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Mechanical Spectroscopy of PVCN with Increasing Cross-Linking Degree

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ABSTRACT: The effect of cross-linking on the dynamics of amorphous poly(vinyl cinnamate) (PVCN) below and above the glass transition temperature (T_g) was studied by means of mechanical spectroscopy. The polymer is cross-linked by irradiating it with ultraviolet light, and it is controlled by the irradiation time, where the kinetics is observed by means of Fourier transform infrared spectroscopy. The evolving links between molecules hinder molecular mobility and thus influence the mechanical loss in the material, leading to (i) a shift of T_g to higher temperatures, (ii) a substantial decrease of the strength of the corresponding α-relaxation, (iii) an increase of Young's modulus, and (iv) an increased damping of PVCN below the glass transition.

1. Introduction

Cross-Linking and Mechanical Response. Cross-linking of polymers involves the formation of intermolecular connections through chemical bonds that occurs randomly. This process results in a three-dimensional network and a reduction of chain mobility, i.e., an increase of the glass transition temperature, T_g. This effect dominates the overall dynamics, and T_g is increased with decreasing cross-link density, x_{cld}. An empirical relation between the two quantities is given by the following equation:[1]

$$\Delta T_g = T_g - T_{go} = 1.2 T_{go} \frac{x_{cld}}{1 - x_{cld}} \quad (1)$$

where T_{go} is the glass transition temperature for zero cross-link density. The cross-link density, x_{cld}, is defined as the ratio of number of cross-links to number of backbone atoms.

In the glassy region, $T < T_g$, the probability of conformational changes is very low and the mechanical response to small stresses (deformations) is basically anelastic, independent of the cross-linking degree. For $T > T_g$, in the rubbery region, the response is both anelastic and viscous. An un-cross-linked polymer is a viscoelastic liquid in the sense that it does not possess any equilibrium compliance and exhibits viscous flow at sufficiently long times. By cross-linking, the flow regions in the material become less pronounced. The elastic modulus of a solid is related to the energy of a bond between neighboring atoms or molecules multiplied by the density of those bonds.[2] In polymers both van der Waals and covalent bonds are present, and the flexibility of the latter with respect to rotation plays an important role too. Thus increasing the number of covalent bonds by cross-linking and the concomitant decrease of segment flexibility lead to an increase of the elastic modulus. However, cross-linking may also give rise to an increase of the average distance between segments due to geometrical constraints and, therefore, decrease the elastic modulus.

In the present study the effect of cross-linking on the α-relaxation or glass transition respectively has been studied for the first time for PVCN by measuring the damping of a thin polymer film on a silicon substrate. Then the film is supported by the silicon, and therefore, its relaxation can be measured even above T_g when the polymer becomes soft. In addition, different from bulk material the thin PVCN film allows a homogeneous cross-linking by UV irradiation, as shown in the following.

Photo-Cross-Linking of PVCN. Regarding its formula polyvinylcinnamate (PVCN) is a copolymer of vinyl cinnamate and vinyl alcohol.[3] Its glass transition temperature is about 77 °C, and the polymer is stable up to 200 °C. Above this temperature the thermal degradation caused by separation of the cinnamate unit from the main chain and thermally induced cross-linking take place.[3] This polymer is well known for its sensitivity to ultraviolet light (UV).[4,5] It is spatially isotropic,[6] and it undergoes a random cross-linking reaction by photoaddition between a UV excited cinnamoyl group of one polymer chain and that of an unexcited cinnamoyl group on different or the same chain, forming a cyclobutyne ring,[7] as schematically depicted in Figure 1. The carbonyl group of the cinnamate segment will not be excited by the UV light used in this study.[8] The electrons in single bonds are usually held too tightly to be excited by near-UV radiation. Therefore only the C═C double bond will cross-link when PVCN is irradiated by UV light.

2. Experimental Section

Sample Preparation. The polymer PVCN was purchased from Aldrich Chemical Co., Inc. with an average molecular weight of 200 000. It was further characterized in ref 3, yielding a mole fraction of 76% of vinyl cinnamate. A solution of 2% PVCN in tetrahydrofuran (THF) is applied on a Si substrate. The film thickness may be varied by the PVCN concentration and by the deposition technique. Spin-coated films are thinner than those produced by spreading the solution over a substrate by a syringe. Both spectra, the mechanical and the FTIR, are not influenced by the deposition technique. The film is then dried in a vacuum of 2 × 10^{-6} mbar in the dark at 90 °C for at least 3.5 h in order to evaporate the solvent and relax stresses in the absence of moisture or UV light.

