

Influence of the Phase Morphology on the Viscoelastic Behaviour of Polymer Blends (*PP-EPR*)

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Summary. Melts of polyethylene-propylene-rubber (EPR, blends of linear polyethylene, linear polypropylene, and *PE-PP* copolymer) show phase separation. The influence of the phase morphology on the viscoelastic behaviour is studied with the aid of the dynamical moduli. The measured moduli of the fraction of the linear homopolymer of an EPR agree with the moduli calculated from the molar mass distribution of this fraction. In contrast, the copolymer fraction shows a strong rubber-like behaviour (represented by a characteristic relaxation time spectrum). Mixtures of 80 wt% linear *PP* and of EPRs with low copolymer content are not rubber-like liquids. In addition, the moduli from them can be calculated from the moduli of the components with the aid of *Palieme's* emulsion model. This clearly reveals that the linear *PP* forms the matrix in this case. Mixtures of 80 wt% linear *PP* and of EPRs with high copolymer content show rubber-like behaviour and *Palieme's* emulsion model is not applicable on them. Obviously, the copolymer fraction forms a physical network.

Keywords. Phase morphology; Ethylene-propylene-rubber; Linear polypropylene; Viscoelasticity; Dynamic moduli.

Introduction

In order to increase the impact strength of polyethylene (*PE*) and polypropylene (*PP*) products, *PE-PP* copolymers which show rubbery behaviour are developed. Usually, a blend of linear *PP* and of *PE-PP* copolymers is produced in one. The melt of these products (usually called ethylene-propylene rubber (EPR)) is not a homogeneous solution. Together with the molar mass distribution (MMD), the content of copolymers and the morphology of the phases influence the viscoelastic behaviour tremendously. Additionally, each flow process will change the phase morphology as long as the equilibrium state is formed.

As the relation between MMD and of material functions (especially of the dynamic moduli) of the melt is known properly, this study focuses on the rubbery

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behaviour of the *PE-PP* copolymers and on the influence of the phase morphology. In order to characterize the rubbery phase of an EPR the *PE-PP* copolymer fraction is extracted with xylene at 25°C. *Atactic-PP* is contained in this XCS (xylene cold solvable) fraction as well. As the concentration of *a-PP* is rather small (<1%), its role is not treated.

To obtain samples hoped to differ in the phase morphology, a linear *PP* is mixed with 4 EPRs variable in *PP* content. The applicability of *Palierne's* emulsion model [1] on these mixtures is used for the discussion on the phase morphology.

Theoretical Basics

Material functions of polymer melts are integral representations of all structural characteristics and are cumulative functions of a relaxation time spectrum ($g_i(\tau_i)$). Such a spectrum specifies the different modes of stress relaxation of deformed structures. In this study the dynamic moduli G^* (storage modulus G' , loss modulus G'') as function of the frequency ω are used because these measurements can be performed with high accuracy. For these moduli the pertinent relation reads (Eq. (1)).

$$G'(\omega) = G_{N_0} \cdot \sum_i g_i \left(\frac{(\tau_i \omega)^2}{1 + (\tau_i \omega)^2} \right); \quad G''(\omega) = G_{N_0} \cdot \sum_i g_i \left(\frac{\tau_i \omega}{1 + (\tau_i \omega)^2} \right) \quad (1)$$

The conversion of moduli into a spectrum is an ill-posed problem usually solved with the aid of a regularisation method. We use the routine of *Paar-Physica* performed by *Kusnezow* [2].

Molar Mass Distribution

The influence of the molar mass distribution on the relaxation spectrum is well studied. Different onsets are known providing proper results. The calculation routine of *Paar-Physica* [2] used in this study is based on the *BSW* spectrum [3] and on the mixing rule of *Schausberger* [4].

The *BSW* spectrum specifies the relaxation modes of linear flexible chains of equal length. In a polydisperse system each component of molecules with the molar mass M_i is represented by such a spectrum. The leading relaxation times $\tau_{i,0}$ of the different molecules scale according to Eq. (2) with τ_e being the relaxation time of molecules with M_e , the entanglement molar mass.

$$\tau_{i,0} = k \cdot M_i^{3,4} \quad \text{or} \quad \tau_{i,0} = \tau_e \cdot \left(\frac{M_i}{M_e} \right)^{3,4} \quad (2)$$

The relaxation strength $g_{i,0}$ of $\tau_{i,0}$ is proportional to w_i , the weight fraction of the component M_i . In a polydisperse system $g_{i,0}$ and $\tau_{i,0}$ are functions of MMD also, which is accounted by a mixing rule.

