

Characterization of Phase Morphology of Polymer Melts (PP/PE Blends) Via Rheology

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ABSTRACT: The viscoelastic behavior of high impact polypropylene (PP) melts, a multiphase system with an isotactic PP matrix and inclusions consisting of mainly amorphous ethylene-propylene copolymer (EP), is strongly influenced by the size of small inclusions. The dynamic moduli of such two-phase systems (reactor products) are well described by Palierne's emulsion model. For this analysis the reactor product is separated into matrix and dispersed phase via the different solubility in xylene. This analysis also provides information on the ratio interfacial tension to particle size of the dispersed phase. With mor-

phology data (particle size) of the solidified heterophasic samples (Transmission Electron Microscopy), we estimate the interfacial tension between PP and EP copolymer via the emulsion model of Palierne and from the relaxation time spectra according to Gramespacher and Meissner. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2294–2298, 2007

Key words: phase morphology; polypropylene ethylene-propylene copolymer blend; viscoelasticity; surface tension; dynamic moduli

INTRODUCTION

The melts of high impact polypropylene (impact PP) are heterophasic systems composed of isotactic polypropylene (i-PP), ethylene-propylene copolymer (ethylene-propylene-rubber: EPR), and of linear polyethylene (PE). The phase morphology has a strong influence on the processing conditions and consequently on the product quality. Several studies have been done to establish the influence of the EPR-particles on mechanical properties like impact strength, scratch behavior, and tensile strength.

This report is to show that simple rheological tests are sufficient for an appropriate characterization of two-phased systems.

The impact PPs are produced mainly by mixing linear PPs and EPRs or by sequential polymerization process in a reactor cascade. In both cases i-PP forms the matrix. Mixing produces EPR inclusion of rather large diameters whereas the reactor product contains rather small EPR inclusions. And as is well known the diameter of the inclusions strongly influences the viscoelastic behavior of the melt. As the optical den-

sity of molten i-PP and EPR is almost equal optical methods can not be used for the characterization of the phase morphology.

This article focuses on the influence of the particle (inclusion) size related to the surface tension on the viscoelastic properties of high impact PP. In a single phase system, the material functions (the viscoelastic behavior) are a function only of the molar mass distribution (MMD). Therefore, the comparison of measured dynamic moduli and of the moduli calculated from the MMD enables us to probe single phase systems. For the analysis of two phase systems the emulsion model of Palierne is used. With the aid of the pertinent equation the dynamic moduli of a suspension can be calculated from the moduli of the components. We studied the influence of surface tension and particle size on the dynamic moduli comparing measured and calculated moduli.

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

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relation reads as:

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

The conversion of moduli into a spectrum is an ill-posed problem usually solved with the aid of a regularization method. We use the routine of Paar-Physica performed by Kusnezov.¹

CALCULATION OF MODULI FROM 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 used in this study is based on the BSW-Spectrum² and on the mixing rule of Schausberger.³

The BSW-Spectrum quantifies 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:

$$B^*(\omega) = \frac{[G_I^*(\omega) - G_M^*(\omega)][16G_M^*(\omega) + 19G_I^*(\omega)] + 4\left(\frac{\alpha}{R}\right)[2G_M^*(\omega) + 5G_I^*(\omega)]}{[2G_I^*(\omega) + 3G_M^*(\omega)][16G_M^*(\omega) + 19G_I^*(\omega)] + 40\left(\frac{\alpha}{R}\right)[G_M^*(\omega) + G_I^*(\omega)]} \quad (2)$$

with τ_e the relaxation time of molecules with M_e the entanglement molar mass.

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 :

$$M_e = \frac{\rho RT}{G_{N_0}} \quad (3)$$

where ρ , density, R , gas constant, T , temperature.

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

EMULSION MODEL OF PALIERNE⁴

Palierne's emulsion model allows the calculation of dynamic moduli ($G^*(\omega)$) of a suspension consisting of a viscoelastic matrix and of included viscoelastic spheres from the moduli of the components.

Blending factor B

$$B^*(\omega) = \frac{[G_I^*(\omega) - G_M^*(\omega)][16G_M^*(\omega) + 19G_I^*(\omega)] + 4\left(\frac{\alpha}{R}\right)[2G_M^*(\omega) + 5G_I^*(\omega)]}{[G_I^*(\omega) - G_M^*(\omega)][16G_M^*(\omega) + 19G_I^*(\omega)] + 40\left(\frac{\alpha}{R}\right)[G_M^*(\omega) + G_I^*(\omega)]} \quad (4)$$

α , surface tension; R , average radius of the inclusions; indexes: M , matrix; I , inclusion.