Photo-cross-linking is performed using a 200 W mercury-xenon lamp (Hamamatsu, L8333) emitting nonpolarized UV light with an intensity of 3500 mW/cm^2 at 365 nm. The sample is placed at a distance of 18 cm from the source in the air at room temperature. Due to the measured divergence of the beam, the UV intensity at this distance is decreased to 10 mW/cm^2. The degree of cross-linking is controlled by the photoirradiation time. The temperature

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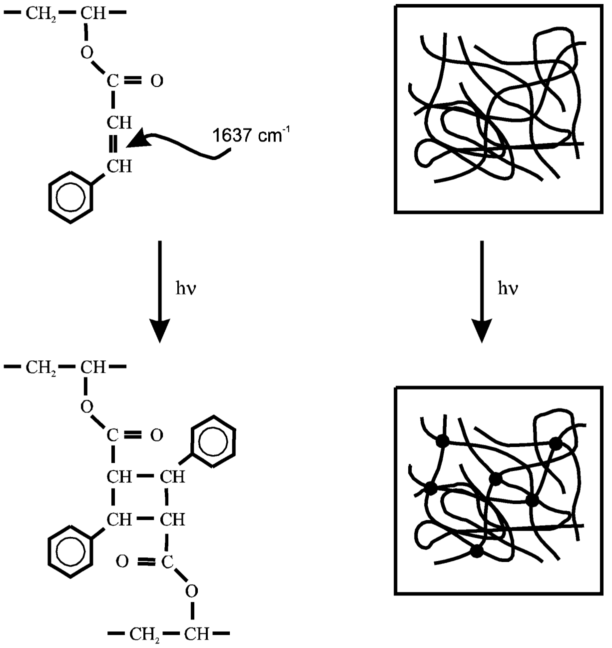

Figure 1. Formula of a segment of PVCN containing the cinnamate group (76 mol % of the polymer) and schematics of cross-linking by photoaddition.

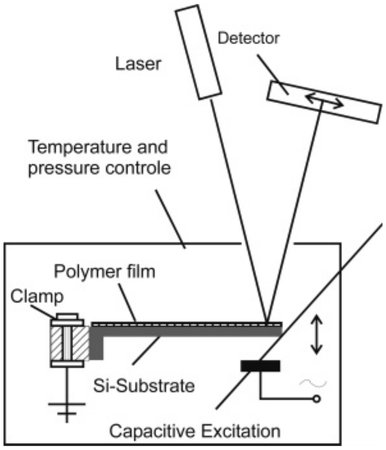

Figure 2. Schematic figure of the vibrating reed apparatus. The vibrating sample being a composite of a thinned Si substrate and the polymer film is clamped with its thick silicon part between copper clamps. Capacitive excitation becomes possible with an adjacent electrode, and the changing amplitude is measured via the deflection of a laser beam exciting a position sensitive detector.

increase in the sample is 2 °C for 2 min exposure and 4 °C for 10 min exposure; hence an effect of the generated heat on cross-linking can be neglected.

The degree of cross-linking is measured by FTIR, using a Bruker Tensor 35 spectrometer with a resolution is 4 cm^{-1}. The transmittance is measured for silicon with and without a PVCN film and evaluated as the intensity ratio of a spectrum with a film and a spectrum of a pure Si substrate.

Mechanical Spectroscopy. Temperature−mechanical spectroscopy of supported PVCN films is performed by means of the vibrating reed technique, and Figure 2 presents a simplified picture of the vibrating reed used. The vibrating reeds were supplied by Prof. Mizubayashi from the University of Tsukuba. They were cut out of single crystalline strips of a Si(100) (p-type-doped with boron) having the dimensions of 3 × 3 × 21 mm^3. The strips were polished to thin reeds with one end left thick for clamping. Therefore only the thinned part of the strip vibrates, reducing the contribution to damping arising from friction between the reed and the clamps dramatically. The top surface of the reed is a mirror surface, and the back surface is smooth, but slightly undulated. The gauge length of the vibrating reed is 15 mm. For the simplest bending mode of vibration the eigenfrequency of the substrate at 300 K is 639.5 Hz for the given thickness of the reed of 105 μm.

The thicker side of the sample is wrapped in Al foil and clamped between two copper plates of the sample holder in order to avoid diffusion of Cu into Si at elevated temperatures (cf. Figure 2). The sample with the silicon substrate being electrically conductive, i.e., being p-doped, could be capacitively excited to vibrations in a simple bending mode. The free decay of the corresponding amplitude is measured by the deflection of a laser beam and a position sensitive detector (PSD). Temperature is obtained from a Pt1000 resistance placed between the copper clamps, and it is changed with a rate of 0.2 K/min. Thus during one measurement of the loss modulus, which lasts 0.4 min, the temperatures changes by only less than 0.1 K. Samples are mounted in the vibrating reed apparatus immediately after spin coating, and the chamber was evacuated afterward. Evaporating the remaining THF solvent and annealing the polymer above T_g, i.e. at 90 °C, are done for more than 3.5 h within the apparatus. The film thickness is obtained both from the shift in the natural frequency of the sample (see following eq 2) and by breaking the sample in liquid nitrogen and looking at the cross-section in a scanning electron microscope (SEM). The latter procedure yielded a film thickness of 5.3 μm.