The sum of all relaxation strengths is the Plateau-modulus G_{N_0} related to M_e (Eq. (3)) with ρ – density, R – gas constant, and T – temperature.

$$M_e = \frac{\rho \cdot R \cdot T}{G_{N_0}} \quad (3)$$

In such a calculation the only two polymer specific parameters are τ_e (depending on temperature) and M_e .

Rubber-like Liquids

In order to describe the relaxation behaviour of rubber-like liquids longer relaxation times have to be added to the spectrum due to the MMD. Following the *Chambon-Winter* spectrum [5] created for cross-linked polymers, we add a spectrum where the strengths of the times growing in a geometrical series decrease according to Eqs. (4) and (5).

$$g_R(\tau_{i+1}) = g_R(\tau_i) \cdot r_{i+1} \quad (4)$$

with

$$r_{i+1} = r_i - k \quad (5)$$

The constants $g_R(\tau_1) = 1000$ Pa and $r_1 = 1.06$ are the same for all cases, and k can be modified in order to change the slope. In this sense k is a measure for the impact of rubber-like molecules. This spectrum called rubber spectrum afterwards is weighted by the volume fraction of the molecules acting rubber-like (Eq. (6)).

$$H_{\Phi R}(\tau) = \Phi \cdot H_R(\tau) \quad (6)$$

Palierne's Emulsion Model

Palierne's emulsion model allows the calculation of $G^*(\omega)$ of a suspension consisting of a viscoelastic matrix and of included viscoelastic spheres from the moduli of the components. In case of *PE-PP* suspensions the surface tension is very small, and therefore the pertinent onset is omitted (Eqs. (7) and (8)).

$$G^* = G_M^* \cdot \frac{1 + (3/2)M}{1 - M} \quad (7)$$

with

$$M = \Phi_I \cdot \frac{2(G_I^* - G_M^*)}{2G_I^* + 3G_M^*} \quad (8)$$

G^* – complex modulus of the blend; G_I^* – complex modulus of the inclusion; G_M^* – complex modulus of the matrix; Φ_I – volume fraction of the inclusion.

Results

In case of the XCU (xylene cold unsolvable) component of an EPR the measured moduli fit quite well the moduli calculated from the MMD and in the low frequency region the curves of G' and G'' come close to the terminal relation: $G' \propto \omega^2$ and $G'' \propto \omega$. That means this component consists only of linear *PP* molecules (Fig. 1).

The values of very small G' (<1 Pa) are lacking in accuracy, therefore should be discarded.

The XCS component shows a behaviour known to gels (physical or chemical networks): in the low frequency region both G' and G'' come to $G' \propto G'' \propto \omega^a$ with

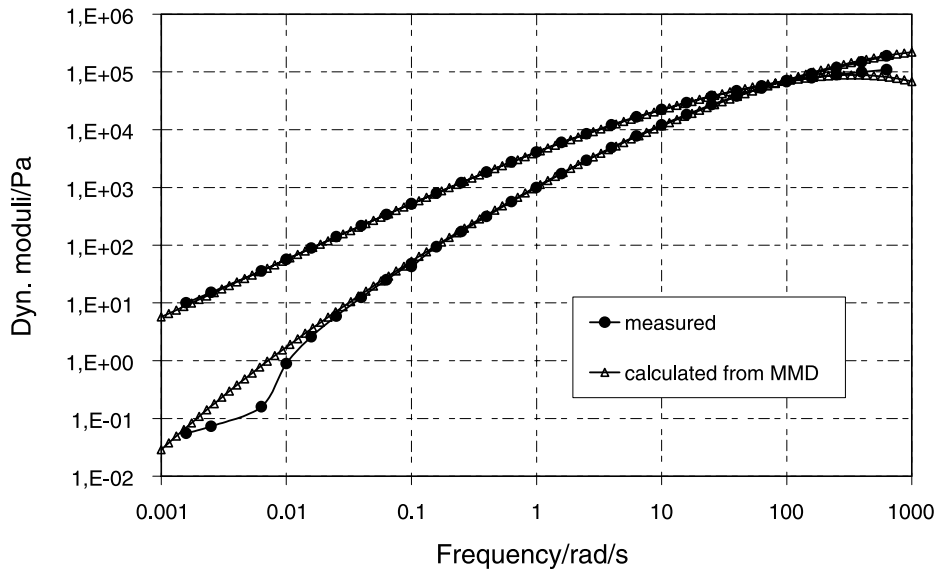


Fig. 1. Dynamic moduli of the EPR-XCU component: ●●● measured, $\Delta\Delta\Delta$ calculated from MMD

