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از نشریات معتبر

Poly(vinyl alcohol)/poly(acrylic acid) hydrogels: FT-IR spectroscopic characterization of crosslinking reaction and work at transition point

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The crosslinking reaction of pure poly(acrylic acid) and its blend with poly(vinyl alcohol) was studied by FT-IR spectroscopy. It is demonstrated that also in blends the anhydride formation characteristic for pure poly(acrylic acid) is the predominant crosslinking reaction upon heating. But the ester formation between poly(vinyl alcohol) and poly(acrylic acid) is detectable due to the ester C=O vibrations and C—O—C vibrations, respectively. The degree of swelling and the Young's modulus of the crosslinked blend in deionized water depend on the time and temperature of the heat treatment. In dependence of the pH-value of the swelling agent the blends swell or shrink. The working energy at the shrinking or swelling process induced by a change of the pH-value of differently treated blends was measured. The values are in a range of technical interests and comparable with other microactuators.

1. Introduction

Polyelectrolytes change their conformation with the degree of dissociation which is a function of such quantities as pH-value, polarity of the solvent, ionic strength and temperature. Thus, the change of conformation in swollen crosslinked polymers results in a dependence of the degree of swelling on the physical properties of the swelling agent. Hence the chemical energy can be converted reversibly into mechanical energy in such gels. The idea to use polymer gels as a muscle-like actuator originates from the work of Kuhn et al. on polyelectrolyte gels [1, 2]. Developments arising from the original idea can be followed in a more recent review [3].

One of the simplest pH-sensitive hydrogels can be prepared by crosslinking a blend of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). There are several ways for the preparation of a network. It is possible to prepare a three-dimensional network by repetitive freezing and thawing cycles of PVA water solutions [4, 5]. It is demonstrated by ¹³C NMR spectroscopy that the junction points are formed by hydrogen bonds [6]. Applying the same cycles to a water solution of PVA and PAA leads to porous gels where the equilibrium degree of swelling depends on the pH-value of the swelling agent. It is assumed that an entanglement network with a high concentration of PVA and PAA chains in the physical junction points is formed [7]. Treatment of the hydrogel with 1 N HCl results in a chemical crosslinking via esterification. The gels are shape resistant and insoluble in boiling water but they are very soft due to their porous nature and not suitable for an application as actuators.

pH-sensitive networks of PVA and PAA can also be formed by crosslinking polymerization of acrylic acid in the presence of PVA followed by crosslinking of the PVA [8]. These interpenetrating networks (IPN) are pH and temperature sensitive depending on their molecular structure [9].

Simply heating PVA and PAA and placing the system into water leads also to a crosslinked hydrogel. It is assumed that a crosslinking of the completely miscible blend system occurs via esterification [10]. According to Zhang et al. the miscibility of the blend system PVA/PAA is caused by strong hydrogen bonds between the COOH- and OH-groups and that during the annealing procedure a polyester is formed [11]. The mechanical properties and the capability to carry out mechanical work is of fundamental importance for the application of thermally crosslinked PVA/PAA blends.

The aim of this study is to understand quantitatively the chemical reactions occurring during the thermal treatment of PVA/PAA blends. FT-IR spectroscopy is applied as a suitable tool for these studies. The degree of swelling and the mechanical properties are studied as a function of the annealing time and annealing temperature of the PVA/PAA blends. The volume related capability of work (working energy) during the change of the pH-value of the swelling agent of hydrogels with a different degree of crosslinking is measured as a function of the mechanical stress and compared to different microactuators.

2. Experimental

2.1. Materials

Table 1 gives the characteristic data of the polymers used.

PVA and PAA were obtained from Aldrich. The molar masses were determined by light scattering in water (PVA) or in dioxane (PAA) at 40 °C. The light scattering apparatus was from SLS Systemtechnik Baur and the refractive index increment was measured using an Otsuka DRM 1020.

2.2. Preparation of polymer blends and films

The polymers were dissolved separately in distilled water under stirring at 80 °C (PVA 15 wt.-% and PAA 7.5

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Table 1. Characterization of the used polymers.

| | Aldrich Catalogue number | M_w^a [kg/mol] | Purity ^a [%] | M_w [kg/mol] | A_2 [mol cm ³ /g ²] | $\langle s^2 \rangle^{1/2}$ [nm] |
|-----|--------------------------|------------------|-------------------------|----------------|--|----------------------------------|
| PVA | 34,158-4 | 50 | 99 | 101 | 1.1×10^{-3} | 65 |
| PAA | 18,128-5 | 450 | 99 | 850 | 7×10^{-5} | 65 |

^a Given by the manufacturer.

wt.-%). The solutions were then mixed in such a manner that 80 wt.-% were PVA and 20 wt.-% PAA. The solution was stirred for 1 h at 60 °C and the homogeneous solution was transferred into a Petri dish. Films were prepared from this aqueous solution by evaporation of water at room temperature. Slow evaporation of water prevents the formation of bubbles and ripples on the film surface. The dried and transparent films had a thickness between 0.1 and 0.2 mm.