The frequency shift, Δf, caused by the deposition of a polymer film is given by[7,9]

$$\frac{\Delta f}{f_s} = \left(\frac{3E_f}{2E_s} - \frac{\rho_f}{2\rho_s}\right)\frac{d_f}{d_s} \quad \textit{for } E_f d_f \ll E_s d_s \tag{2}$$

where d_s is the thickness of the substrate, ρ_s its density, and E_s its Young's modulus, d_f is the thickness of the PVCN film, ρ_f its density, and E_f its Young's modulus, and f_s is the frequency of the substrate without the film. In the present study both the thickness of the polymer film as well as Young's modulus is orders of magnitude smaller than the corresponding values of the silicon substrate, and therefore, the condition described by the inequality in eq 2 is fulfilled.

The damping of the reed or the internal friction, respectively is expressed by an inverse quality factor of the composite (the film on the substrate), Q_c^{-1}, which is defined by

$$Q_c^{-1} = \frac{1}{2\pi}\frac{\Delta W_c}{W_c} = \frac{1}{2\pi}\frac{\Delta W_s + \Delta W_f}{W_s + W_f} \tag{3}$$

where the subscripts c, s, and f refer to composite, substrate, and film, respectively, ΔW is the energy dissipation per period of vibration, and W is the elastic energy stored in the corresponding material. Using equivalent definitions for Q_s^{-1} and Q_f^{-1} leads to

$$Q_c^{-1} = \frac{Q_s^{-1} + Q_f^{-1} W_f/W_s}{1 + W_f/W_s} \tag{4}$$

Expanding the right-hand side into a series of the small quantity W_f/W_s and neglecting quadratic and higher order terms yields

$$Q_c^{-1} = Q_s^{-1} + Q_f^{-1}\frac{W_f}{W_s} - Q_s^{-1}\frac{W_f}{W_s} \approx Q_s^{-1} + Q_f^{-1}\frac{W_f}{W_s} \tag{5}$$

The latter approximation is due to the fact that $Q_s^{-1} \ll Q_f^{-1}$ holds. Thus the increase of damping caused by the polymer film is given by

$$\Delta Q^{-1} = Q_f^{-1}\frac{W_f}{W_s} \tag{6}$$

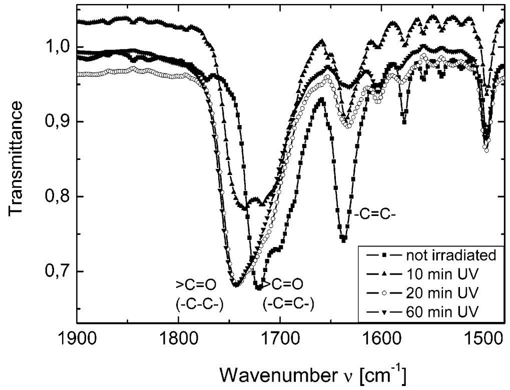

Figure 3. FTIR of PVCN presented for an interval of the wavenumber that is relevant for this study. The intensity of the C═C band decreases with increasing time of UV irradiation due to an increasing cross-link density.

Integrating over the elastic energy of the substrate and the film finally leads to

$$\Delta Q^{-1} = \frac{3E_f d_f}{E_s d_s} Q_f^{-1} \qquad (7)$$

3. Results and Discussion

FTIR. Observing the intensity of the band characteristic of the C═C at 1637 cm^{-1} and that of the C═O between 1700 and 1750 cm^{-1} provides information on the cross-linking degree.[8] As depicted in Figure 3 the intensity of the peak corresponding to the C═C double bonds decreases during the cross-linking reaction. On the other hand the number of carbonyl or phenolic hydroxyl functional groups remains rather constant. However, a peak shift is observed, because before the UV exposure all the carbonyl groups are of the unsaturated ester type (i.e., C═C−CO−C), whereas after exposure to UV radiation those involved in the cross-linking reactions are now saturated esters.[8]

The most dramatic changes in the infrared spectrum occur in the first 10 min. The bands of the C═C double bond and that of the carbonyl group of the unsaturated ester decrease with the exposure time. Concurrently, a new band, attributed to a saturated ester carbonyl stretching band, occurs and its intensity increases. According to ref 10 PVCN will cross-link nearly 100% after 48 h of irradiation. In order to avoid the effect of slight changes of the overall intensity, the integrated intensity of the C═C band is divided by that of the stretching C−H band (not shown in Figure 3) and normalized to 100% for nonirradiated PVCN. The ratio of these integrated intensities is shown in Figure 4 as a function of time. Independent of the exposure intervals, the kinetics seems to be the same and the results are reproducible.