Dynamic moduli G^*

$$G_B^* = \frac{1 + 3\Phi B^*(\omega)}{1 - 2\Phi B^*(\omega)} \cdot G_M^* \quad (5)$$

Φ , volume fraction of the inclusions; index: B , blend.

MATERIALS

The heterophasic polypropylene (PP)-EP copolymer blends used in this study were produced in the spherulite pilot plant with a Ziegler Natta Catalyst and external donor by a sequential polymerization process in a reactor cascade. The molecular parameters of the matrix (PP) are kept constant within these series. The EP copolymer produced in the second step is varied in the ethylene-propylene content. Since we know the high reactivity of ethylene during the formation of the copolymer, additional crystalline PE will be formed especially at high gas phase ratio.

To separate the reactor product the polymer is solved in hot xylene ($\sim 130^\circ\text{C}$, ~ 5 h, stabilized with 0.2% Ionol). In the cold solution ($\sim 25^\circ\text{C}$) the i-PP (and also the linear PE) forms a semicrystalline solid phase (xylene cold unsolvable XCU), whereas the EPR remains solved (xylene cold solvable XCS).

The two reactor products (RP) of this study differ in the XCU/XCS fraction: RP 1: 75/25, RP 2: 68/32, and in the C2/C3 ratio of the EPR: RP 1 - 63/37, RP 2 - 27/73.

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

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

RESULTS

Characterization of the components

We test the phase status of the components by comparing the measured moduli and the moduli calculated from MMD (Table I). In case of the XCU compo-

TABLE I
Molecular Data for Conversion of MMD to Moduli

Sample	G_{N_0} (Pa)	M_e (g/mol)	τ_e (s)
XCU_RP 1	3.5×10^5	9230	7×10^{-7}
XCU_RP 2	2.4×10^5	8450	9×10^{-7}
XCS_RP 1	15×10^5	1970	0.7×10^{-7}
XCS_RP 2	8.2×10^5	3600	0.2×10^{-7}

G_{N_0} , plateau modulus; M_e , entanglement molar mass; τ_e , entanglement relaxation time.

ment of RP 2, 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 is a single phase system and consists only of linear PP molecules (Fig. 1).

When the XCS component of the RP 2 is tested in this way (Fig. 2) the moduli differ and the measured moduli look like the moduli of a two phase system (as will be discussed later).

After testing the solubility we assume that this XCS component contains linear PE which was included in the inclusions of the reactor product and was not separated by the xylene fractionation.

In contrast, the XCU component of the RP 1 (Fig. 3) is two-phased (remarkable differences between measured and calculated moduli), whereas the XCS component of RP 1 (Fig. 4) is a single phase system.

This means that in the xylene fractionation process of RP 1 the linear PE has been dissolved totally and was able to crystallize in the cold solvent. Therefore it was filtered together with linear PP. In the cooling process i-PP crystallizes first. Thereby, in the molten XCU component i-PP will form the matrix and the linear PE will form inclusions of rather large diameters. The results shown in Figure 3 indicate this phase structure (more details of the evaluation of differences

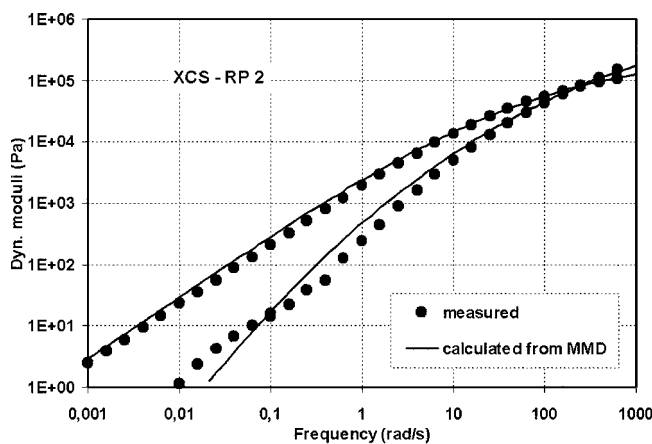


Figure 2 Dynamic moduli of the RP 2 – XCS component: ● measured, — calculated from MMD.

shown in Figure 3 will be given later). Despite the fact that the moduli of this XCU fraction are not exactly the moduli of the i-PP matrix of the RP 1 they are used in the analysis of the morphology of RP 1.

The reason for this different fractionation process is not clear.

Fortunately, the incomplete fractionation of RP 2 provides exactly these samples required for analyzing the phase morphology.

