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The polydienes epoxidation is a good method to modify the backbone chain, improving some of its properties. The epoxidation rate changes with the time and reaction temperature, epoxidizer agent and polymer microstructure. There are two kinds of different kinetic behavior during the reaction of epoxidation, which are related to the epoxidation of trans 1,4 and cis 1,4 double bonds. An increase in the epoxidation content leads to an increase in the glass temperature (T_g) in all materials studied. Tailor-made linear polydienes modified by epoxidation also show shifts of the flow region of the viscoelastic spectra to lower frequencies and significant changes in the dynamic mechanical storage and loss moduli. With higher side group density, the plateau modulus decreases due to lower entanglement density and the frequency limits of the rubber elastic region shift to lower values. Higher molecular weights shift the onset of the flow region towards lower frequencies extending the rubbery plateau. The predictions of refined tube models, which are derived directly from molecular considerations are in good correlation with the experimental data.

Introduction

Chemical modifications of polydienes are of great interest to the rubber properties. The introduction of a reactive group into the polymer chain is a method which has demonstrated good results to improve some properties of polydienes as such oil and solvent resistance, air permeability resistance, better bonding to ceramics, metal and the textile, and principle good wet-skid resistance. These chemical modification can be carry out by different methods as such epoxidation, carboxylation, sulfonation etc.

In this work the epoxidation methods was used, as well as known to natural rubber (1). The epoxidation method has been applied by Cheremisinoff et al and by Danuta (1,2), who have studied factors that could influence the epoxidation reaction, as microstructure of polymer, epoxidation agent and so on.

There are some different methods to epoxide polydienes, one of the most used is the preparation of peracid *in situ*. This seems to be one of the best methods to epoxidation due to the easy availability, low cost of reagents and good results in terms of epoxidation content.

Tailor-made linear polydienes with modifications in molecular weight as well as in microstructure (amount of vinyl, cis-1,4-butadiene, styrene) show significant

changes in the dynamic mechanical storage and loss moduli. With higher side group density, the plateau modulus decreases due to lower entanglement density and the frequency limits of the rubber elastic region shift to lower values. Higher molecular weights shift the onset of the flow region towards lower frequencies extending the rubbery plateau. The predictions of refined tube models, which are derived directly from molecular considerations are in good correlation with the experimental data.

The use of rubber as material places demands upon the polymer, depending on process and the desired end properties. The viscoelastic properties of a polymer depend mainly on the microstructure (constituent groups) and the macrostructure (degree of polymerization). An understanding of the structure property relationship of polymers is the foundation for the best selection.

The effects of micro- and macrostructures can be investigated particularly well using systematically tailor-made polymers, which is demonstrated as follows.

Based upon a simple tube model, major characteristic properties of polymers become understandable. Further refinements of the model improve the conformity of curve fittings with the experimental

behavior of polymers and provide new insights into the dynamic chain motions.

The basis for understanding the flow properties of polymer melts is molecular rheology. The tube model, initially suggested by de Gennes (3, 4) and later reformulated by Doi and Edwards (5), provides particularly successful predictions for the behavior of melts. It describes the motion of a Rouse chain in a tube.

Experimental

In this work some different kind of commercial styrene butadiene rubber (SBR) and polybutadiene (BR) were used without any further purification.

SBR 32 (statistic Vinyl-SBR, Mw = 187000, 25% Styrol, 32% Vinyl).

low molecular weight BR (Mw = 137000, cis1,4 = 40%, trans 1,4 = 50% and vinyl = 10%)

high molecular weight BR Mw = 265000, cis1,4 = 40%, trans 1,4 = 50% and vinyl = 10%).

All SBR and BR were supplied by Bayer AG. Company.

The hydrogen peroxide (Merck, 30%) was titrated against KMnO_4 and used in different concentration, 30% to SBR epoxidation and 15% to BR epoxidation.

Formic acid (98% Fluka), toluene (Fluka) and all others reagent grade were used without further purification.

The epoxidation reactions were carried out in specific conditions. To SBR epoxidation: temperature: 50°C, 35°C, 20°C and 5°C to reactant mol ratios: $\text{H}_2\text{O}_2/\text{C}=\text{C}$ 1,5/1 and $\text{H}_2\text{O}_2/\text{HCOOH}$ 2/1 and to BR: temperature 50°C, reactant mol ratios $\text{H}_2\text{O}_2/\text{C}=\text{C}$ 1,5/1 and $\text{H}_2\text{O}_2/\text{HCOOH}$ 3/1. In a typical epoxidation reaction (6).