For the reaction to take place an unsaturated cross-linker has to come within a short reaction radius, r_x, of an excited cross-linker. This process is controlled by diffusion. Since the glassy polymer at room temperature has a rather high activation energy for long-range diffusion, there must be a critical concentration of excited cross-links in the film, leading to a high probability of finding the unsaturated couple in the nearest neighborhood by slight local rearrangements of polymer segments. After the reaction has started the number of cross-links decays with the logarithmic time dependence and then reaches a constant nonzero value; that is, the final state still contains about 20% of non-cross-linked C═C bonds. This occurs because the cross-linking itself leads to a spatial confinement of the chains. They can explore only a rather small volume in order to look for linking partners.[11] However, it might also be that after prolonged exposure up to 48 h the amount of non-cross-linked C═C bonds reaches zero, as observed by Matsuguchi et al.[10]

The PVCN film is assumed to be homogeneously cross-linked, because the absorption coefficient[12] for UV light is 13.9 μm^{-1} and the reflectance[14] of the silicon substrate at the wavelength of 365 nm is about 50%. Thus the UV intensity throughout the thickness of the 5 μm thick film is rather constant. In addition, Matsuguchi et al.[10] observed only slight changes in the kinetics of cross-linking for a film thickness varying between 2 and 4 μm.

Peak Position and Shape of the α-Relaxation. The temperature−mechanical spectra of PVCN with different degrees of cross-linking provide information on how the cross-linked structure influences the glass transition and how the mechanical properties change depending on temperature.

Figure 5 depicts temperature−mechanical spectra of the PVCN film with an increase in cross-linking degree. The substrate spectrum, i.e., the logarithm of Q^{-1}, was described by a polynomial of second order that was obtained by least-square fitting to the data. The polynomial was subtracted from the PVCN data, yielding the ΔQ^{-1} spectra presented in Figure 6. This procedure appeared to be useful, because the damping of the silicon substrate was not measured at the same temperatures as the composite PVCN/silicon samples. It can be seen that substantial changes in the spectrum occurred after the sample was exposed for 10 min to the UV irradiation, which corresponds to the cross-linking degree of about 30%. In the glassy state the internal friction or damping, respectively, increases, whereas the relaxation strength during glass transition decreases. Damping is expressed in terms of Q^{-1} as calculated from the logarithmic decrement, λ, of the damped oscillations by $Q^{-1} = \lambda/\pi$. The onset of the α-relaxation, which is sometimes identified with the glass transition temperature, T_g, and the temperature at maximum peak heights shift to higher values. With further irradiation this tendency continues consistently. After 120 min the relaxation almost vanishes.

The relaxation peaks are symmetric and fit nicely to Gaussian functions, allowing a direct comparison. This is proven in Figure 7a, where the spectra were shifted to the zero baseline and normalized to the same heights. In order to compare the width, the peaks were moved parallel to the abscissa and centered on the maximum peak temperature of the nonirradiated sample (see Figure 7b). In the present study the glass transition temperature, T_g, is defined as the intercept of the tangent through the inflection points of a Gaussian curve fitted to the experimental data and the baseline before the glass transition (cf. Figure 7a).

Frequency Changes. The eigenfrequencies of the samples are presented in Figure 8 as a function of temperature and irradiation time. There is a slight increase of the absolute value of the slope of the curve describing the eigenfrequency dependence on temperature of the composite (−0.023 Hz/K) compared to the pure Si reed (−0.020 Hz/K). Because of the precision of the technique, this small difference is significant, and it reveals that the modulus of the cross-linked polymer is more temperature sensitive than that of Si(100).

After the film is applied the mass of the composite sample increases, and as a consequence, the eigenfrequency decreases by about $\Delta f = -5.2$ Hz. By inserting the following values into eq 2—silicon thickness $d_s = 105$ μm, density of Si $\rho_s = 2.33$ g/cm^3, elastic modulus of Si(100) $E_s = 163 \times 10^9$ Pa, polymer density $\rho_f = 0.9$ g/cm^3, elastic modulus of non-cross-linked polymers[13] $E_f = 3 \times 10^9$ Pa—the thickness of the PVCN film is calculated to be $d_f = 5.18$ μm. This is in very good agreement with the result obtained by SEM analysis of 5.3 μm.

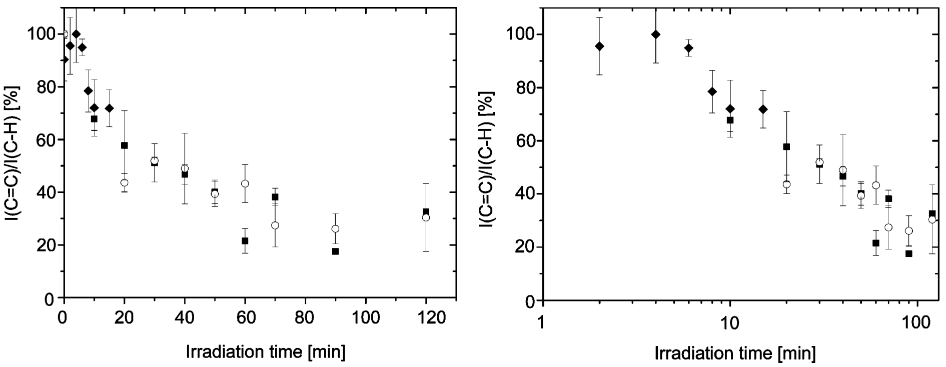

Figure 4. Intensity of the C═C band normalized to that of the C−H band as a function of time for three different samples presented by different symbols. The time dependence is shown with a linear (a) and a logarithmic (b) scale, in order to reveal the attainment of a steady state and an incubation period, respectively. The intensity ratio is assumed to correspond to the fraction of C═C bond not yet cross-linked; that is, subtracting this from unity or 100%, respectively, yields the cross-linking degree.

