbouring peaks at lower temperatures, however, are suppressed or narrowed by water absorption.
- Even a ‘water peak’ is reduced when the main glass transition is shifted to its neighbourhood.

This means that the ‘water peak’ does not suppress damping peaks of the same temperature range. It suppresses only the next peak at lower temperatures (i.e. a peak characterized by a lower activation energy). For the different polymers considered, the ‘suppressed’ peaks originate from mobilities of chemically different groups. It can be concluded therefore that the process of suppression is a universal one.

5.2. Moduli

The moduli of polymers are controlled by:

- binding forces (mainly Van-der-Waals forces),
- unfreezing of molecular mobilities (dispersion steps).

The former is responsible for the elastic behaviour, the latter for viscoelasticity. At very low temperatures, the polymer chains are stiff and the moduli are controlled mainly by the Van-der-Waals forces (force constant). At glass transition, mobilities of segments unfreeze and the chains become flexible, which results in a modulus decrease (dispersion step). The dispersion or modulus step is roughly proportional to the maximum loss factor of the relevant peak. The exact value is given by the Kramer Konig’s relation which correlates the modulus step to the area of the damping peak integrated over the inverse temperature.

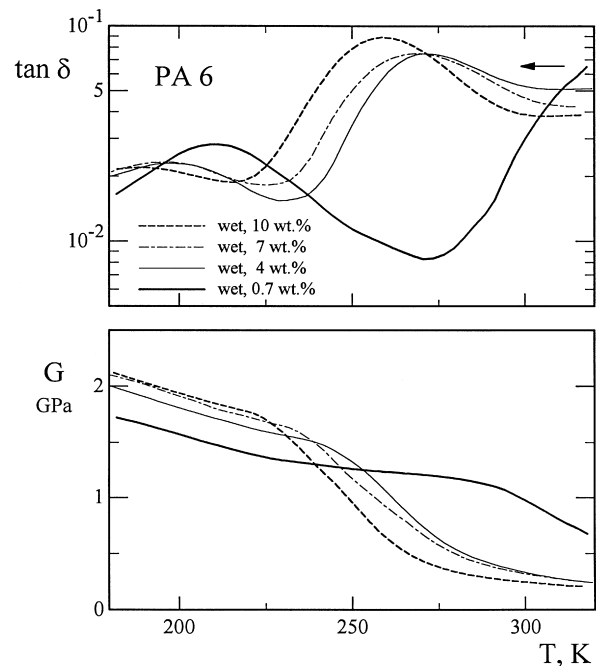


Fig. 9. Shift of main glass transition temperatures by increased water absorption in PA 6 (0.7–10 wt.%)

For a rough estimate a ‘water peak’ can be characterized by $\Delta \tan \delta_w = (\tan \delta_{\text{wet}} - \tan \delta_{\text{dry}})$. Without going into quantitative details, the results are these:

- A modulus step occurs in the temperature range of the ‘water peak’
- No correlation exists between the height of the ‘water peak’ and the magnitude of the modulus step:

For PES, even a small (superimposed) ‘water peak’ causes a relative large modulus step and vice versa for PEI and PEEK.

PA 12 and PA 6 (with 0.7 wt.% H₂O) is in between.

There are general tendencies found for the influence of water on moduli:

- Nearly all polymers considered exhibit a higher modulus below the ‘water peak’ (stiffening effect). This could be explained by water attached as a side group to the polymer chains. Below the temperature of the ‘water peak’ it gets frozen and makes a polymer stiffer.
- In the broad temperature range within the ‘water peak’ and main glass transition there is no influence of water on the modulus (neutral range). This makes the explanation with a ‘water side group’ less powerful. Even in the unfrozen state water should act as a spacer.
- In the vicinity of the main glass transition temperature water strongly reduces the modulus (softening effect). If water acts as a spacer, why is its effect only strong at the main glass transition? Is there a conglomeration of water?
- For PA 12 and PA 6 (with ≈ 0.7 wt.% H₂O) there is a modulus increase only in the small range between the ‘water peak’ ($T \approx 200$ K) and the existing peak ($T \approx 140$ K), which is narrowed by water. Below this peak there is no influence of water at all.
- PA 6 with a high water content (4–10 wt.%) exhibits a modulus increase in the temperature range between absolute zero and the (shifted) main glass transition temperature, where a strong modulus decrease follows. The modulus increase also exists below the existing peak at 140 K, which is suppressed by a high water concentration. It seems that different mechanisms prevail when water is connected to PA 6 at low and high concentrations.

A final remark should make clear that obvious errors (e.g. swelling of the specimens or desorption of water) in the measuring procedure are not the reason for these strange findings. The values of damping and moduli were correlated to the cross-section of specimens in the wet and dry states, respectively. Measurements were started directly after conditioning. Cross-checks were performed at RT before and after the experiments; the values of the loss factor and the modulus were nearly the same. The loss of water during the experiments was relatively small (see Table 1).

5.3. Thermal expansion

Several parameters control thermal expansion of polymers:

- modes of vibration,
- glass transitions.

At very low temperatures interchain vibrations dominate; above 80 K intrachain vibrations are activated. The latter are rather insensitive to temperature, but depend on the mode of vibration: longitudinal vibrations yield a low positive expansion coefficient, while transverse (or rotational) ones produce a small negative one [16].

The vibration-based expansion is similar for most amorphous and semi-crystalline polymers, respectively. Major changes occur as a result of the influence of glass transitions, where more free volume is generated by unfreezing of molecular mobilities. A damping peak is an indicator of the onset of unfreezing. The main increase arises at the temperature of the main glass transitions and, to a lesser degree, by secondary ones [16]. It is surprising, however, that the ‘water peak’ is nearly uncorrelated to thermal expansion. Obviously, the free volume is not changed. In fact, the opposite tendency has been observed. If thermal expansion is at all changed by water, it is not increased but decreased slightly. For example, the thermal expansion coefficient of PA 12 is decreased by approx. 10% in the wet state (Fig. 6). Thus, the specific volume is decreased slightly by water. This is in contradiction to common expectations. A large increase of thermal expansion occurs, however, in the vicinity of the main glass transition when shifted to much lower temperatures by attachment of water as is shown for PA 6 (Fig. 8).

6. Conclusions

Wanted: The process which kills all damping peaks at very low temperatures and, in a secret way, establishes ‘water peaks’ without passing any information to thermal expansion. Protected by main glass transitions shifted to low temperatures by water, the process is even able to kill a ‘water peak’. This has been proven for PA 6. Several results indicate that the process changes mechanical properties, probably by attaching water to its victims by hydrogen bonds. Several traces have been found by i.r.-spectroscopy. It cannot be excluded that water agglomeration is involved. The process appears as a stiffening effect below the ‘water peaks’ and as a softening agent in the range of the main glass transitions. In between, it is not active for whatever reason. Readers are asked to save no water in discovering and imprisoning the process.

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