Mechanical relaxation behavior of polyurethanes reinforced with the in situ-generated sodium silica-polyphosphate nanophase

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Further exploration of hybrid organic/inorganic composites (polyurethane based with inorganic material sodium silica polyphosphate) properties with mechanical relaxometer gives ability to analyze microstructure of such materials in terms of chain reptation tubes filler’s fractal aggregates and stress amplification.

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I. INTRODUCTION

Segmented polyurethanes (SPU) is a generic name for polyblock copolymers which are usually obtained by polyaddition reaction between long-chain di- or polyols, and diisocyanates\(^1\). Due to poor compatibility between polyol and diisocyanate chain fragments (commonly referred to as soft and stiff segments, respectively), the latter usually self-associate and segregate as nano-size domains from a continuous phase of the former. Depending on the relative content and the intrinsic properties of soft and stiff nano-phases (i.e., molar weight, polarity, chain stiffness, etc.), the mechanical performance of SPU can be readily varied over an unusually broad range, from soft rubbers to hard thermoelastoplastics\(^2,3\). The relatively easy synthesis of SPU combined with their unique properties make them attractive for different practical applications; however, their commercial value is severely limited by quite a few deficiencies, the intrinsically high flammability being among the most notorious\(^4\). An apparently straightforward way to minimize these deficiencies by, e.g., compounding of SPU with mineral fillers, proved to be of little feasibility in so far as their other important properties significantly deteriorated. An attractive alternative route for synthesis of SPU with improved performance can be based on sol-gel technology which ensures a homogeneous, in situ generation of inorganic\(^5\) nanoparticles throughout a continuous polymer matrix. Using this route to generate a ceramic-type nanophase (silicates, aluminates, phosphates, etc.), a series of SPU-based nanocomposites (SPUN) with significantly improved weather-, radiation- and flame-resistance was developed. This paper is aimed at the further characterization of the same samples\(^6\) by mechanical relaxation technique.

II. EXPERIMENTAL

A. Materials

As described\(^6\), the organic/inorganic hybrids (segmented polyurethane-based nanocomposites, SPUN) were prepared by reaction between the organic precursor [macrodiisocyanate, MDIC, from propylene oxide glycol oligomer (\(MM = 1052\)) and 2,4-toluene diisocyanate], and the inorganic precursor (sodium silica-polyphosphate, SSP)

Thin films of the SPUN for physical characterization were cast from solutions using methyl cellulose as a surfactant, and dried overnight in a vacuum oven at 150\(^\circ\) C to constant weight.

B. Experimental method

The step-wise loading (stretching)/unloading (contraction) cycles were measured (with the estimated mean errors below 2 %) at room temperature with the mechanical relaxometer on basis of stretching calorimeter described in details\(^7\). Each specimen was stretched at a constant velocity \(q_+ (10\% \text{ of the total specimen length per minute})\) to a predetermined \(\lambda_i\), stored at fixed \(\lambda_i\) to the full completion of mechanical relaxations, and thereafter allowed to contract at the same velocity \(q_-\) to zero force. The typical difference between fixed extensions in two successive steps, \(\Delta \lambda = \lambda_{i+1} - \lambda_i\), varied from several digits in the fourth place to a few digits in the third place. Prior to each measurement, the previous mechanical history was erased by several successive pre-stretchings to the maximum extension \(\lambda_{lim}\), free relaxation to zero stress and subsequent storage in an unloaded state overnight. Then the specimen was stretched to a predetermined fixed extension \(\lambda_f < \lambda_{lim}\), and the time dependence of the stress \(\sigma\) was monitored at \(\lambda_f = \text{const.}\)
III. RESULTS AND DISCUSSION

A. Main models

There’s a lot of possibilities to use relaxation method. Usually for uncrosslinked polyurethanes the stress-relaxation phenomena considered as a set of physical processes, such as: breaking of weak chemical linkages (urethane, allophanate, etc.), disrupting of hydrogen and other secondary bonding, decreasing the number of free entanglements and slippage of trapped entanglements\(^8,9\). Well known that hysteresis phenomena caused by high stress-orientation mechanism in hard domains (HD) of PU, at large strains HD even can be broken, and high mobility of soft segments is a pledge of fast stress relaxation and shape recovery\(^10\). Several popular models are used for explaining of relaxation datas. First was Maxwell’s models. There are different variations, but general is that solid body presented as a set of viscous and elastic modes. Amount of different modes depends on morphological models. Fast and slow modes referred to different morphological units (e.g. microdomains\(^11\), entropic elasticity of back bone segments in the filler-reinforced matrix\(^12,\) etc.)

