TRENDS IN NON-CRYSTALLINE SOLIDS

Proceedings of the Third International Workshop on Non-Crystalline Solids

Editors
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World Scientific

LOCAL DEFORMATION INHOMOGENEITY IN DYNAMIC MECHANICAL BEHAVIOUR OF BLOCK COPOLYMERS

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ABSTRACT

Models which describe the relationship between macroscopic complex modulus and the spatial inhomogeneities of the properties of block copolymers are presented. Both the inhomogeneity of the composition of the interfacial layers and the distribution of local deformations were investigated. The structures of block copolymer samples were studied by X-ray scattering employing synchrotron radiation at HASYLAB in Hamburg.

1. Introduction

The temperature dependence of the loss modulus $G''(T)$ of block copolymers(BC) forming domain structures cannot be described within the models which only take into account the homogeneous properties of the components. In this paper we propose an approach which also considers the inhomogeneities of the properties. The calculations are compared with the experimental data obtained for butadiene-styrene block copolymers.

2. Results and Discussion

In the previous publications[1,2] the role of the interfacial layers was investigated. The composition of the layer where the components were mixed varied in space[2] and hence its dynamic mechanical properties were spatially inhomogeneous. The interfacial layer was presented as a composition

of n phases. There was obtained:

$$G^*(T)=G'(T)+iG''(T)=(G_a^*G_b^*)^{1/2} \qquad (1)$$

$G_a^*=(\sum_i^n f_i/G_i^*)^{-1}$, $G_b^*=\sum_i^n f_iG_i^*$ are complex moduli of the regions of the sample where domains are oriented to the external force perpendicular or paralelly, n is number of phases, f_i, G_i^* are the volume fraction and the modulus of i-phase. In the model and in the experiment we varied the absolute and relative fractions of the interfacial layer. Good description of the relative changes of $G'(T)$ and $G''(T)$ was obtained[3]. However the experimental values of $G''(T)$ in the range between T_g of the components were much higher.

Next we investigated the role of the spatial distribution of stresses. Each inclusion of a certain component acts as a stress concentrator in the medium of another component[4]. It produces different amplitudes of deformation in different volume elements. Assuming that we can write the modulus of the composite:

$$G_k''=G''\sum_i (e_i/e)^2V_i/V \qquad (2)$$

G'' is modulus for a given component, e_i is amplitude of deformation for i-th volume element, V_i/V is volume fraction of i-element. $B_i^{-1}=e_i/e$ characterises the change of the amplitude of deformation.

The values of G_k' and G_k'' measured by torsional pendulum at frequency of 1 Hz are presented in Fig.1. Calculated values are denoted by points. The corresponding values of B_i are indicated by numbers.

From these data one can conclude that in the temperature range between T_g of the components the mechanical model of the type (1) with constant B_i is quite good for quantitative description of the experimental data.

The domain structures of the BC were studied by small angle X-ray scattering employing synchrotron radiation at HASYLAB in Hamburg. The data concerning with the structure