2.3. Thermal treatment and degree of swelling

The dried films were cut into stripes of 35 mm × 8 mm and isothermally annealed in an oven between 125 and 180 °C for periods between 15 and 80 min. Below an annealing temperature of 110 °C the films remain soluble in agreement with literature data [10]. The crosslinked films were extracted by keeping them in distilled water. The mass loss was less than 3 wt.-%, somewhat less than discussed in the literature [10]. From the extracted samples, the degree of swelling as the ratio of the swollen to unswollen masses of the crosslinked polymer in equilibrium with deionized water ($Q_m = m_{\text{swollen}}/m_{\text{dry}}$) was determined.

2.4. Mechanical testing

The Young's modulus of the blends which were annealed at different temperatures and for different times, was determined at room temperature with a Miniature Material Tester (PL Thermal Sci.). The samples were cut into stripes and glued on aluminum plates and placed into the test apparatus (deformation rate: $de/dt = 3$ mm/min, for data evaluation the linear range for $\epsilon < 10\%$ was used). The working energy at the point of transition from the swollen to the unswollen state (related to the volume of the swollen polymer) was measured with the apparatus shown in Fig. 1.

Similar to the apparatus described by Suzuki [12], the sample is placed in a temperature controlled test chamber which is filled with the test liquid. The sample is fixed on one side. The sample can be loaded with a fixed force F . The change of the length of the sample ds which is connected with the change of the degree of swelling, is recorded stepwise with an incremental lengthmeter. The working energy w_v normalized to the reference volume V_{swollen} is calculated by

$$w_v = \frac{1}{V_{\text{swollen}}} \int_{s_0}^{s_n} F \cdot ds \quad (1)$$

Displacement pick-up Tractive force sensor

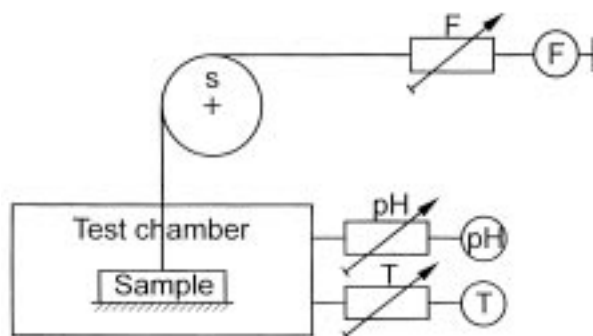


Fig. 1. Schematic drawing of the apparatus for measurements of the working energy.

2.5. Thermal analysis

The glass transition temperatures of PVA/PAA blends were determined by using differential scanning calorimetry (MDSC 2920, TA Instruments). The heating rate was 3 K/min modulated with a temperature gradient of 0.5 K/40 s. The thermal stability of the polymers and their blends was measured by thermogravimetry using a TGA of TA Instruments under nitrogen with a heating rate of 3 K/min.

2.6 FT-IR spectroscopy

The films of the pure polymers and the blends were cast from 2 wt.-% solutions in water. A drop of the solution was placed on a Teflon film and the sample was isothermally annealed in a vacuum oven at 60 °C for 3 days. The dried films were peeled off the Teflon support and placed between two KBr plates. The films were then placed into the FT-IR spectrometer (Bruker IFS 88) equipped with a temperature chamber. An MCT detector was used. The resolution was 4 cm⁻¹ and for the kinetics measurements 50 spectra were averaged.

3. Results and discussion

3.1. FT-IR spectroscopy

Figure 2 shows the FT-IR spectra of pure PAA and pure PVA, respectively, taken at room temperature. The complete assignment of the bands can be found elsewhere [13]. The C=O band at about 1711 cm⁻¹ is important for further discussions. The position of this band indicates that the carboxylic acid groups form dimers [14]. The most characteristic band for PVA is located at wavenumbers larger than 3000 cm⁻¹ and it belongs to the OH group. There is no absorption of PVA in the C=O region of interest. Prior to the observation of the crosslinking behavior of PVA/PAA blends, it is interesting to study the network formation in pure PAA since it has been known that the anhydride formation in PAA is a dominant process during network for-

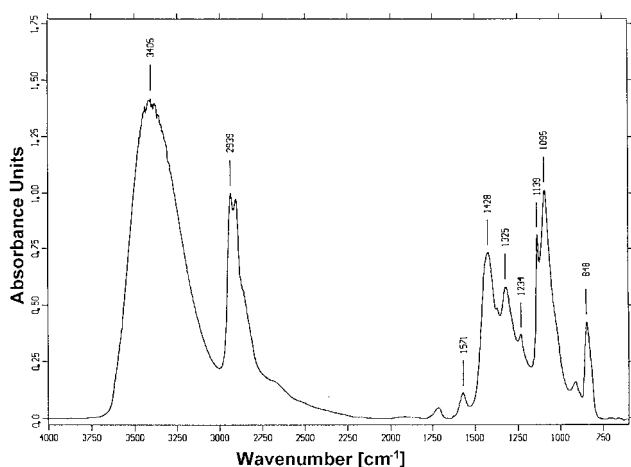
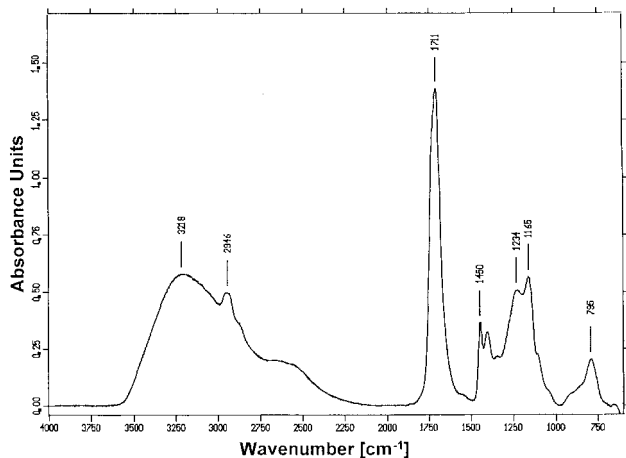