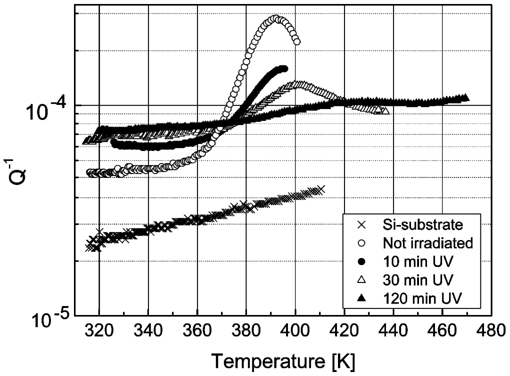

Figure 5. Temperature−mechanical spectra of PVCN with increasing cross-linking degree as obtained by various irradiation times (shown in the inset). Measurements for the shorter irradiation times were not extended above 410 K, in order to avoid cross-linking by thermal excitation.

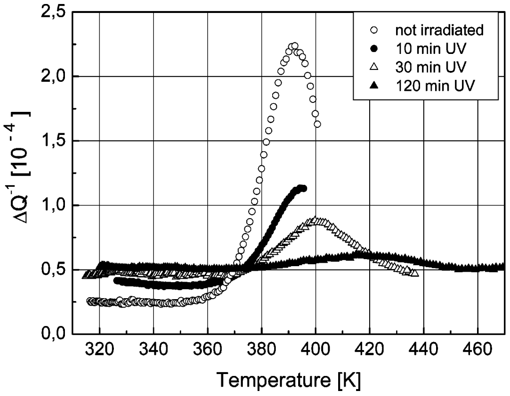

Figure 6. Spectra of Figure 5 after subtraction of the substrate spectrum.

The good agreement between calculated and measured frequency decrease proves that Δf in eq 2 is mainly caused by the mass of the film, i.e., the product $\rho_f d_f$ being the mass per unit area. However, during UV exposure additional minor positive changes, $\Delta\Delta f$, could be measured as shown in Figure 9. Since the mass remains constant, the effect has to be explained by an increase of the elastic modulus, ΔE_f, of the cross-linked structure given by eq 2 as

$$\frac{\Delta\Delta f}{f_s} = \frac{3\Delta E_f d_f}{2E_s d_s} \tag{8}$$

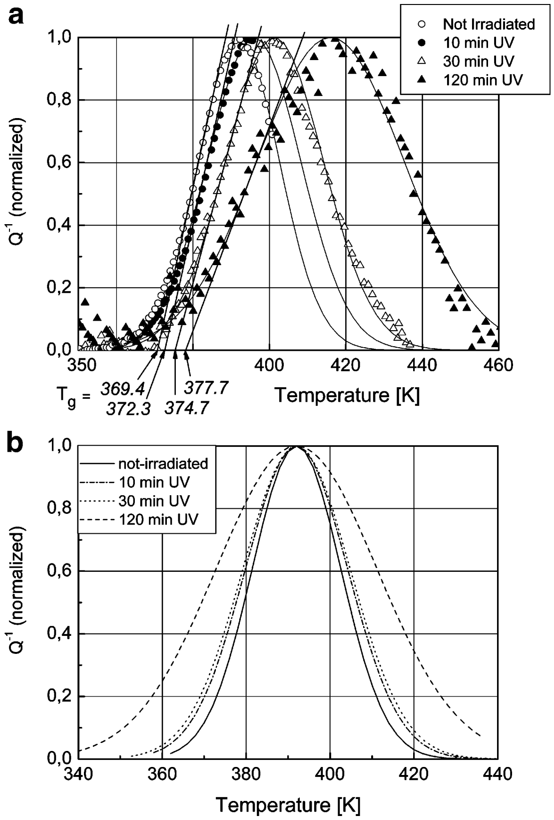

Figure 7. (a) Gaussian fits of the temperature−mechanical spectra in Figure 6 normalized to the same baseline and amplitude. The width and the temperature of the relaxation peak increase with increasing the cross-linking degree. The glass transition temperature (T_g) was determined from the intercept of tangents through the inflection points of the Gaussian fit curves as shown in the figure. (b) Gaussian fits of the temperature−mechanical spectra in Figure 6 normalized to the same amplitude and centered with respect to the maximum peak temperature.

Thus using the measured frequency changes, $\Delta\Delta f$, shown in Figure 9 as an enlargement of a part of Figure 8 for a temperature of 307 K, the changes of Young's modulus, ΔE_f, is calculated and presented in Figure 10. Frequency changes at higher temperatures were not taken into account, because the α-relaxation or glass transition, respectively, reduce the modulus of the polymer film, leading to an additional change of the frequency. This is clearly seen for the nonirradiated sample around 390 K.