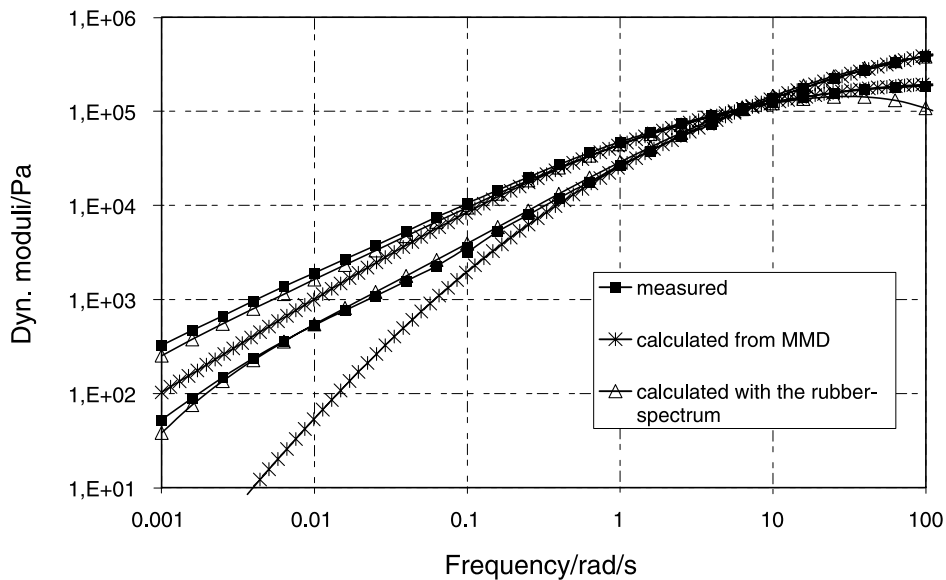


Fig. 2. Dynamic moduli of the EPR-XCS component: ■■■ measured, + + + calculated from MMD, $\Delta\Delta\Delta$ calculated with the rubber-spectrum

$a < 1$ (parallel lines with a slope a in a double logarithmic plot, Fig. 2). That means to the spectrum given by the MMD ($H_{\text{MMD}}(\tau)$) another spectrum has to be added representing the relaxation of gels ($H_{\Phi\text{R}}(\tau)$; Eq. (6)). The volume fraction Φ and the constant k are adjustable parameters in this calculation and are a measure of the rubbery behaviour (parameters $k = 0.000225$, $\Phi = 20$) (Fig. 3).

The melts of EPR 2, 3, and 4 are rubber-like liquids as shown by the dynamic moduli and much more obviously by the comparison of the measured moduli and

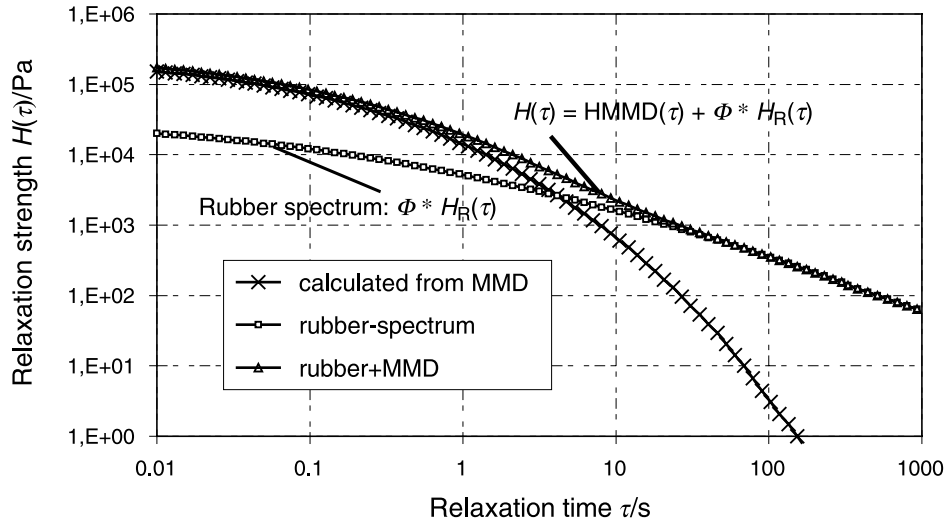


Fig. 3. Relaxation time spectra of the EPR–XCS component: addition of the rubber-spectrum to the spectrum calculated from the MMD in order to obtain the complete spectrum of the rubber-like component