Fig. 2. FT-IR spectra at room temperature (a) PAA, (b) PVA.

mation [15]. Figure 3 shows FT-IR spectra of pure PAA taken in increments of 5 min during isothermal annealing at 170 °C. Figure 3a depicts the time development of the FT-IR spectra during 1 h and Fig. 3b the corresponding difference spectra. It is clearly indicated that the anhydride formation occurs connected with the growth of the respective bands of the C—O—C stretching vibrations at 1032 cm⁻¹ and the C=O stretching vibrations at 1803 and 1759 cm⁻¹. Simultaneously the C=O stretching vibration of the acid at 1713 cm⁻¹ decreases. The vibrations are also temperature sensitive and change slightly as a function of temperature. In the difference spectra the peaks of the bands at 1699 and 1803/1768 cm⁻¹ appear well separated and they can thus be integrated. Just by visual inspection it can be seen that the band at 1803 cm⁻¹ is stronger compared to the band at 1768 cm⁻¹. This is a clear indication that the anhydride formation occurs mainly in the linear intermolecular form and to a minor extent as the cyclic intramolecular anhydride [13]. Furthermore, the C—O—C band of the anhydride is well separated. There are other bands influenced by the anhydride formation and they can be assigned to C—O or O—H vibrations sometimes coupled with C—H vibrations [13].

The temperature dependence of the reaction kinetics is demonstrated in Fig. 4. The reaction kinetics is monitored

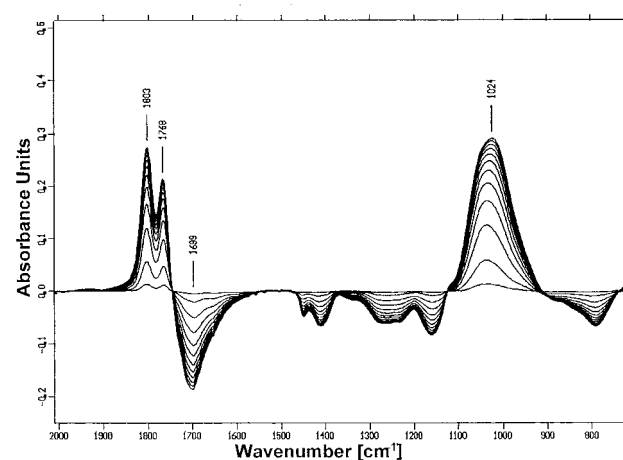
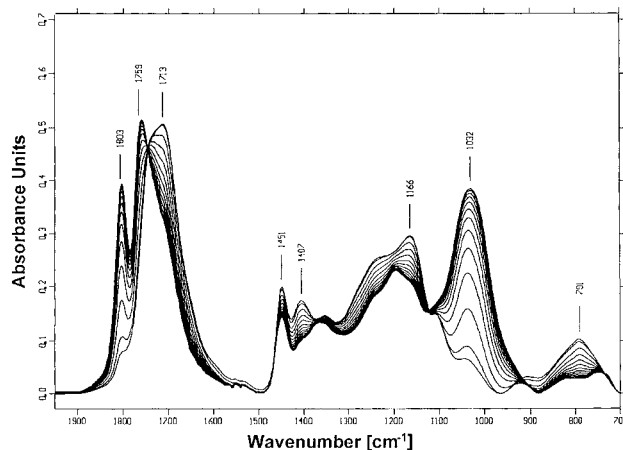


Fig. 3. a) Change of the FT-IR spectra of PAA during the reaction at 170 °C. The spectra are recorded for 60 min in intervals of 5 min. b) The corresponding difference spectra to a).

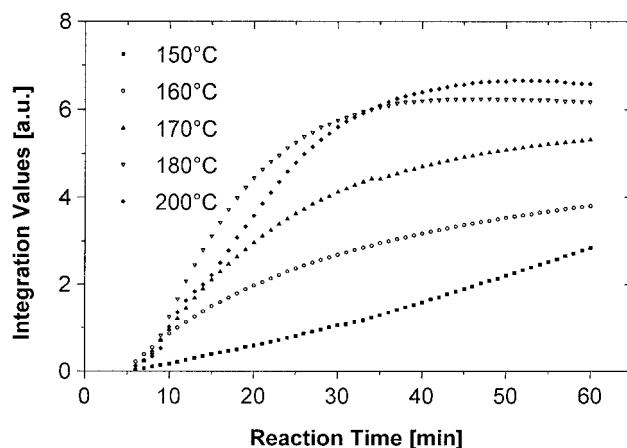


Fig. 4. Temperature dependence of the reaction kinetics measured by the change of the relative integral absorbance values of the anhydride bands at 1803 and 1768 cm⁻¹ as a function of time.