The parameter τ_e and M_e needed for the MMD to moduli conversion are polymer specific but depend on factors like content on molecules with $M < 2M_e$, PP/PE ratio in case of EP copolymers and on the PE content in case of PP/PE suspensions when the phase separation is not treated separately. Therefore, we do not try to calculate these parameters *a priori* but take them as the result of a proper comparison between measured and calculated moduli.

The small differences in the parameters of the XCU components reflect the fact that the RP 1 component is a PP matrix with a few PE inclusions. In a copolymer

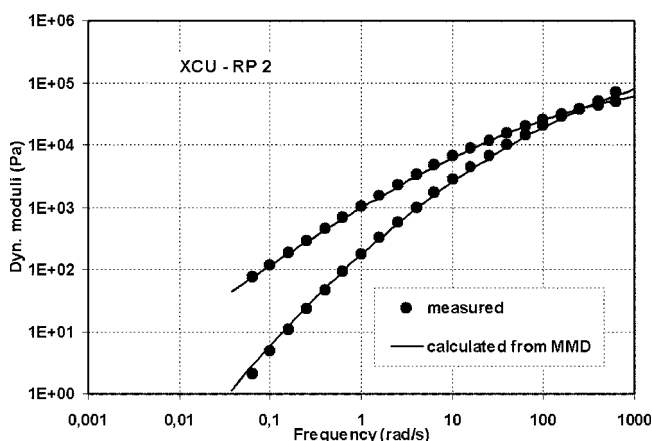


Figure 1 Dynamic moduli of the RP 2 – XCU component: ●, measured; —, calculated from MMD.

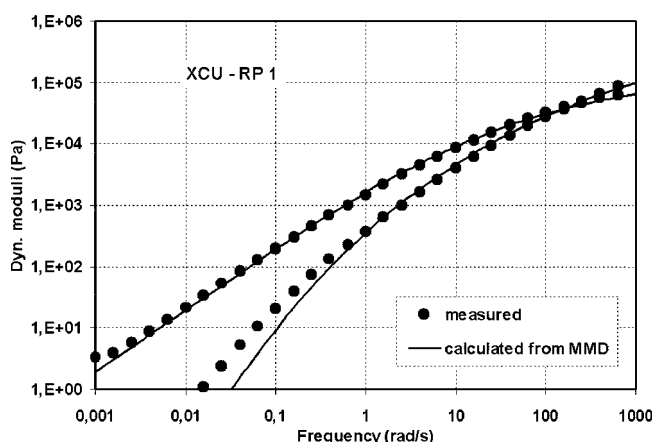


Figure 3 Dynamic moduli of the RP 1 – XCU component: ●, measured; —, calculated from MMD.

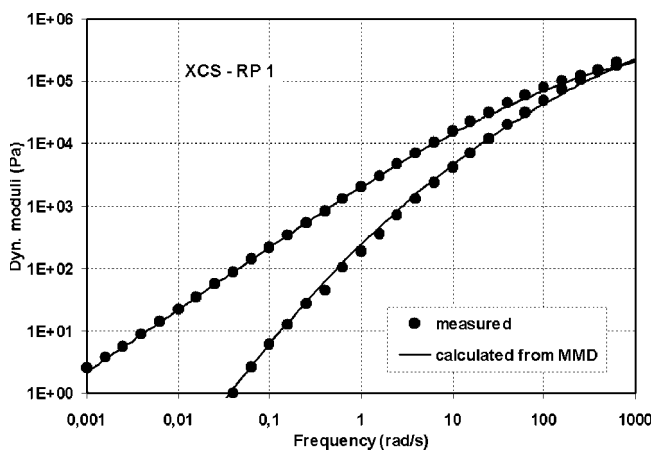


Figure 4 Dynamic moduli of the RP 1 – XCS component: ●, measured; —, calculated from MMD.

the PE content increases the Plateau modulus and shortens the relaxation times.

The XCU component of RP2 and the XCS component of RP1 are not exactly single phase systems, but in lack of better samples they are considered as single phased in the following.

Analysis of two phase systems (reactor products)

For one type of analysis we use Palièrne’s equation (eq. 5). As we know, the moduli of the suspension (reactor product) and the moduli of the components (XCU = matrix, XCS = inclusions) and the volume fraction Φ of the components, the only adjustable term is α/R the ratio of surface tension to particle size. Rather good agreements are found for RP 1 with $\alpha/R = 50$ Pa and for RP 2 with $\alpha/R = 150$ Pa (Figs. 5 and 6).

