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Hydrogen Bonding in Polyurethane-Silica Nanocomposites

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Summary: Thin films of polyester-based polyurethane-silica nanocomposites with 34% hard segments and different concentrations of nano SiO_2 filler (0, 0.5, 1.0 and 3 vol.%) have been prepared. The hydrogen bonding and orientational behaviour of hard and soft segments were analysed using infrared linear dichroic measurements. The number of hydrogen bonded NH and C=O groups and orientation function were calculated from polarized FTIR spectra. The presence of nanosilica slightly increased the number of hydrogen bonded carbonyls. The soft segments in nanocomposite films display increased orientation in comparison to the neat polymer film. The addition of 3% nanosilica significantly reduced elongation at break. The results were compared with hydrogen bonding and orientational behaviour of thin film of polyether-based silica nanocomposites.

Keywords: infrared linear dichroism; polyurethane; silica nanocomposites

Introduction

Polymer based nanocomposites are extensively studied because they exhibit significantly improved properties in comparison with neat polymer materials. The improvements include electrical and mechanical properties, thermal stability, radiation resistance resulting from interactions between nanofiller and polymer matrix.[1–3] Polyurethanes (PU) are important polymeric materials with a wide range of applications in modern technology such as coatings, adhesives, foams, thermoplastic elastomers and fibers.[4] Segmented PU elastomers are polymers with alternating hard and soft segments that separate into domains formed from respective hard and soft segments. The structure of segmented PU depends on the relative amount of hard and soft segments.[5] The addition of silica nanoparticles improves thermal, rheological and mechanical properties of PU.[6]

Recently, we have reported the results of our research on hydrogen bonding and orientational behaviour of hard and soft segments in the stretching direction of thin films of polyether-based PU silica nanocomposites (ETPU).[7] The objective of this study is to investigate the hydrogen bonding and orientation of segments during applied mechanical force in polyester-based PU silica nanocomposites and compare the results with those reported for ETPU silica nanocomposites).[7] In both synthesized PU matrix hard segments were based on diphenyl methane-4-4′-diisocyanate (MDI) with 34% hard segments content (HSC). The series of ESPU and ETPU nanocomposite thin films were prepared with addition of the same volume fraction of nanosilica (0, 0.5, 1, and 3 vol %). Infrared linear dichroism was used to analyze the influence of nanofiller on hydrogen bonding between hard and soft segments and to the orientation of hard and soft segments.

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Experimental Part

Preparation of Polyurethane Elastomer

The synthesis of PU elastomer was carried out by a two-step method as follows: Step I: prepolymer was prepared by reacting the diphenyl methane-4-4′-diisocyanate (MDI) from Mobay Chemical (Pittsburgh, PA) and poly (caprolactone glycol) (PCL) of 1250 molecular weight from Union Carbide (Danbury,CT) at NCO/OH equivalent ratio of 2/1.[8] The reaction was carried out under a stream of nitrogen at 80 °C.

Step II: The prepolymer, preheated to 90 °C, was mixed with 1, 4-butanediol (1.4-BD) as chain extender under high-speed stirring for 60 s. The PU elastomer was compression moulded in a Teflon-coated aluminium mould for 30 min at 100 °C in a Carver hydraulic platen press. The PU elastomer was postcured in an oven for 24 h at 105 °C immediately after molding.[8] The HSC of the prepared elastomer was 34%. PU with 30% HSC is soft thermoplastic elastomer.[9] The chemical structure of ESPU and ETPU is shown in Figure 1.

Preparation of Polyurethane Nanocomposite

Aerosil 200, a type of hydophilic pyrogenic nano-silica (nano-SiO_2), with primary particle size of 12 nm and specific surface area 200 m^2/g provided by Degussa was used as filler in the polyurethane composite. Synthesized polyurethane films were dissolved in dimethylformamide without and with the addition of 0.5; 1 and 3 vol.% of nano-SiO_2 and homogenized with magnetic stirrer (500 rpm).

The solution was cast onto the glass plate to a uniform thickness using hand coater (designed to provide a certain film thickness). The samples were dried at the room temperature to the constant weight. The final thickness of prepared films was approximately 30 μm.

Infrared Measurements

The IR dichroic measurements were performed on the films that were cut in strips of dimension (20 × 10) mm^2. The stretching of samples was performed manually by a home-made extensor in 5 mm steps starting from the initial length $L_0 = 20$ mm.