The elastic modulus of the cross-linked PVCN changed remarkable by cross-linking becoming almost 50% larger for a cross-linking degree of 69%. This is qualitatively explained by

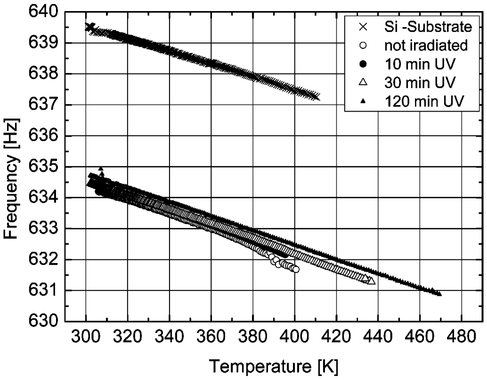

Figure 8. Eigenfrequencies of the substrate and composite sample with different cross-linking degree.

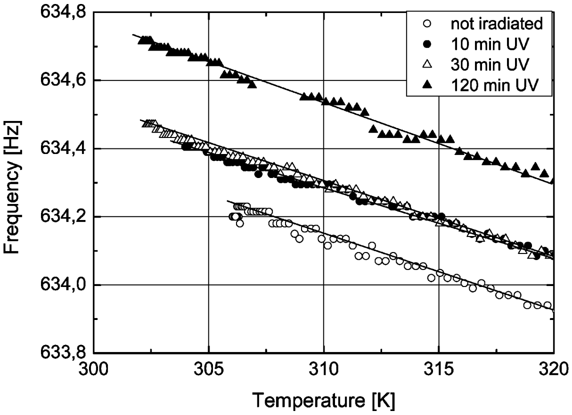

Figure 9. Enlargement of a part of Figure 8 revealing frequency changes, $\Delta\Delta f$, as caused by UV irradiation. Straight lines are drawn through data points, in order to average over statistical fluctuation. The difference between these lines at 307 K is used for calculating the modulus change, ΔE_f, according to eq 8.

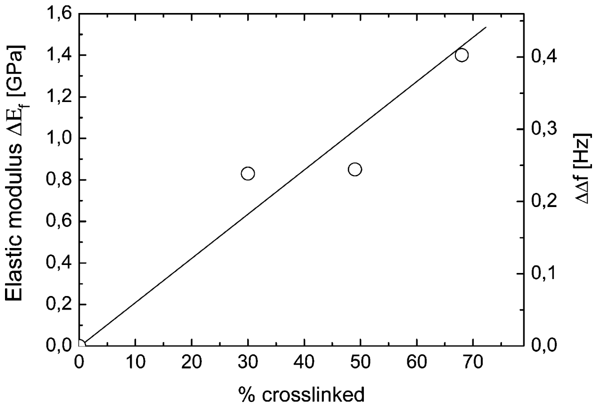

Figure 10. Change of Young's modulus ΔE_f as calculated via eq 3 from the frequency changes (cf. Figure 9) and plotted versus the degree of cross-linking. The straight line is drawn to guide the eye.

the formation of new covalent bonds, leading to a higher overall energy of bonding and thus a higher elastic modulus.[12]

Glass Transition Temperature and Width of the α-Relaxation. Since the α-relaxation of polymers is caused by the movements of chains and segments, the hindrance through the cross-links leads to a lower internal friction during the relaxation process. Following an analysis of the glass transition by de Gennes,[15] only the standard WLF (Williams−Landel−Ferry) jumps, as he calls the jumps of polymer segments, take place, because the sliding process is increasingly inefficient for cross-linked polymers.

A polymer with a backbone that exhibits higher flexibility will have a lower T_g, because the activation energy for conformational changes is lower. Contrary, in order to excite the cross-linked molecular net of high molecular weight, higher energy (or temperature) is required, so the relaxation takes place at higher temperatures and the average relaxation time becomes longer. The new structure entails heterogeneity of the chain environment and the length of the units participating in the relaxation process. This leads to the large distribution of the relaxation times and thus implies a broadening of the relaxation, as shown in Figure 7b.

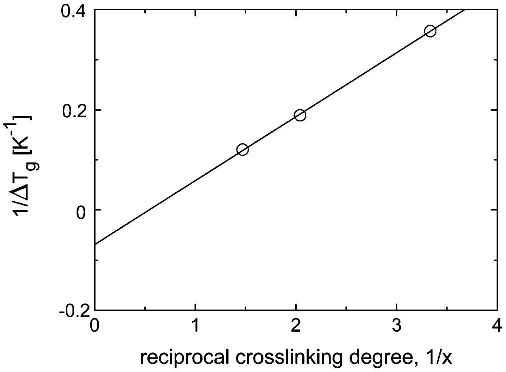

Figure 11. Inverse of the changes of the glass transition temperature, ΔT_g (cf. Figure 7a), plotted versus the inverse degree of cross-linking, x (cf. eq 9).