In the literature we did not find values for the surface tension between PE and PP. This is not surprising because it is not possible to measure directly the expected small values of these high viscous fluids. On

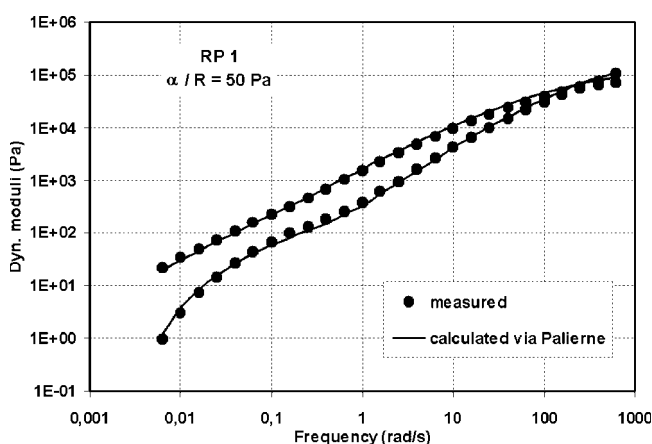


Figure 5 Dynamic moduli of RP 1 with XCU as matrix and XCS as inclusion: ●, measured; —, calculated via Palièrne.

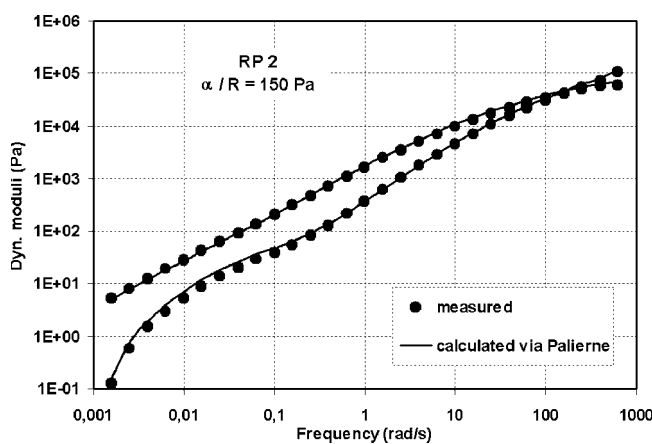


Figure 6 Dynamic moduli of RP 2 with XCU as matrix and XCS as inclusion: ●, measured; —, calculated via Palièrne.

the other hand, with information on the particle size the above cited values of α/R allows the calculation of α . Unfortunately, the particle sizes in the melt can not be estimated by optical methods. But one may assume that the solidification process does not change the phase distribution remarkably because due to the high viscosity of the melt no efficient material transport takes place. Therefore, transmission electron microscopy will provide proper information on the particle size (dark areas in Figure 7).

With the average radii of the inclusions for RP 1: $R = 0.23 \mu\text{m}$ and for RP 2: $R = 0.07 \mu\text{m}$ the surface tension in the reactor products is found to be between 11.5 and 10.5×10^{-6} Pa m.

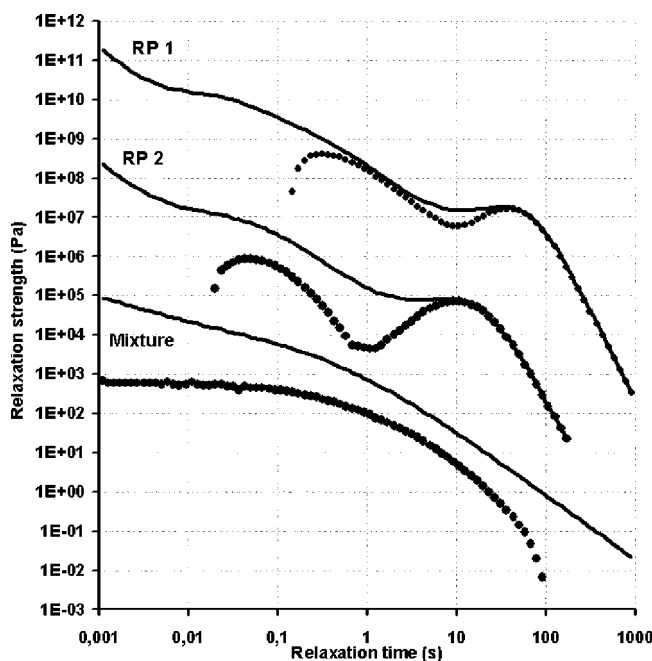


Figure 7 Transmission electron microscopy of RP 1 (left) and RP 2 (right).