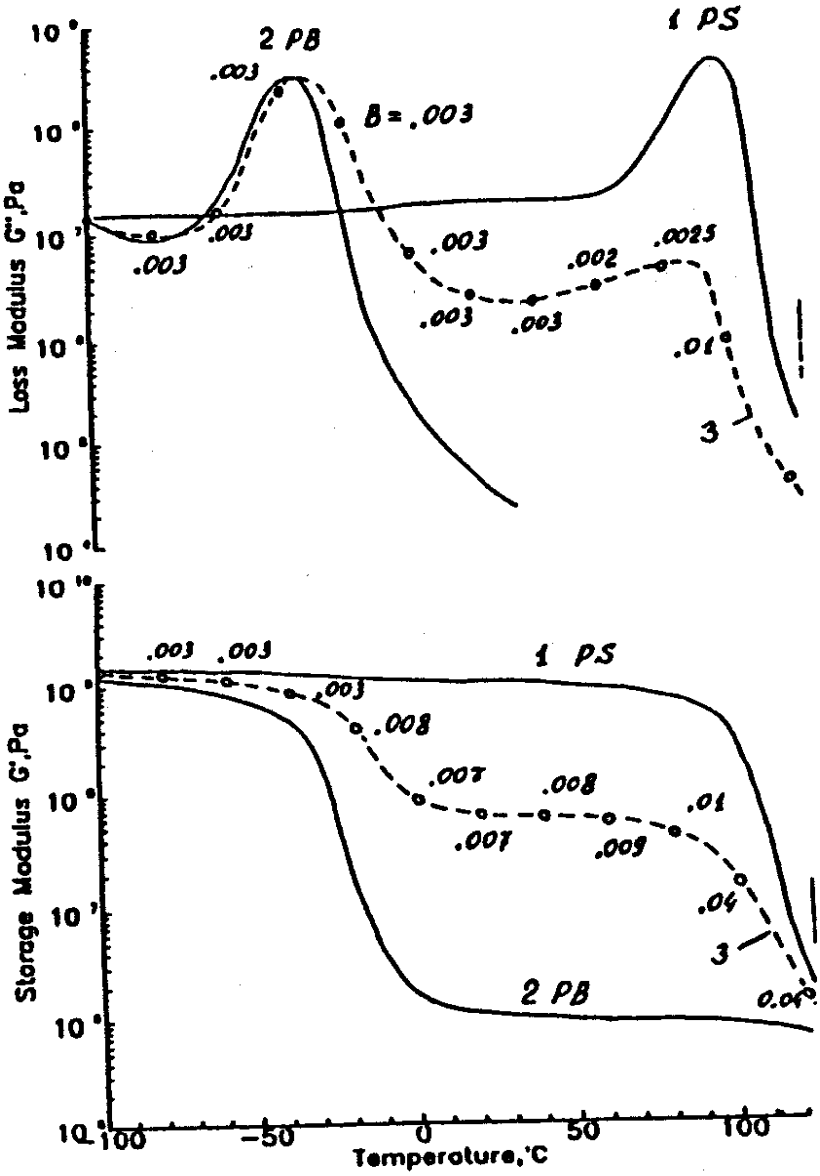

Fig.1. Dynamic storage modulus and loss modulus vs temperature for polystyrene(curve 1), polybutadiene(2) and styrene-butadiene BC(3). Calculated values are denoted by points with B_i values numbers.

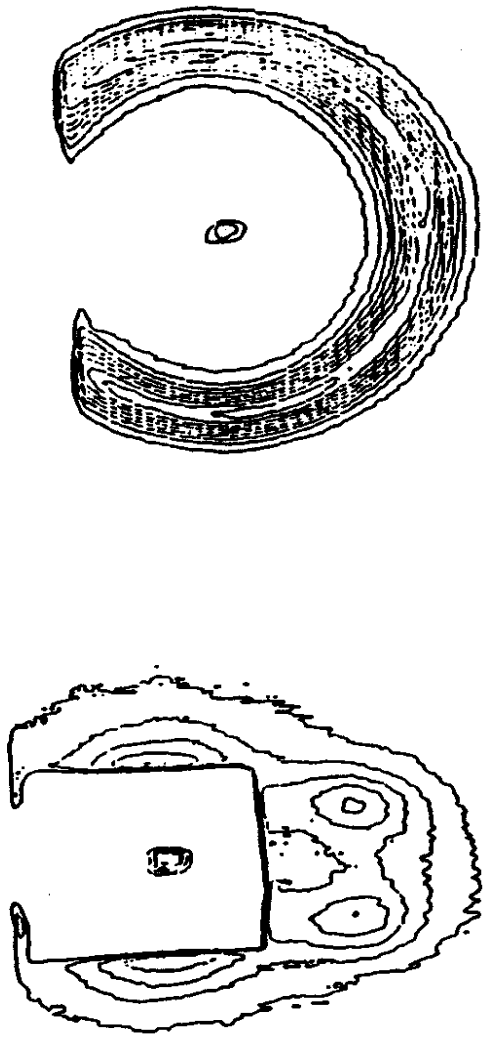

Fig.2. Two-dimensional scattering pattern of three-block copolymer sample as obtained by the VIDICON detector (HASYLAB)
1 - without elongation
2 - 100% elongation.

are necessary to choose the proper parameters for the mechanical model. Using the Vidicon system[5] it is possible to obtain a two-dimensional scattering pattern. The stretching of the sample which causes the orientation of the domains enables one to get a detailed information about the struc-

ture. Typical scattering patterns of three-block copolymer sample forming the domain structure of hexagonally packed cylinders are presented in Fig.2. The long period of the structure is 285Å.

3. Conclusions

The model which takes into account the spatial distribution of the interfacial layer composition allows to obtain a quite good description of the relative changes of the storage and loss moduli due to variation of the relative fractions of the interfacial layer. Complete quantitative description of these moduli is possible if one takes into account the spacial distribution of the amplitudes of deformation in the sample.

Acknowledgment: This work was in part supported by the German Federal Minister of Science and Technology (BMFT) under the contract number 05405HXB. One of the authors (A.V.) thanks the Deutsche Forschungsgemeinschaft for financial support.

4. References

1. Ju.S.Lipatov, Physical Chemistry of Filled Polymers (Nauka, Moscow, 1977).
2. N.M.Khasilov, A.D.Vilesov, V.P.Volodin and et.al., Vysokomol.soed. 31(1989)1745.
3. N.M.Khasilov, A.D.Vilesov, V.P.Volodin and et.al., Vysokomol.soed.32(1990)19.
4. K.Zener, Elasticity and anelasticity of metals (Chicago, 1948).
5. G.Elsner, C.Riekel and H.G.Zachmann, Adv.Pol.Sci. 67(1985).