by the change of the relative integration values of the anhydride bands at 1803 and 1768 cm⁻¹ as a function of time. There is a delay time of approximately 5 min until the reaction starts. From the initial slope it can be seen that the reaction proceeds relatively slow at 150 °C and much faster

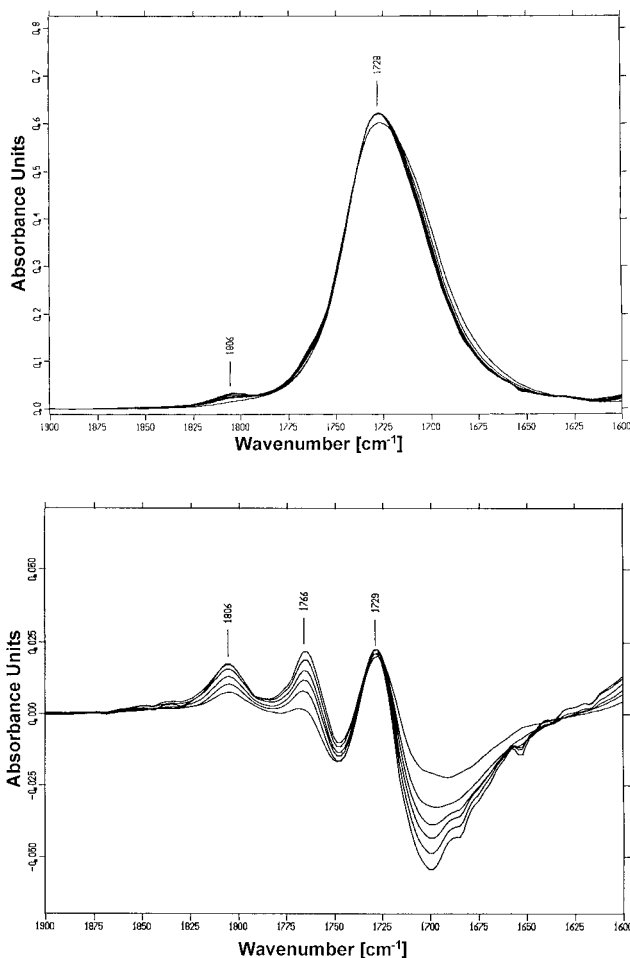


Fig. 5. a) FT-IR spectra of the reaction of PVA/PAA (80/20 wt.-%) at 200 °C taken over 60 min in the time intervals of 10 min. b) The corresponding difference spectra to a).

at 200 °C. At temperatures between 180 and 200 °C a plateau value of the crosslinking reaction is obviously reached after 40 min indicating a possible equilibrium.

It is now interesting to compare the crosslinking reaction in PVA/PAA blends. Fig. 5a shows the change of the FT-IR spectra of PVA/PAA (80/20 wt.-%) blends in the range from 1450 to 1900 cm^{-1} during the annealing at 200 °C. As discussed above for the crosslinking reaction of pure PAA, all bands characteristic for the anhydride formation can be found in the carbonyl region (bands at 1803 cm^{-1} and 1759 cm^{-1}). In contrast to the difference spectra obtained during the annealing of pure PAA, the blends show an additional increase of an absorption at 1729 cm^{-1} (see Fig. 5b). This band can be unambiguously assigned to the ester C=O vibration.

An additional indication for the ester formation in the blend is found in the region of the C—O—C ether vibration. The time dependence of this absorption band can be seen in the difference spectrum of Fig. 6. In the beginning there is an increase of the band in the range of 1031 cm^{-1} . This is already discussed for the anhydride formation. But with increasing reaction time, there appears a shoulder at 1004 cm^{-1} . Again this is an indication for a C—O—C ester

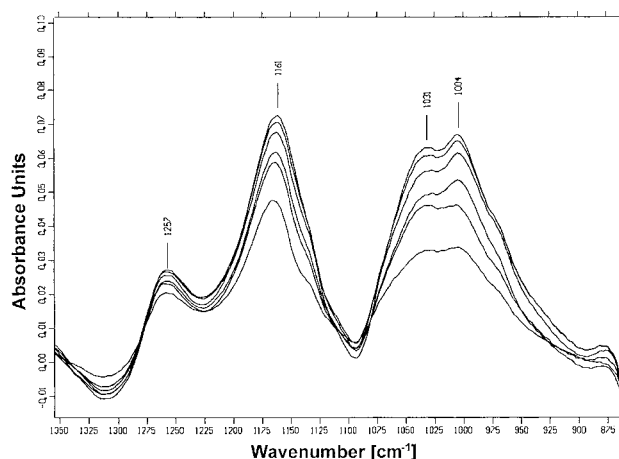


Fig. 6. Evaluation of the C—O—C ester vibration at 200 °C taken in intervals of 10 min (difference spectrum).

vibration. In conclusion it can be said, that in the blends the predominant crosslinking reaction is still the anhydride formation observed also for pure PAA. But additionally an ester formation can be monitored by FT-IR spectroscopy.