The FTIR absorbance spectra of neat ESPU and ESPU-silica nanocomposite thin films were recorded using a Bomem MB 102 spectrometer. The extensor containing the stretched sample was placed in the spectrometer arid zone. A ZnSe IR polarizer placed in front of the sample was used to produce an incident beam of parallel and perpendicular polarization to the stretching direction. The two kind of spectra, A_p (parallel polarization) and A_n (perpendicular polarization), were collected with a resolution of 4 cm^{-1} by co-adding the results of 10 scans. The spectra were always collected from a sample that was first stretched and then kept at a given length for 20 minutes to allow for relaxation in the stretched state.[10] A reference spectrum was collected before each measurement.

Results and Discussion

FTIR spectra of ETPU and ESPU with 34% HSC based on MDI are presented in Figure 2. The spectra are very similar in position of vibrational bands characteristic of the functional groups. There are

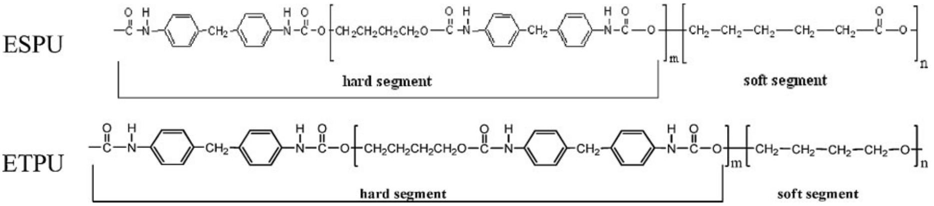

Figure 1.
Chemical structure of ESPU and ETPU.

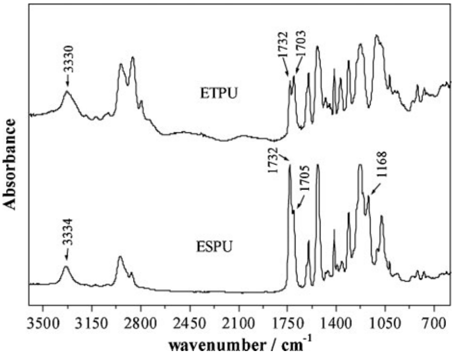

Figure 2.
Absorbance spectra of ESPU and ETPU films stretched to 350%. In highly stretched films all vibrational bands could be resolved.

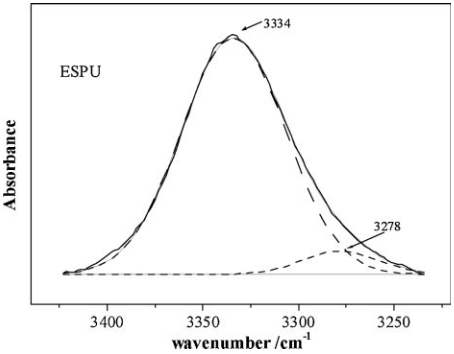

Figure 3.
Absorbance spectrum of neat ESPU film in the NH stretching region.

significant differences concerning the band intensities in the CH (3100-2800 cm^{-1}), C=O (1800–1600 cm^{-1}) and C–O–C (1200–1000 cm^{-1}) stretching region.[7,10] The comparison has shown that band observed at 1168 cm^{-1} in spectrum of ESPU corresponds to the CO stretching vibrations of ester C–O–C groups.

Hydrogen Bonding

The analysis of NH and C=O stretching vibrations gives information about possible interactions between hard and soft segments. In polyester PU hydrogen bonds can be formed between NH groups and proton accepting oxygen in: urethane and ester C=O groups, urethane alkoxy groups and ester C–O–C groups. The part of the spectrum corresponding to the NH stretching region is presented in Figure 3. The broad asymmetric band consists least of two overlapping bands. Therefore, we used curve fitting of IR absorption spectrum to facilitate data interpretation. In curve fitting, the experimental spectrum is modelled as a sum of individual spectral contributions. The curve fitting of the NH stretching region gave two Gaussian band connected to hydrogen bonded NH groups. The intensive band at 3334 cm^{-1} is ascribed to the vibrations of NH group bonded to carbonyl groups suggesting hydrogen bonding between either the hard segments or between hard and soft segments. The band observed at 3278 cm^{-1} is, according to the literature, assigned to the stretching modes of NH groups hydrogen bonded to urethane alkoxy or ester C–O–C groups.[11]