In order to compare the results of this study with eq 1, it is assumed that the cross-linking degree, x, as determined by IR spectroscopy and shown in Figure 4, is proportional to x_{cld}, i.e., $x = kx_{cld}$. Then eq 1 is rearranged to become

$$\frac{1}{\Delta T_g} = \frac{1}{1.2T_{go}}\left(\frac{k}{x} - 1\right) \tag{9}$$

According to this relation, a plot of the inverse glass temperature changes versus inverse cross-linking degree is presented in Figure 11. In agreement with eq 9 the data points can be described by a straight line with an intercept of -0.069 ± 0.006 and a slope of 0.128 ± 0.003 obtained by a least-square fit. Dividing the two values yields k being very close to unity. Thus the cross-linking degree, x, as determined by IR spectroscopy and shown in Figure 4 is equal to x_{cld}, and the glass transition temperature diverges for $x = 1$. The equality is in agreement with the definition of x_{cld}, because at $x = 1$ there is only one carbon atom in the backbone between two adjacent cross-links. However, the factor in front of the brackets in eq 9 should be $1/(1.2 \times 392\ \text{K}) = 0.0021$, which is orders of magnitude smaller than the value of 0.128 as obtained from the data in Figure 11. Thus cross-linking in PVCN is less effective on the glass transition temperature than predicted by the empirical eq 1, which was set up for different polymers and different ways of producing cross-links.

The discrepancy between eq 1 or eq 9, respectively, and experimental data is overcome by a comparison with more recent theoretical treatments by Couchman and Karas,[16] Venditti and Gillham,[17] and Pascault and Williams.[18] They proposed the following relationship based on the work of DiBenedotti[19] and experimental data for thermosets and polymers cross-linked by radiation:

$$\frac{\Delta T_g}{\Delta T_{g\infty}} = \frac{T_g - T_{go}}{T_{g\infty} - T_{go}} = \frac{\lambda x}{1 - (1 - \lambda)x} \tag{10}$$

where $T_{g\infty}$ is the glass transition temperature for 100% cross-linking ($x = 1$) and λ is an adjustable parameter between 0 and

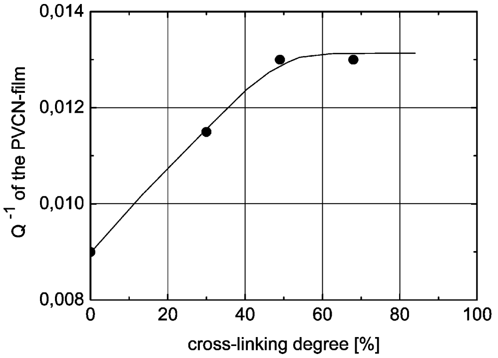

Figure 12. Damping of PVCN below the glass transition temperature between 320 and 350 K as a function of cross-linking degree. The line is drawn to guide the eye.

1 that is related to physical measurable quantities.[18] Rearranging eq 10 yields

$$\frac{1}{\Delta T_g} = \frac{1}{\Delta T_{g\infty}\lambda}\left[\frac{1}{x} - 1 + \lambda\right] \tag{11}$$

Comparing this equation with the slope and the intercept in Figure 11 leads to values of $\Delta T_{g\infty} = 17 \pm 2$ K and $\lambda = 0.46 \pm 0.05$. The latter is in good agreement with values obtained for a variety of different cross-linked polymers.[20]

After the sample was exposed for 120 min to UV light the relaxation peak corresponding to the glass transition almost vanished. As confirmed by the IR spectra (Figure 4), PVCN is not completely cross-linked after 120 min and the remaining relaxation may be attributed to the fraction of the polymer that had not been cross-linked yet.

The measured broadening of the α-peak of PVCN with increasing cross-linking density (cf. Figure 7b) has been observed in other polymers as well.[21−27] The phenomenon is explained by an increase of the widths of activation energies[24] that may arise from a broader distribution of the average chain length between cross-links[21,23] and/or a distribution of the local free volume.[25,27]

Damping in the Glassy State. Contrary to the decrease of the relaxation strength at the glass transition (peak heights), the inverse quality factor increases in the glassy state with increasing cross-linking degree. This can be attributed partly to an increase of Young's modulus, E_f, of the polymer film as expected from eq 7 and as determined from the frequency shifts (cf. Figure 10). However, this effect contributes only partly to the measured increase of ΔQ^{-1}, because at 300 K and at the highest cross-linking degree E_f had increased from 3×10^9 Pa to 4.4×10^9 Pa, i.e., by a factor of 1.47, whereas ΔQ^{-1} had increased by a factor of 2. Thus the observed increase of ΔQ^{-1} in the glassy state is also caused by an increase of Q_f^{-1}, i.e., increased film damping after cross-linking. The corresponding changes were calculated from eqs 7 and 8 and are presented in Figure 12.