3.2. Thermal analysis

Prior to crosslinking, the blend shows a single glass transition temperature T_g in agreement with literature data [11]. The glass transition T_g is located between the T_g of PAA at 106 °C and that of PVA at 85 °C [16]. The relatively low glass transition temperatures of the blend given in Table 2 are the result of small amounts of water in the films. For one film the glass transition temperature defined as the deflection point at the c_p step is measured as a function of the thermal annealing regime. The samples were heated from room temperature to the maximum temperature with 3 K/min then cooled with 20 K/min and the cycle was repeated. It can be seen that the T_g increases with increasing annealing time or temperature. This could be the result of the higher crosslinking density which reduces the mobility of the polymer chains.

In order to exclude thermal degradation during the crosslinking reaction, the thermal stability of the pure polymers and the blends was measured by thermogravimetric measurements. Figure 7 shows the first derivatives of the thermogravimetry traces of PVA, PAA and the 80/20 (wt.-%) blend of PVA and PAA. The thermal degradation of a PVA film starts at 220 °C. The weight loss trace has two distinguished maxima at 260 and 410 °C. Also for

Table 2. Glass transition temperature of the blend in dependence on the heating cycles.

| Cycle | 1 | 2 | 3 | 4 | 5 |
|--------------------------|------|------|------|------|--------------------------|
| Maximum temperature [°C] | 68 | 116 | 153 | 215 | 241 |
| T_g [°C] | 39.4 | 48.3 | 71.8 | 91.9 | no T_g , decomposition |

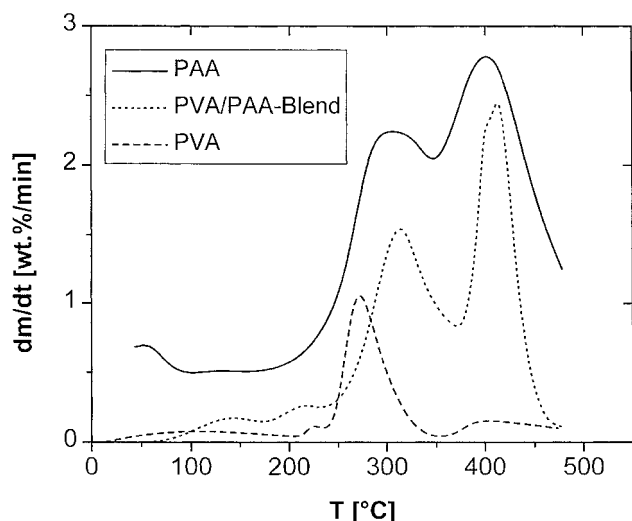


Fig. 7. Thermogravimetric measurements of PAA, PVA and the PVA/PAA blend.

PAA powder a weight loss is found at 200°C. There are two incompletely separated maxima at 300 and 410°C. A two-step mechanism for the thermal degradation of PVA is discussed in the literature [17]. The first process is a dehydration and starts at 200°C. This process yields predominantly macromolecules with a polyene structure. This structure is destroyed at elevated temperatures and carbon as well as hydrocarbons are formed. For PAA two- and three-step mechanisms for thermal degradation are discussed [18], which are connected with an anhydride formation (dehydration at approximately 170°C) and CO₂ evolution due to anhydride decomposition (starting at 230°C). The decomposition temperatures are a function of the tacticity. The blend starts to decompose at 250°C. The maximum of the decomposition temperature is reached at 315°C and it occurs thus at higher temperatures compared to the blend components. Previous results indicated that the decomposition should start at lower temperatures in the blends compared to the pure components [11]. These data are not in agreement with our measurements. Additionally to the mass loss connected with the decomposition of the PVA and PAA two small peaks at 145 and 214°C are detected which cannot be interpreted.

3.3. Mechanical data

For PVA/PAA networks prepared by freeze/thaw cycles a Young's modulus of 0.3 to 0.5 MPa is given in the literature [19]. For PVA gels a Young's modulus of 2 MPa is reported [4]. The increase of the Young's modulus as a function of the crosslinking time and crosslinking temperature can be seen in Fig. 8. The Young's modulus increases with crosslinking temperature to a maximum value of about 5 MPa. The time dependence is rather negligible indicating that at the temperatures under investigation the equilibrium of the crosslinking reaction is reached rapidly. There is obviously a steep increase of the modulus at temperatures higher than 150°C. As discussed for the

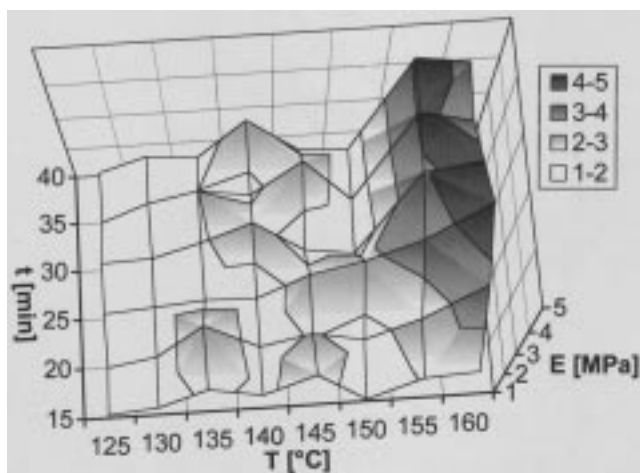


Fig. 8. Young's modulus as a function of the time and temperature of crosslinking.