The model polymers were produced in anionic polymerization, whereby a selective control of the initial concentrations of the monomers and the reaction parameters makes it possible to selectively adjust the micro- and macrostructures of the polymers. The dynamic/mechanical measurements were made with the Rheometrics Dynamic Analyzer RDA II and also ARES. In view of the considerable differences between the viscoelastic properties of the characteristic polymers, a plate-plate arrangement was selected as the best measurement geometry. The measurement was carried out with an amplitude of 0.5 % across a frequency range of 0.1 to 100 rad/s at temperatures graduated accordingly, so that all regions of the viscoelastic spectrum were recorded overlapping. In accordance with the time-temperature superposition principle, a master curve was created for a temperature of 20 C.

The epoxidized polymers were analyzed for their oxirane content by proton and carbon nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) in a NMR equipment-Varian XL-20. The secondary reaction and also the content of oxirane were

controlled by the Fourier transform infra-red (FTIR) on a Nicolet 60-Nexus. The T_g were studied by differential scanning calorimetry (DSC) measurements using a DSC Polymer Laboratory Thermal equipment with the heated rate was 10°C/min, from -80°C to 50°C.

Results and Discussion

Epoxidation

Although a variety of peracids may be used for epoxidation of polydienes, "in situ" formed performic acid was chosen due to its availability, reactivity and economy. The "in situ" epoxidation is performed by two consecutive steps. The first step, the formation of the peracid is a slow and endothermic reaction, while the second step, the addition of the oxygen to the double bond is a fast and endothermic reaction. (7).

Previous work on the epoxidation of polybutadiene has showed that the reactivity of the double bonds of the pendant vinyl groups were found to be less reactive than the double bonds in the mainly chain (2). Some authors report that the reactivity of the epoxidation of polydienes depends on the microstructure of the rubber but there is no agreement as the effects of the composition of SBR, influence of the styrene content, and the vinyl content on the epoxidation of SBR and BR rubbers. It has been shown that the reactivity of the trans units \cong cis units \gg vinyl units.

Figure 1 shows the results of the epoxidation of the SBR at different temperature.

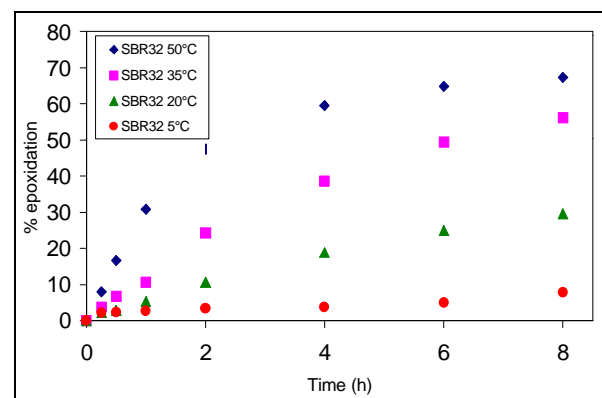


Figure 1: % epoxide versus time for SBR at different temperatures

Assumed that the first step, the formation of peracid is the slower step, the conversion can be formulated as a second order reaction depending on the concentration of the peracid, that should be depending on the peroxide concentration and the acid concentration. The acid concentration is constant because after the introduction of oxygen on the double bond the acid is regenerated. Due to the complexity of the heterogeneous reaction, exact kinetics analysis is difficult to do. But a simple formulation as function of concentration of the double bonds and the

concentration of peracid can be done, with an apparent constant reaction, k_{app} ,

$$d \frac{[C=C]}{dt} = k[C=C][peracid] \quad (\text{Equ.1})$$

It must be remembered that the [peracid] depends on the $[H_2O_2]$ because the determined step of the in situ epoxidation is the formation of the peracid, which depends on the concentration of the acid, and the peroxide. In first time, the concentration of the peroxide is higher than the concentration of the double bond, so a pseudo-first reaction can be formulated,

$$- \frac{d[C=C]}{dt} = \kappa_{app} [C=C] \quad (\text{Equ.2})$$

after integration, eq.2 leads to

$$\ln \frac{[C=C]_0}{[C=C]_t} = k_{app} t \quad (\text{Equ.3})$$

where $[C=C]_0$ and $[C=C]$ are the concentrations of unsaturated double bonds at the beginning and time t , respectively. equation (3) can be further expressed in terms of epoxidation degree, X :

$$\ln \frac{1}{1-X} = k_{app} t \quad (\text{Equ.4})$$

In figure 2 the results of the data from figure 1 plotted followed equation 4. For reaction time up to 2 hours a linear relationship between $\ln[1/(1-X)]$ and t was obtained. For times longer than 2 hours, another apparent kinetic constant was found.