FTIR spectrum in the carbonyl stretching region is presented in Figure 4. The band centred at 1732 cm^{-1} correspond to the stretching vibrations of free C=O groups. The band observed at 1705 cm^{-1} was assigned to the stretching mode of hydrogen bonded carbonyl groups. It was not possible to distinguish hydrogen bonded carbonyl groups originated from hard or soft segments. This means that band at 1705 cm^{-1} contains contributions from hydrogen bonding within hard domains and

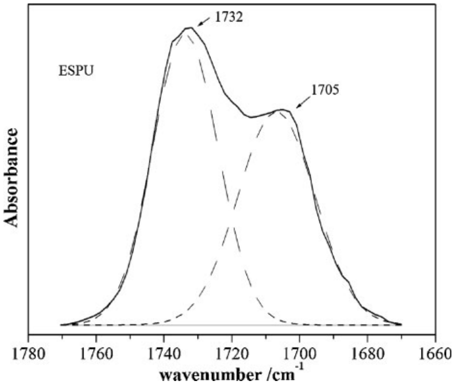

Figure 4.
Absorbance spectrum of ESPU film stretched to 350% in the C=O stretching region.

also from hydrogen bonding in intermediate phase (between hard and soft segments).

The degree of hydrogen bonded NH or C=O groups can be determined from the integrated intensities of the absorbance bands using relations for the degree of phase separation (*DPS*):

$$DPS = \frac{A_{\text{bonded}}}{A_{\text{bonded}} + A_{\text{free}}} = \frac{N_{\text{bonded}}}{N_{\text{bonded}} + N_{\text{free}}} = \frac{N_{\text{bonded}}}{N_{\text{total}}}$$

where A_{bonded} and A_{free} are the intensities of the absorbances of stretching vibrations of hydrogen bonded groups and free groups, respectively. N_{bonded} is the fractions of hydrogen bonded groups and N_{free} is the number of free groups ($N_{\text{total}} = N_{\text{free}} + N_{\text{bonded}}$).

The analysis of spectra has shown that all of the NH groups in ESPU were hydrogen bonded ($N_{\text{free}} = 0$). According our estimation 93% of NH groups was hydrogen bonded to carbonyl groups, while 7% was bonded to alkoxy urethane or C–O–C ester groups. The addition of nanosilica does not significantly affect the number of hydrogen bonded NH groups. No significant changes in number of hydrogen bonded NH groups with straining have been observed. In ETPU nanocomposite films 62% NH groups were hydrogen bonded to urethane carbonyl.[7] This difference is a consequence of different concentration of carbonyl groups.

The analysis of vibrational band observed at 1705 cm^{-1} shows that in neat ESPU and in ESPU +0.5% SiO_2 sample 47% of carbonyl groups were hydrogen bonded. Further addition of nanofiller content increased the number of hydrogen bonded carbonyls to 48% and 50% in ESPU +1.0% SiO_2 and ESPU +3.0% SiO_2, respectively. It is evident that hydroxyl groups on the surface of nanosilica form hydrogen bonds with ESPU carbonyls. According to the published results, silica preferentially interacts with ester carbonyl groups in soft segments of PU.[12] For comparison, in ETPU films 62% C=O groups were hydrogen bonded.[7] The analysis of ETPU nanocomposites had shown that silica interact with C–O–C ether groups.

Orientation Function

The orientation of polymer chains under stress can be described by the second moment orientation function.[13]

$$f \equiv \langle P_2(\cos\theta)\rangle = \frac{1}{2}\left(3\langle\cos^2\theta\rangle - 1\right) = \frac{R_0 + 2}{R_0 - 1}\cdot\frac{R - 1}{R + 2} \qquad (1)$$

where$R_0 = 2 \cdot ctg^2\beta$, β is the angle between the transition moment and the local chain axis (in the gas phase approximation here applied it is assumed that the absorption from the whole polymer is just the linear sum of the absorptions of independent molecular groups) and θ is the angle between stretching direction and the local chain axis of the polymer or any directional vector characteristic of a given chain segment. R is dichroic ratio defined as:

$$R = \frac{A_p}{A_n}$$

where A_p and A_n are integrated absorbances of the investigated band measured with the light polarized parallel and perpendicular to the stretching direction, respectively. They are evaluated by integrating the respective absorption bands after the baseline corrections. The Gaussian functions were fitted to the experimental bands and the half-widths and intensities were allowed to vary during iteration. The maximum error associated with the fit was estimated to be less than 5%.

The R value of all analysed fundamentals observed in absorbance spectra of all unstretched films was nearly 1.0, which suggests that the corresponding transition moment were randomly oriented.