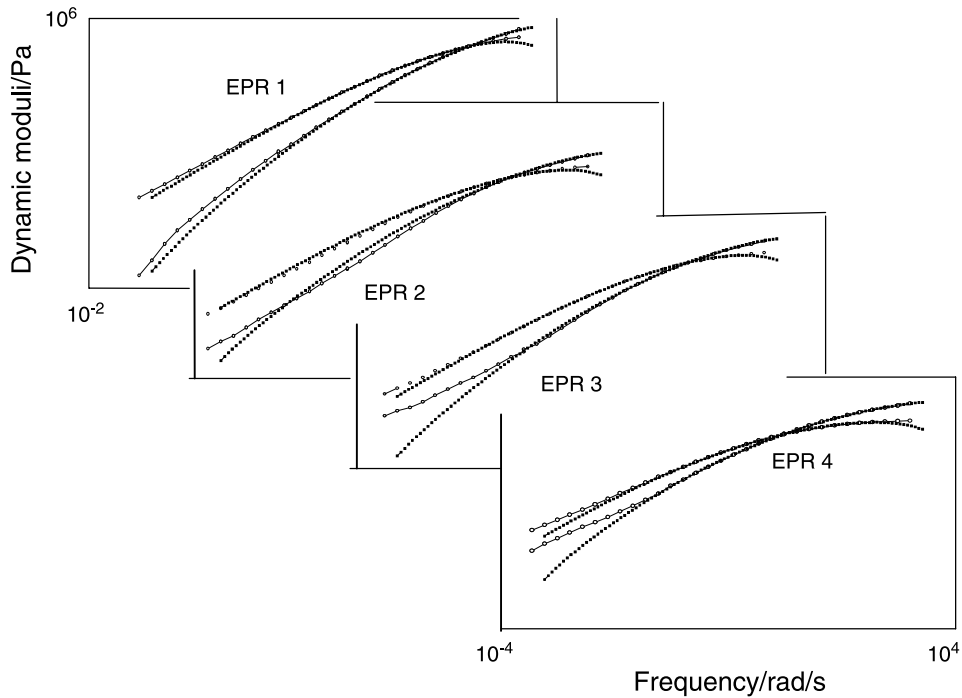


Fig. 4. Dynamic moduli of the EPRs of Table 1: ○○○ measured, ●●● calculated from MMD

of the moduli calculated from the MMD. In case of EPR 1 there is only a slight difference between the measured and calculated moduli, but the curves of the moduli do not look like curves of rubber-like liquids (Fig. 4).

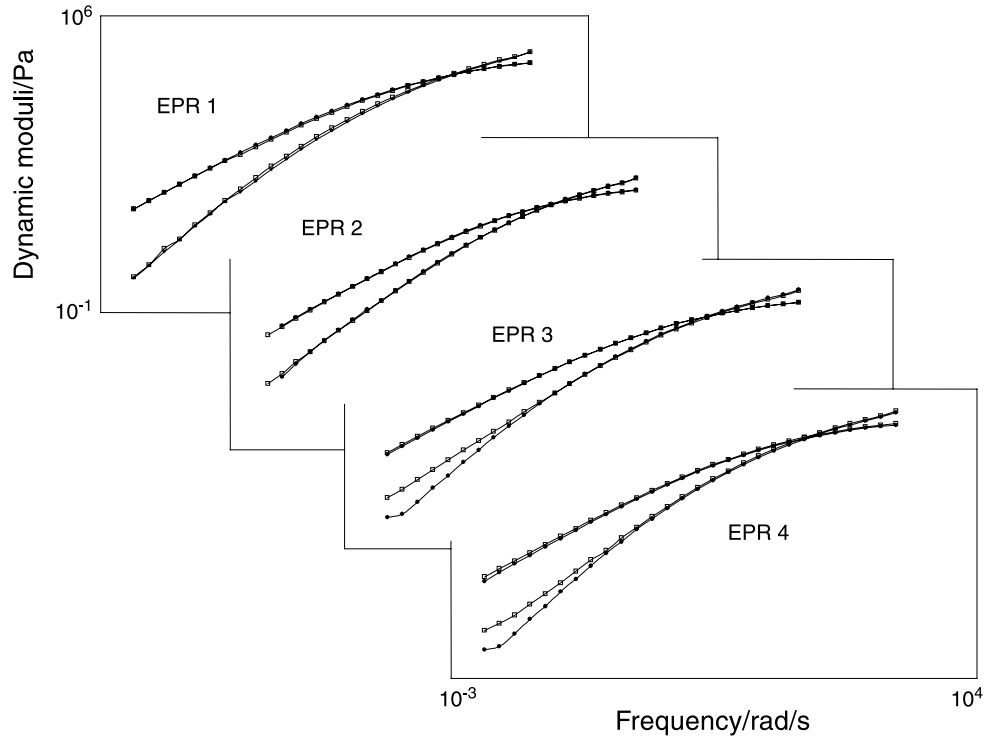


Fig. 5. Dynamic moduli of mixtures of linear PP with EPRs: $\square \square \square$ measured, $\bullet \bullet \bullet$ calculated via *Palierne*