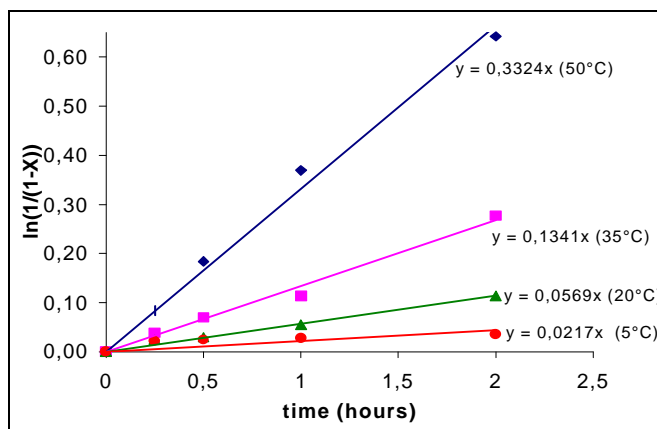


Figure 2: Kinetic treatment for SBR epoxidation reaction

Different factors can contribute to this behavior as for example the isomerism of the double bonds. If the reactivity of the 1,4-cis and 1,4-trans units is higher, after a certain time the system was poorer in this kind of units, also the concentration of the peroxide was changed, peroxide is not only consumed in the

epoxidation, but also decomposed with temperature and time.

What could be also observed, was that when the epoxidation temperature is lower, the reaction shows a trend to a linear behavior. This behavior can be explained due the epoxidation rate, that is lower at lowers temperatures.

As shown in figure 3, the activation energy (E_a) can be determined from the slope of the $\ln k_{app}$ versus $1/T$ curve, and this E_a is basically related with the consum of cis-1,4 and trans-1,4 double bonds.

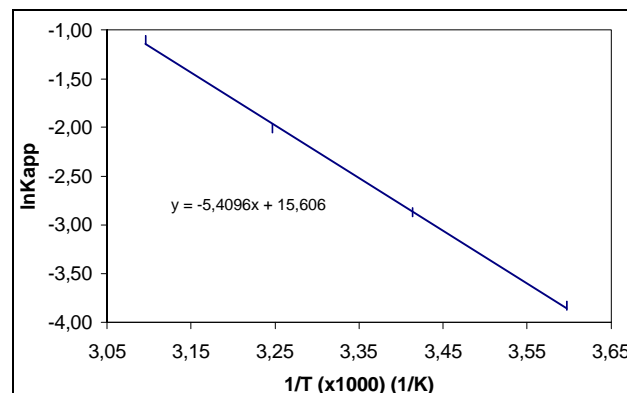


Figure 3: Determination of activation energy from an epoxidation reaction to styrene-butadiene (SBR).

The DSC measurements have shown that with the increase for the polydienes epoxidation content, the values from T_g are higher (figu.4). This can be explained by the motion for the chains. Since the polydienes are epoxidate, a new rigid group is introduced into the chain and then the movement from these chains come to be slow.

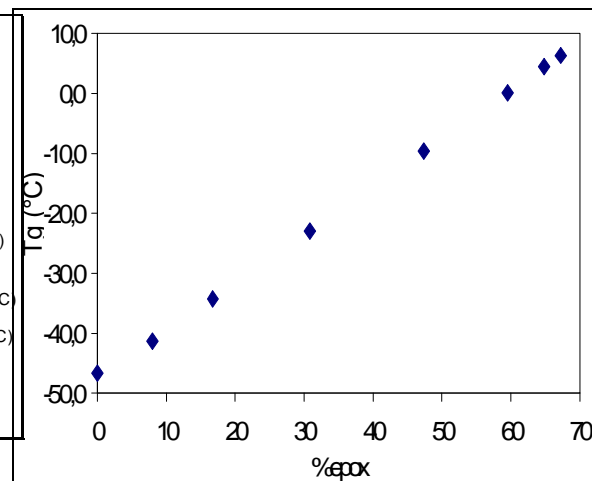


Figure 4: Behavior of T_g 's of the SBR with the content of epoxidation

Some changes in the viscoelastic properties can be seen in figure5 and 6, where it can be observed that the viscoelastic properties in the flow region depend heavily upon the molecular weight and also

epoxidation content, as can be seen for samples with low-vinyl butadienes and for epoxidized samples. For all polymers, the logarithmic increase in the storage moduli is close to two and the increase in the loss moduli is close to one, in agreement with the predictions of the tube model for the flow region