One of the drawbacks of this models is limited set of relaxation modes and as a result is impossibility to include all relaxational spectra in mathematical description.

Recent times reptational theories based on the tube model of de Gennes, Edwards and Doi. It was shown in\(^13\), that mechanism of relaxation in networks Model of Kolraush-Watts-Williams (KWW) based on a simple termodinamical principles leads to a common fractional power law and consider this problem via introduction of stretched exponent which should reflect a common shape of relaxation spectra\(^14\). Main equation should be written as:

\[
\sigma(t) = \sigma_{inn} + \sigma_0 e^{-(t/\tau_p)^{1-n}}
\]  

where \(n\) - coupling parameter, \(\sigma_{inn}\) - non-relaxing part of overall modulus, \(\sigma_0\) - relaxing part, \(\tau_p\) - effective time. Here \(n\) represents microscopically the strength of coupling between a relaxing species and it’s surroundings and macroscopically – the breadth of relaxation. The higher the coupling strength between primitive species with it’s envirement, the closer \(n\) to unity.

Complications appears when nonlinear effects of stretching gonna be included into discussion. In this case the popular stochastic reptational models are hardly fits experimental datas well. Main distinguishing nonlinear processes during large step-strain experiments assumed as: chain retractions, convective constraint releases (CCR), partial strand extensions (PSE) and non-affine deformations\(^15\).

Modification of KWW model concerning nonlinear effects gives a dependend of coupling factor \(n\) from time as \(n(T_f(t))\), where \(T_f\) is a fictive temperature, which ascribes volume changing during relaxation as

\[
T_f - T = (V - V_\infty)/V_\infty \Delta a(T),
\]

where \(\Delta a(T)\) is the difference between liquid and glassy state thermal expansion coefficients. Main equations should be written as:

\[
\sigma(t) = \sigma_{inn} + \sigma_0 e^{-(t/\tau_p)^{1-n(T_f)}}
\]

\[
\tau_p = [(1 - n(T_f))\omega_0^{n(T_f)}\tau_0^{1/1-n(T_f)}]
\]

IV. EXPERIMENT AND DISCUSSION

A. Parameter \(k = 1 - n\)

Experimental data was calculated accordingly to simple KWW model\(^14\).

As can be seen from summary picture for \(k\) (Fig.1), in the wide range of elongations parameter \(k\) does not depend from elongation, which can suggest linearity of relaxation process. Moreover, the whole set of samples this parameter has approximately the same values of \(k\): in the range of 0.45 – 0.7. According to this one can say, that \(n\) is in the range of 0.3 – 0.55. The most important results is the absence of large divergencies between coupling mechanisms in pure PU and filled samples. However \(k\) for pure PU slightly lower than for filled samples. That could indicate on weak coupling mechanisms in filled samples in the reason of domination of phase separation above chemical bonding. It means that coupling forses mostly specified by interactions of spieces with hard domains even in the case of large filler contents.
FIG. 2. Values of $\frac{\sigma_{\text{inf}}}{\sigma(0)}$ calculated from KWW model. Filler content (mas.): red symb. - 10%, green - 20%, blue - 30%, cyan - 40%, magenta - 50%, yellow - 60%. Hollow symbols - predeformed samples. Squares - MDI, circles - SPh (+MC), triangles - SPh (+PMS), upset triang. - SAPh (+PMS), diamonds - SAPh (+MC)

B. Stress $\sigma$

The value of reduced $\sigma_0$ usually is out of consideration. Main interest is the behavior of $\sigma_{\text{inf}}$. For the most relaxation models this value is out of relaxation spectra dependence and connected with density of crosslinks. Classical theories of rubber elasticity in the case of Maxwell’s model for equilibrium modulus gives\(^\text{16}\):

$$E_{\text{inf}} = \frac{\sigma_{\text{inf}}}{\epsilon} = \frac{3RTd}{M_c}(1 - \frac{2M_c}{M_n})$$

(4)

where $R$ – gas constant, $d$ – density, $T$ – temperature, $M_c$ – average molecular weight of segment between two crosslinking points, $M_n$ – number average molecular weight of chain.