FT-IR measurements, the anhydride formation in the range of 150°C is rather slow and the complete reaction needs more time than 25 min. But after 25 min the modulus does not further increase. Thus it can be concluded that mainly in the early stage of the reaction intermolecular anhydride formation occurs connected with crosslinking. The later stage might be connected with the formation of cyclic anhydrides by intramolecular reactions.

3.4. The swelling behavior

The mass degree of swelling Q_m as a function of crosslinking conditions is shown in Fig. 9 and supports the data discussed above. A higher degree of crosslinking results in a smaller amount of water uptake. This leads to the smaller mass degree of swelling with increasing crosslinking time and crosslinking temperature. Thus the improvement of the mechanical strength with crosslinking time and crosslinking temperature of the hydrogels is the result of the higher crosslinking density.

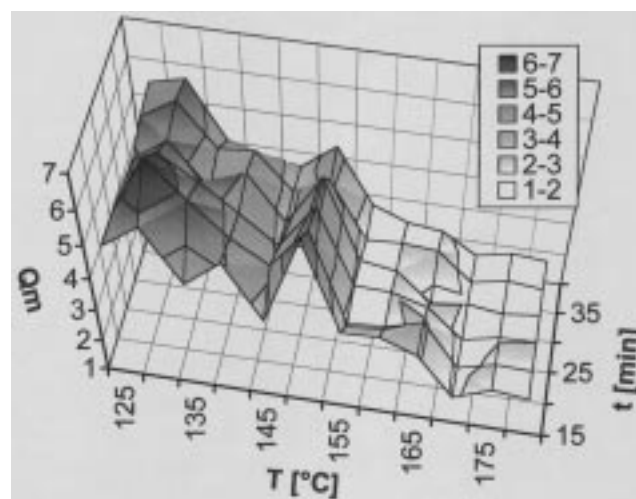


Fig. 9. Mass degree of swelling (Q_m) as a function of the time and temperature of crosslinking for pH = 11.

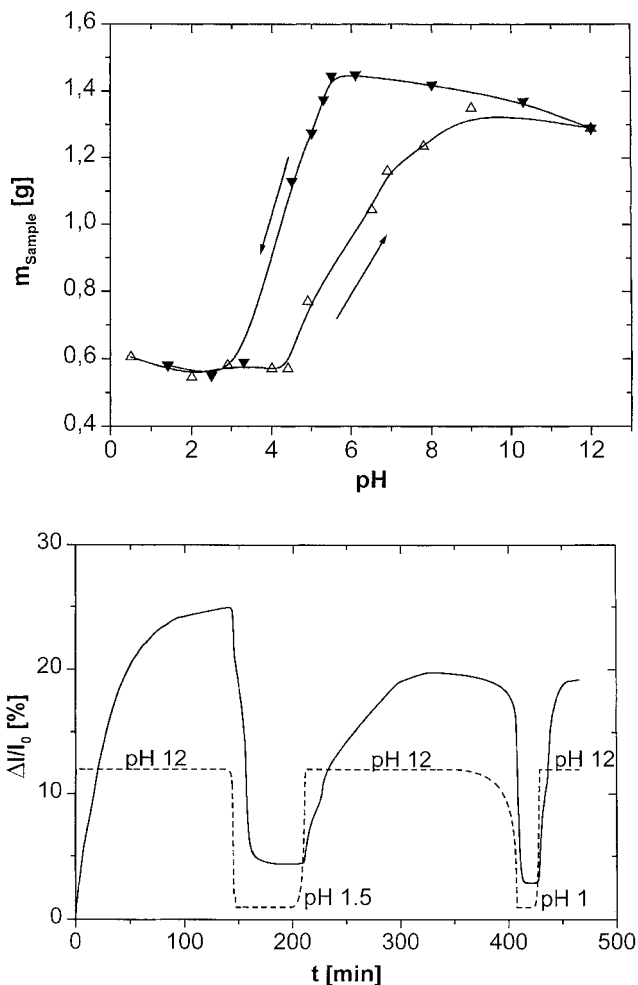
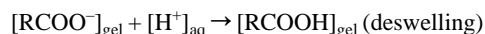


Fig. 10. pH dependent swelling of the hydrogel PVA/PAA. a) Change of mass as a function of pH-value. The open symbols represent the trace from acidic to basic medium and the full symbols represent the opposite trace. b) Time dependence of the relative change of length (full line) as a function of pH-value (dashed line).

In agreement with the data on the Young's modulus, the mass degree of swelling decreases strongly at temperatures higher than 150 °C. Thus it is possible to prepare within one sample areas with different crosslinking densities and different mass degrees of swelling. Again the annealing time has only a small influence on the degree of crosslinking. The mass degree of swelling at pH = 2 is only weakly dependent on the crosslinking conditions (1.5 to 2.5). Q_m at pH = 11 decreases with increasing annealing temperature and shows qualitatively the behavior demonstrated in Fig. 9. The difference of the degrees of swelling defined by [Q_m (pH = 11) - Q_m (pH = 2)] decreases with increasing crosslinking temperature.