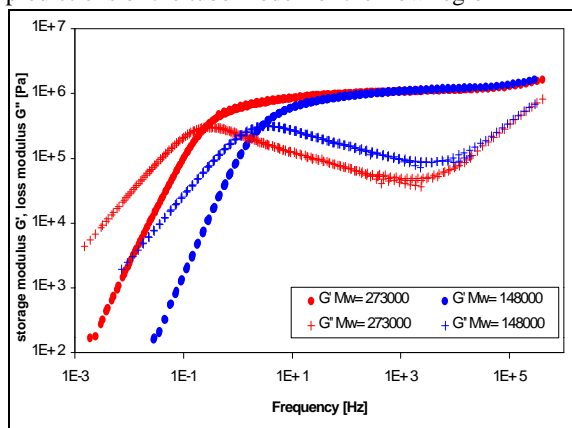


Figure 5: Effect of the molecular weight on the linear-viscoelastic properties of low-vinyl butadienes (50 % trans, 40 % cis, 10 % vinyl)

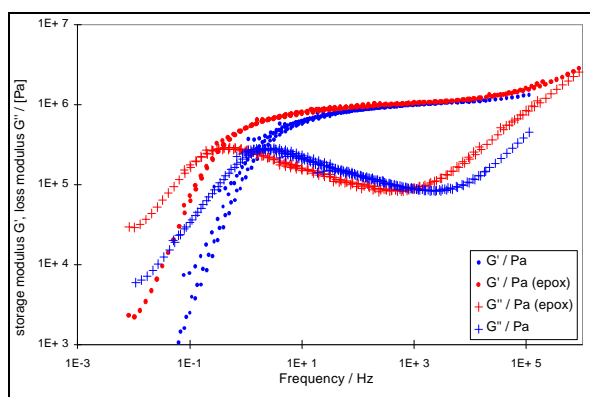


Figure 6: Effect of the epoxidation on the linear-viscoelastic properties of low-vinyl butadienes (50 % trans, 40 % cis, 10 % vinyl)

The positions of frequency of the individual storage and loss moduli curves are clearly frequency-shifted against each other in the region of lowest frequencies up to the crossover, according to the molecular weights and epoxidation content. This behavior is caused by the dominance of flow processes whose relaxation times are scaled to the molecular weight according to equation 5.

$$h_0 \propto t_{rep} \cong \frac{z_{mon} a^2}{k_B T M_{mon}} \frac{M^3}{M_e^2} \left(1 - \sqrt{\frac{M_e}{M}} \right)^2 \quad (\text{Equ.5})$$

$$\eta_0 \propto M_w^{3,4} \quad (\text{Equ.6})$$

In the rubber-elastic region of intermediate frequencies, the trends of the curves of the various polymers gradually merge, since as the frequency increases the relaxations of entanglement segments

that depend on only the microstructure above a critical mass dominate to an ever-greater extent. At even higher frequencies, glass transition takes place, so that bond deformations provide the predominant relaxation contribution.

In a previous study (8) it was shown that at the same ratio of 1,4-cis to 1,4-trans-monomer units in each case, the plateau modulus decreases by more than half as the vinyl content increases from 10% to 93%. This effect can be explained by the fact that the high vinyl butadienes have a larger chain cross-section due to the much more common 1,2 configuration. This leads to a lower probability of entanglement and therefore to a lower plateau modulus.

However as can be seen in figure 6 the behaviour to polybutadiene epoxidized shows a trend to a very similar values to plateau modulus as the plateau modulus to polybutadiene no epoxidized. This effect shows that there is a very similar probability to have entanglement in polybutadiene epoxidized and no epoxidized and so there is no pronounced effect in the plateau modulus.

Conclusions

It was found two different kinetic behaviour during the epoxidation reaction, what can be related with the consumption of trans 1,4 and cis 1,4 double bonds from polydienes studied. To reaction time until two hours the activation energy can be determined from the slope to the curve from figure 3 and it was found an $E_a = 15,6$ Kcal/mol of double bond.

The T_g 's of the SBR and BR increase with the increase of epoxide content. This behaviour occurs due to epoxidation of the polymer chains. As the polymer chains are epoxidized then the chains mobility decreases.

The viscoelastic properties in the flow region dependent from the molecular weight and also from epoxidation content.

Acknowledgement

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