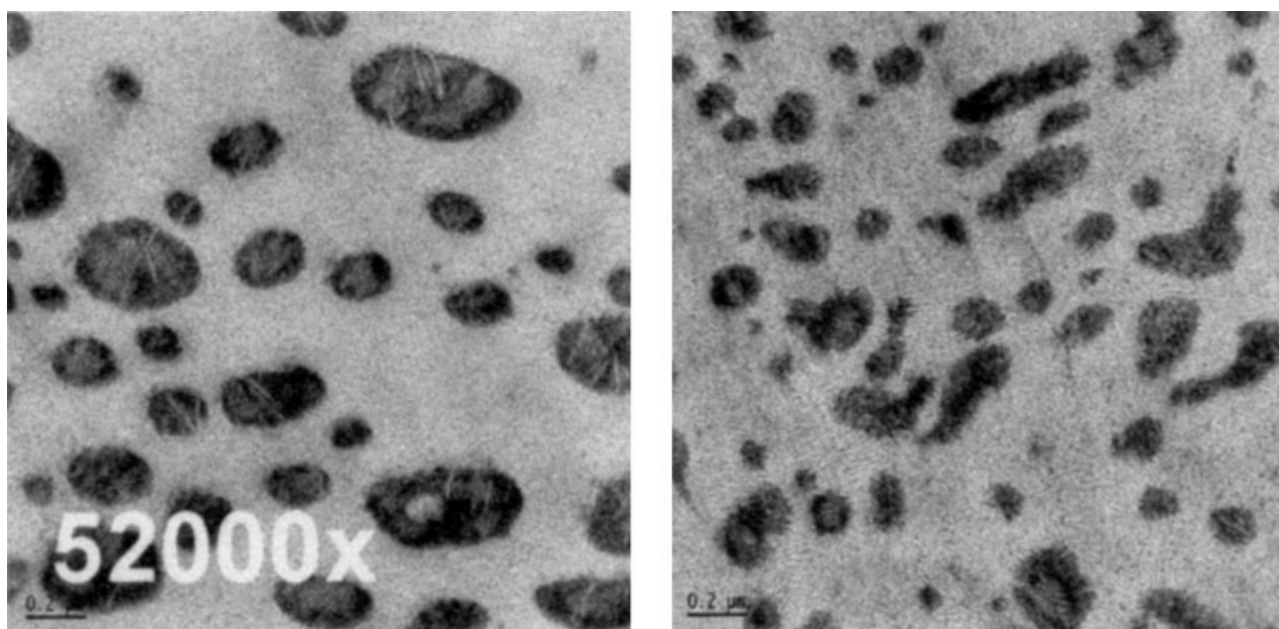


Figure 8 Relaxation time spectra calculated from: —, measured dynamic moduli of mixture, of the RP 1 (y -axis $\times 10^3$) and of the RP 2 (y -axis $\times 10^6$), respectively, ●, difference.

Relaxation time spectra allow another type of analyses. In Figure 8, we show the spectra of two phase systems and the differences of these spectra to the spectra obtained by the volume weighted summation of the spectra of the components. These differences quantify the influence of the phase morphology.

To complete the picture of the influence of the particle size the spectra of a mixture of 80% i-PP and 20% EPR are shown in Figure 8 also. As reported von Vincze-Minya and Schausberger⁵ in such a mixture the ratio α/R is near to zero and the strengths of the relaxation times created by such a phase morphology are rather small compared with the strengths of the pertinent single phase melt. The same fact is found for the XCU fraction of RP 1.

Figure 8 shows that smaller particles create an additional relaxation process. The strongest relaxation time of this process depends on the particle size (and the surface tension of course). Gramespacher and Meissner⁶ quantify the relation between this relaxation time and the ratio α/R . With $\tau = 14$ s, $R = 0.23$ μm (RP1) and $\tau = 50$ s, $R = 0.07$ μm (RP2) the pertinent calculation gives α between 11.9 and 10.1. 10^{-6} Pa m. This result is very close to that of the analysis according Parlierne.

CONCLUSIONS

In addition to a previous article from Vincze-Minya and Schausberger⁵ on the phase morphology of PP-EPR blends (mixture of PP and of EPR) this article is focused on the influence on the particle size of the inclusions. While mixing procedures make rather large particles the reactor process produces a more fine-grained morphology. Smaller particles strongly influence the viscoelastic

behavior at low shear rates on the one hand. On the other hand this effect can be used for the characterization of the phase morphology. We apply Palierne's emulsion model successfully. Calculations like Gramespacher and Meissner reported provide equally good results. With data on the particle size distribution obtained via TEM on solidified samples we estimated values for the surface tension. Despite these values being results of some fitting and averaging procedures, they are findings never reported before.

For such analyses the dynamic moduli of the components has to be known separately. A given suspension (reactor product) is separated into the components by the different solubility in xylene (cold solvable or cold unsolvable). The single phase status of the components is tested with the aid of the moduli calculated from the molar mass distribution (provided by size exclusion chromatography).

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