The next fact of interest is that only the moduli of the mixtures with EPR 1 and 2 calculated from the moduli of linear *PP* as matrix and of the EPR as inclusion according to *Palierne* (Eq. (7)) resemble the measured moduli. In case of EPR 3 and 4 the calculated and measured curves differ remarkable (Fig. 5).

Calculations with EPR as matrix and linear *PP* as inclusions give senseless results for all mixtures.

Discussion

If the dynamic moduli in the low frequency range scale with $G' \propto \omega^2$ and $G'' \propto \omega$ (slopes 2 and 1 in a double logarithmic plot) it is rather sure that the longest relaxation times are counted. If then, in addition the moduli calculated from the molar mass distribution equal the measured moduli it is sure that only the MMD but no other structural characteristic influences the viscoelastic behaviour. That's the case with the XCU (linear *PP*) component of an EPR, but not with the XCS (*PE-PP* copolymer) component. The latter shows further much longer relaxation times not created by the movement of linear molecules in a bulk of linear molecules. A similar behaviour is found for gels [4]. Therefore, we account this rubber-like behaviour with the so called rubber-spectrum, well-considering that the *PE-PP* copolymers are not cross-linked chemically as they are soluble. Probably a high degree of branching makes these systems rubber-like. The factor k in

Eq. (5) (and the slope of G' , G'' curves in the low frequency range) is a measure for this rubber-likeness (larger k – smaller slope – more rubber-like).

The applicability of *Palierne's* suspension-modulus of the mixture of linear *PP* and *EPR* 1 and 2 indicate that the linear *PP* forms the matrix of this inhomogeneous system. This is why such a system does not behave rubber-like despite the fact that it contains a rubber-like liquid. Therefore, we know that even at low concentrations of *PE-PP* copolymers (mixtures with *EPR* 1 and 2) phase separation occurs. Consequently, the mixtures with higher concentrations of copolymer are also inhomogeneous. But in contrast, these mixtures (linear *PP* with *EPR* 3 and 4) are rubber-like liquids as it is clearly revealed by the measured dynamic moduli. Actually, this proves that the copolymer acts as a physical network. Probably it even forms the matrix.

Conclusions

We have investigated the viscoelastic behaviour of the melt of *EPRs* and of their components. The *EPR* melts are inhomogeneous blends of linear *PP* and of *PE-PP* copolymer. The *PE-PP* component is a rubber-like liquid.

In case of *EPRs* with a small fraction of copolymer (like *EPR* 1 and mixtures of linear *PP* and *EPR* 1 and 2), the *PP* component forms the matrix, and these *EPRs* do not show a rubber-like behaviour. In the other case, the *EPRs* are rubber-like liquids. That means the copolymer component acts like a physical network.

The emulsion model of *Palierne* describes properly the blends with linear *PP* as matrix and *PE-PP* copolymer as inclusion.

Experimental

The samples used in this study are products of BOREALIS GmbH Linz. Table 1 lists molecular data of the samples used in the mixtures.

The GPC measurements were performed by the producer with trichlorobenzene as solvent at 135°C in a standard device of Waters.

Granules of the mixtures were produced with a twin screw mixer at 220°C. These mixtures always contain 80 wt% linear *PP*.

The dynamic moduli were measured with a UDS 200 from *Paar-Physica* at 200°C at deformations smaller than 2 in a parallel plate device. For these measurements, the samples were pressed to plates in a vacuum oven at 200°C.

Table 1. Molecular data of the samples used in the mixtures

Sample	<i>PP</i> Content/wt%	Rubber G_0 /Pa	M_e /kg/mol	τ_e /s
lin <i>PP</i>	100	6×10^5	4.9	7.5×10^{-8}
<i>EPR</i> 1	87	5.5×10^5	5.4	9×10^{-8}
<i>EPR</i> 2	64	8×10^5	3.7	5.5×10^{-8}
<i>EPR</i> 3	45	11×10^5	2.7	3×10^{-8}
<i>EPR</i> 4	34	13×10^5	2.3	1.5×10^{-8}

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