The degree of swelling of the crosslinked blends depends on the properties of the swelling agent as can be seen in Fig. 10a. At a pH-value smaller than the pK_a -value of acrylic acid (4.7), the acid is in its nonionic protonated form. When the gel is placed into a water/KOH solution, the carboxylic groups are ionized. The electrostatic repulsion between the anionic groups is the driving force for the swelling process.

When the gel is placed into an acidic environment, it will collapse because of the protonation of the ionic groups. The reason for the changes of the degree of swelling is the change in the ionic charge within the gel schematically shown below.



Furthermore, the swelling/deswelling process has a hysteresis.

Figure 10b shows the time dependence of the degree of swelling of the gel when changing the pH-value. The swelling process (from pH = 1.5 to pH = 12) takes place much slower compared to the deswelling process (from pH = 12 to pH = 1.5). Both processes, i. e. from the beginning of swelling/deswelling until the equilibrium degree of swelling is reached, differ by a factor of 10 in their rate, e. g. for a gel that is annealed for 15 min at 130 °C, the time of swelling is about 150 min and the time of deswelling (shrinkage) is about 15 min (depending on the sample thickness).

According to [20] it is necessary that during the shrinkage protons diffuse into the gel and neutralize the negatively charged carboxylate. A neutral layer of the polymer that shrinks is formed around the inner part of the polymer which is still ionized and swollen. During the further deswelling process the protons must then diffuse across the neutral polymer layer. This process is characterized by a $[Dt/R^2]^{1/2}$ -dependence, where R is the initial layer thickness, t is the diffusion time and D is the diffusion coefficient. During the swelling process it is necessary that the hydroxide ions are transported into the neutral gel. A Donnan-potential is formed in the swollen gel that opposes the transport process. The Donnan-potential is a function of the base concentration (pH-value) [21]. Thus the kinetics of the ion exchange dominates the kinetics of the volume change even though the ion exchange reactions are usually fast. The formation of the neutral layer can be prevented by stirring in such a manner that the swelling kinetics is influenced. We found, that the time dependence of the deswelling process (from pH = 12 to pH = 1.5) is identical with that of the swelling process of a dry sample in deionized water. Using the time dependence of the degree of swelling for a film with a thickness of 0.28 mm in the unswollen state (crosslinked at 130 °C for 25 min) yields a diffusion coefficient of $3 \cdot 10^{-7} \text{ cm}^2/\text{s}$ according to the mathematical procedure given by [22]. Under large stresses the swelling process takes a longer time.

3.5. Crosslinking density

Using the equilibrium degrees of swelling it is possible to calculate M_c values according to the Flory-Rehner-equation [23]

$$M_c = - \frac{\rho_B V_A (A \eta \phi_B^{1/3} - B \phi_B)}{\ln(1 - \phi_B) + \phi_B + \chi \phi_B^2} \quad (2)$$

The memory-term is $\eta = 1$ and for affine deformation $A = 1$, $B = 0.5$. V_A is the molar volume of the swelling agent and ϕ_B is the volume fraction of the polymer.

With known values of the density of the unswollen polymer blend, $\rho_B = 1.288 \text{ g/cm}^3$, and the mass degree of swelling, it is possible to calculate the volume fraction of the polymer ϕ_B in the swelling equilibrium. The main problem when using the Flory-Rehner-equation for the estimation of M_c is the proper value of the Flory-Huggins interaction parameter χ . According to [8] it is possible to calculate the χ -parameter of PVA/PAA networks in deionized water from the interaction parameters of the pure components with water; $\chi_{\text{PAA}} = 0.50$ and $\chi_{\text{PVA}} = 0.494$. The weighted interaction parameter with respect to the blend composition is then $\chi = 0.498$. Furthermore, it is necessary to account for the interaction between the polymer by introducing the polymer-polymer interaction parameter $\chi_{\text{PVA/PAA}}$ [10]. This parameter can be calculated from the solubility parameters $\delta_{\text{PVA}} = 25.8 \text{ (J/cm}^3)^{1/2}$ [24] and $\delta_{\text{PAA}} = 23.68 \text{ (J/cm}^3)^{1/2}$ [10]. The overall χ parameter is then corrected according to

$$\chi = \phi_{\text{PVA}}\chi_{\text{PVA}} + \phi_{\text{PAA}}\chi_{\text{PAA}} - \phi_{\text{PVA}}\phi_{\text{PAA}}\chi_{\text{PVA,PAA}} \quad (3)$$

where ϕ_{PVA} is the volume fraction of PVA and ϕ_{PAA} is the volume fraction of PAA, respectively, in the blend. The last term in Eq. (3) yields a value of 0.07 and its influence on M_c is thus negligible. All estimations yield M_c values in the range of 6000 g/mol ($Q_m = 6$) which is by far too small. Thus, other methods for the estimation of M_c must be applied.