Internal friction can be increased by (i) increasing the number of relaxation centers, i.e., the group of segments or side groups that rearrange on the molecular scale under varying external stress, (ii) the relaxation strength (proportional to the difference between the initial and final strain), or (iii) decreasing the activation energy. The activation energy of a cross-linked structure is expected to increase, and therefore, the reason for this behavior is caused by either an increased number of relaxation centers or an increase of the relaxation strength. An increase of the number of relaxation centers is consistent with an increase of the cross-linking density.

4. Summary and Conclusion

Within this work the temperature−mechanical spectrum of a composite system containing a Si substrate and a PVCN film was measured. The film thickness was determined from the frequency shift and by SEM analysis of the cross-section of the composite. The polymer was cross-linked by UV radiation, where the cross-linking degree of the polymer was measured by the FTIR as a decrease in a band attributed to the C═C double bond that saturates during the cross-linking. The amount of cross-linking was easily controlled by controlling the time of exposure to UV light. The cross-links inhibit the molecular mobility, leading to an increase in T_g and a reduction of the relaxation strength. Below T_g the elastic modulus of the cross-linked structure increased by about 50%, leading to a higher damping of the composite. In addition, the mechanical loss in this temperature range shifted to the higher Q^{-1} values probably due to the increase in the number of relaxation centers. After 2 h exposure of the PVCN film to UV light leading to a cross-link density of about 70% the α-relaxation almost vanished.

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References and Notes

(1) (a) Nielsen, L. E. *J. Macromol. Sci.* **1969**, Part C3, 69, (b) van Krevelen, D. W. *Properties of Polymers*; Elsevier, Amsterdam, 1990; p 148.
(2) Jones, R. *Soft Condensed Matter*; Oxford University Press: New York, 2003.
(3) Kim, H.-T.; Park, J.-K. *Polym. Bull.* **1998**, *41*, 325.
(4) Minsk, L. M.; Smith, J.; Deusen, W.; V.; Wright, J. *J. Appl. Polym. Sci.* **1959**, *2*, 302.
(5) Robertson, E. M.; Deusen, W. P. V.; Minsk, L. M. *J. Appl. Polym. Sci.* **1959**, *2*, 308.
(6) Yaroshchuk, O.; Sergan, T.; Kelly, J.; Gerus, I. *Jpn. J. Appl. Phys.* **2002**, *41*, 275.
(7) Kinsler, L. E.; Frey A. R. *Fundamentals of Acoustic*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1962.
(8) Coleman, M. M.; Hu, Y.; Sobkowiak, M.; Painter, P. C. *J. Polym. Sci. B* **1998**, *36*, 1579.
(9) Mizubayashi, H.; Yoshihara, Y.; Okuda, S. *Phys. Status Solidi A* **1992**, *129*, 475.
(10) Matsuguchi, M.; Miura, J.; Sakai, Y. *J. Appl. Polym. Sci.* **2000**, *78*, 1744.
(11) Grest, G.; Kremer, K.; Duering, E. *Europhys. Lett.* **1992**, *19*, 195.
(12) Bryan-Brown, G. P.; Sage, I. C. *Liq. Cryst.* **1996**, *20*, 825.
(13) Van Krevelen, D. *Properties of Polymer*, 3rd ed.; Elsevier Science B.V.: Amsterdam, The Netherlands, 1990.
(14) Haapalinna, A.; Kärhä, P.; Ikonen, E. *Appl. Opt.* **1998**, *37*, 730.
(15) de Gennes, P. *Eur. Phys. J. E* **2000**, *2*, 201.
(16) Couchman, P. R.; Karas, F. E. *Macromolecules* **1978**, *11*, 117.
(17) Venditti, R. A.; Gillham, J. K. *J. Appl. Polym. Sci.* **1997**, *64*, 3.
(18) Pascault, J. P.; Williams, R. J. J. *J. Polym. Sci. B* **1990**, *28*, 85.
(19) DiBenedetto, A. T.; Nielsen, L. E. *J. Macromol. Sci.* **1969**, *3*, 69.
(20) Boey, F. Y. C.; Qiang, W. *J. Appl. Polym. Sci.* **2000**, *78*, 511.
(21) Shimizu, K.; Yano, O.; Wada, Y.; Kawamura, Y. *Polym. J.* **1973**, *5*, 107.
(22) Nielsen, L. E. *Mechanical Properties of Polymers*; Van-Nostrand-Reinhold: New York, 1962.
(23) Hill, D. J. T.; Perera, M. C. S.; Pomery, P. J.; Toh, H. K. *Polymer* **2000**, *41*, 9131.
(24) Glatz-Reichenbach, J. K. W.; Sorriero, L. J.; Fitzgerald, J. J. *Macromolecules* **1994**, *27*, 1338.
(25) Ward, I. M. *Mechanical Properties of Solid Polymers*, 2nd ed.; John Wiley & Sons: New York, 1990; p 171.
(26) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley & Sons: New York, 1980; p 420.
(27) McCrum, N. G.; Read, B. E.; Williams G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: New York, 1967; pp 35−37, 398−405.

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