The orientation function graphs were generated using relation (1). The hard segment orientation were analysed with vibrational band observed at 1598 cm^{-1}, which were assigned to the C=C aromatic stretching of MDI.[10] The CO stretching vibrations of C–O–C ester group observed at $1168\,cm^{-1}$ is representative of the orientation of soft segments. The transition dipole moments of C=C aromatic stretching and CO stretching was taken to be parallel to the chain axis.[10]

The orientational behaviour of hard and soft segments is presented in Figures 5. and 6., respectively. The changes in orientational function showed parallel alignment of the transition moments connected with C=C and CO stretchings. The alignment of hard segments in neat ESPU film was grater in comparison to results obtained for ETPU films.[7] The incorporation of nano SiO_2 slightly increased the orientation of hard segments for 0–200% strain. All nanocomposites show almost identical behaviour in that region. At higher ε' the orientation of hard segments in ESPU +1.0% SiO_2 sample was the greatest.

The alignment of soft segments along the stretching direction in pure ESPU showed similar behaviour as the alignment of hard segments. It is interesting to emphasise that alignment of soft segments in pure ETPU sample was almost negligible.[7] The observed orientation of soft segments in ESPU is a consequence of reduced mobility of soft segments due to the presence of ester carbonyl and hydrogen bonding with hard segments. In ESPU nanocomposites the addition of nanosilica increased the alignment of soft segments. It has been also found that the alignment of soft segments in ESPU nanocomposites was enhanced in comparison with alignment of hard segments. For example, at $\varepsilon = 200\%$ the value of orientation function $f = 0.2$ for hard segments, while for soft segments $f = 0.25$. The increased orientation of soft segments was connected with the hydrogen bonding between silanol groups on the nanosilca surface and ester carbonyl group.

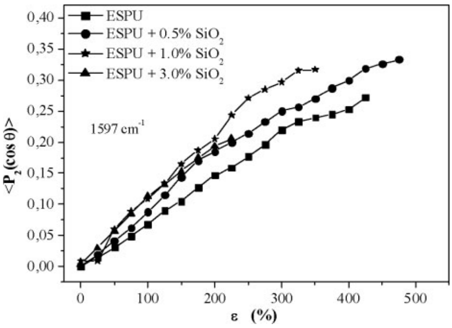

Figure 5.
The variations of the orientation function of hard segments upon stretching.

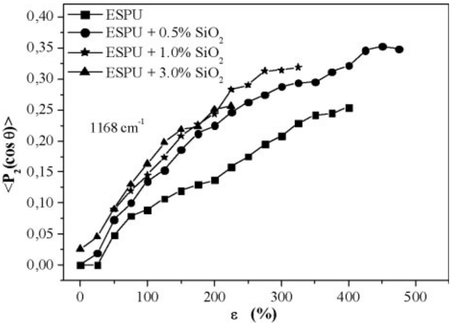

Figure 6.
Soft segments orientation as a function of applied strain.

The incorporation of nano SiO_2 in ETPU matrix does not significantly changed elongation at break ($\varepsilon_b \sim 500\%$).[7] In neat ESPU film elongation of break was $\varepsilon_b \sim 400\%$. The addition of 0.5 and 1% of nanosilica slightly changed ε_b, but in ESPU +3.0% SiO_2 film ε_b was reduced to 200%.

Conclusion

This research compared the hydrogen bonding and orientational behaviour of two series of polyurethane-silica nanocomposites with different soft segments, but with same hard segments as well as the same hard segment content. In both polyester and polyether polyurethane all NH groups from hard segments were hydrogen bonded. In ESPU sample the interaction between NH groups and ester carbonyl results in stiffer network, greater orientation of hard segments in the stretching direction and reduced elongation of break in comparison to ETPU. The behaviour of soft segments was quite different. In ETPU the alignment of soft segments was almost negligible. In ESPU the hydrogen bonding between ester carbonyl and NH group reduced the mobility of soft segments and enhanced the values of orientational function.

The number of hydrogen bonded NH group remains constant after the addition of nano SiO_2 in both polymers, while the number of hydrogen bonded carbonyl groups slightly increased. The results of our spectroscopic investigations had shown that nanosilica primarily interact with soft segments in ESPU as well as in ETPU nanocomposites. The incorporation of 1 and 3 vol% nano SiO_2 significantly reduced elongation of break only in ESPU samples. The maxima of elongation of break in both series of PU nanocomposites were observed in nanocomposites with 0.5 vol% fraction of filler.

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