To this end uniaxial compression measurements were carried out on samples swollen in deionized water. A plot of the stress σ versus $|\lambda - \lambda^{-2}|$ was linear at small deformation ratios λ ($\lambda < 0.9$). Assuming validity of the RET-equation

$$\sigma = A\eta \frac{\rho_B}{M_c} RT\phi_B^{-1/3}|\lambda - \lambda^{-2}| \quad (4)$$

yields an M_c value of approximately 70000 g/mol (crosslinking conditions: 130°C, 25 min). The parameters were $A = 1$ (affine deformation) and $\eta = 1$ (memory-term).

3.6. Working energy

The working energy was measured for crosslinked PVA/PAA networks with different crosslinking densities as a function of stress and stimulation by changing pH-values (change from pH = 11.5 to pH = 7 and from pH = 7 to pH = 2). According to [2] the maximum restoring force of the deformed chain is only a function of the segment length of the polymer chain and thus independent of the crosslinking density. This hypothesis cannot be supported by our data. We found two important quantities that influence the working energy. Firstly, there is a dependence on the parameters of the synthesis and thus on the crosslinking density. At the maxima of the degree of swelling at $T = 130^\circ\text{C}$ and at $T = 150^\circ\text{C}$ shown in Fig. 9 also the working energy

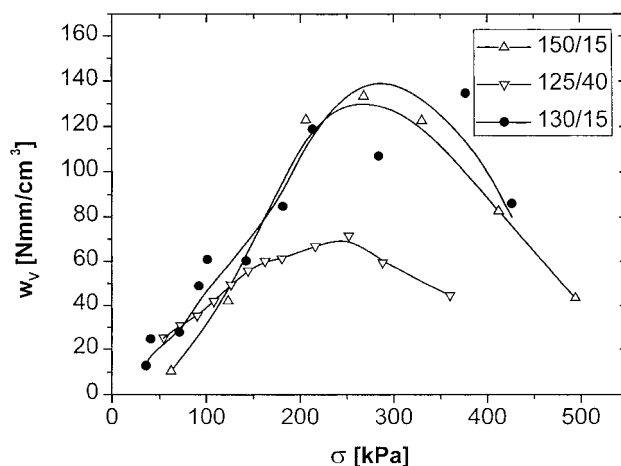


Fig. 11. Working energy as a function of applied stress for different crosslinking parameters (temperature/time).

shows maxima. Furthermore, the working energy is a function of the acting stress (see Fig. 11). This is reasonable, since the working energy at too small stresses is restricted by the maximum possible change of the length of the gel. On the other hand if the stress is too strong the working energy is limited by the maximum force of the hydrogel which can be reached. The position of the maxima changes with increasing crosslinking density to higher stresses. At too high stresses there is a decrease of the working energy. This phenomenon was also observed for temperature sensitive (poly-N-isopropylacrylamide) gels [25].

The application relevance for hydrogel actuator effects should be reached when a w_v -value of at least 100 Nmm/cm³ is reached. The value of 13.2 Nmm/cm³ obtained for freeze-thawing gels based on the PVA/PAA system and poly(allyl amine)hydrochloride by stimulating the work via changing acetone/water ratio is too small in order to be used as effective actuators [12]. Our maximum value of $w_v = 135 \text{ N mm/cm}^3$ seems to be a promising way to obtain effective actuators.

4. Conclusion

FT-IR spectroscopy is able to detect the crosslinking reaction in PAA and in PVA/PAA blends quantitatively. It is demonstrated that the crosslinking reaction of pure PAA occurs via anhydride formation. The intermolecular and intramolecular anhydride formation can be observed but can not be distinguished quantitatively. The ester formation during the crosslinking reaction of PVA/PAA blends occurs only to a minor extent. By choosing different crosslinking conditions, it is possible to produce blends with different crosslinking densities and different maximum degrees of swelling. The application potential of the hydrogels for the use as microactuators is shown in Table 3 in comparison to the other systems.

The advantage of hydrogels is their large change in length and also in the volume dimension. Simultaneously, the hydrogels show viscoelastic, sometimes linear visco-

Table 3. Properties of various actuator principles.

| | Working energy [N mm/cm ³] | Applicable normalized length change [%] | Cycle time [ms] |
|---------------------------------|---|--|----------------------|
| Electromagnets | 10 | non descript | 1 |
| Piezo elements | 30 | <2 | 5 |
| Hydrogels (PVA/PAA) | 135 | 70 | 60 × 10 ³ |
| Magnetostrictive actuators | 475 | 0.2 | 5 |
| Shape memory alloy actuators | 5000 | 8 | 500 |

elastic behavior. A certain disadvantage are the long cycle times, which can, due to the diffusion control of the swelling or deswelling process, only be improved by using very thin layers. A frequently discussed application of such hydrogels are miniaturized linear motors which are called artificial muscles or biomimetic actuators due to their analogs in the nature. A criterion for these applications is that the stimulation is frequently done by electric fields which reduces the useful polymers e.g. to conductive materials [26]. Such actuators need fast dynamics which cannot be achieved with the present hydrogels. Better application examples for the present hydrogels are given by actuator-sensor systems for process control with relatively slow dynamics. Thus, it should be possible to vary the flow of liquids or gases e.g. as a function of temperature or pH-value. These actuator-sensor systems would not need any external energy supply.

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