It could be seen from Fig. 2 that whole group of results can be devided onto two filler containant-dependent zones as it shown with straight lines. A visible decrease of equilibrium stress with increasing of filler content in the whole range of elongations indicates on lowering of number of crosslinking points (crosslinking density). Comparing this with moduli dependance it could be pointed that decreasing of filler content leads to lowering of crosslink dencity, but it does not mean lowering of moduli. So inorganic hybryd fillers plays in PU reinforcing role even in the case of in-situ reaction process. Calculation of experimental data in accordance with eq. (4) gives that if $M_n \approx 1000$ than for pure MDI $M_c$ lies in the range from above zero to 450, and for 50% - 60% wt. filled samples $M_c$ lies from 450 to 765.

FIG. 3. Values of $\tau_p$ calculated from KWW model. Filler content (mas.): red symb. – 10%, green – 20%, blue – 30%, cyan – 40%, magenta – 50%, yellow – 60%. Hollow symbols – preddeformed samples. Squares – MDI, circles - SPh (+MC), triangles – SPh (+PMS), upset triang. – SAPh (+PMS), diamonds – SAPh (+MC)

C. Parameter $\tau_p$

As can be seen from Fig. 3, whole set of datas can be divided onto two parts the same way as for $\sigma$ datas. Low concentration datas are extremely high then datas for highly filled samples. As shown in\(^\text{14}\), effective relaxation time and ”true” relaxation time has found to be identical. As far as $\tau_p$ connected with temperature as Vogel-Fulcher-Tamman-Hesse-like equation:

$$\tau_p \propto \exp\left[\frac{B}{T - T_v}\right]$$

(5)

and main equation (3) which determine value of $\tau_p$ is connected both with cooperative response time (frequency) and independent relaxation time of primitive species it could be supposed dependence of relaxation time from values of free volume\(^\text{17}\). Also it can be related to the crosslink dencity\(^\text{8}\). Interesting interpretation also gave Irjak\(^\text{18}\) who related relaxation time with concentration of equilibrium physical junctions and conformation of chains in the network. Analizing Fig. 3 it can be supposed, that there is a linear dependance between crosslink dencity (density of equilibrium junctions) and stretching ratio. In-situ generated filler could decrease density of crosslinks and lowers relaxation times. But it can be seen that predeformation increases relaxation times only in cases of big amount of fillers. May be it was caused by better interaction between already broken clusters of filler with flexible matrix in relation to small filler containing samples.

V. CONCLUSIONS

1) Shown that even in filled samples coupling mechanismus determinied mostly with interactions be-
tween hard domens of PU and matrix of PU.

2) There is no or completely small nonlinear effects in the range of elongations up to 300%.

3) In the case of in-situ process of synthesys of hybrid organic/inorganic materials, inorganic filler acts as reinforcising agent for PU.

4) Crosslinking density slightly reduced as filler content increasing.

5) Preddeformation does not affect relaxation times in case of small filler content, but increases $\tau_p$ in case of filler content $\geq 40\%$, which can be related to a greater increas of crosslink density after preddeformation.

VI. ADDITIONS

1) Great plastic deformation occurs in the hard phase of PU and leads to hysteresis$^{19}$.

2) Relaxation mechanism in microblocs with two relaxation processes, proposed by Irjak$^{18}$ looks like KWW – Doi, Edwards idea with $w_c$ and $w_0$.

3) Stress can be stored mostly in the filler in the reason of increasing acting region between phases$^{12}$.

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