

Creep measurements on “in situ” compatibilized polypropylene/polyamide-6 blends

S. Schlag, J. Rösch*, and Chr. Friedrich

Institut für Makromolekulare Chemie, Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg i. Br., Stefan-Meier-Strasse 31, W-7800 Freiburg i. Br., Germany

Summary

Rheological properties of Polypropylene/Polyamide-6 blends at different degrees of compatibilization were studied at 240°C. The compatibilizing agent was synthesized in situ during the mixing procedure. Creep measurements at constant stress levels were performed on a Rheometrics Stress Rheometer.

The morphology of the blends was determined by scanning and transmission electron microscopy before and after the shear experiments. No changes of the morphology occurred during the experiments.

In the creep experiments the flow zone was reached. Data of that region such as zero shear viscosity, creep compliance and terminal retardation time were determined.

The values of these quantities increased with increasing amount of the compatibilizing agent.

Introduction

Mixing of polymers attracts growing interest for the preparation of new materials. In most cases, however, it is not enough to combine two incompatible polymers in order to yield the desired properties. It becomes more and more obvious that the proper choice of a suitable compatibilizer plays an important role in improving the material's properties. In most cases block copolymers are used as compatibilizing agents. They can be prepared separately or in situ during the mixing process. Their mode of operation in mixtures of incompatible polymers is close to that of soaps in oil/water mixtures. They lower the surface tension between the components which leads to a decrease of the domain size. This effect can be shown by microscopic methods. An other important effect of compatibilizers is the improvement of adhesion between the two components. The latter depends on the block length of the compatibilizer */2,3/* as well as on interaction parameters. An overview on the entropic and enthalpic interactions in the interface depending on the compatibilizing agent is given by Braun et al. */13/*.

In the case of the blends it is the aim to yield the desired domain size and an optimum adhesion between the immiscible phases. The latter is not necessarily reciprocally proportional to the interface tension as stated by Wu */1/*. This was shown by Kramer et al. who studied the effect of compatibilizer on the strength of the interface */2/*. Further research in that area was done by them with the help of forward recoil spectrometry */3/*, and measurements of the fracture toughness */4/*. Electron microscopic methods are often used for the morphological characterization of blend materials. From TEM-pictures not only the domain size can be determined but also a qualitative evaluation of the adhesion can be made from the state of the cut or broken surface.

As compatibilization influences the domain size and the interfacial tension, the rheology of these materials is changed. Ide and Hasegawa were the first who tried to explain this relationship for polypropylene/polyamide blends */5/*. By experiments with their materials in the solid state they demonstrated the influence of the compatibilizer. In recent time Muller and coworkers */6/*, Valenza et al. */7,8,9/*, and Utracki and Sammut */10/* studied the same question on closely related materials. Their results differed in some aspects. While in */6/* hardly no changes in the rheological behavior were found as far as different degrees of compatibilization are concerned other authors found remarkable dependencies on that

*Corresponding author

feature. Though such dependencies were found, the rheological properties were not examined in a systematic dependence of the degree of compatibilization. One reason why this was not done might be that in the case of these systems it is experimentally very difficult to get data as Newtonian zero shear rate viscosity or a terminal relaxation time. Such data should show a good correlation with the morphological changes. Normally dynamic experiments are used for the rheological characterization of the blends in order to get no modification or destruction of the morphology during the experiment. These measurements are only possible in a limited frequency range from which often no characteristic points are available. The time-temperature superposition often does not work or even if it works the terminal zone cannot be reached because of the thermal degradation which occurs at elevated temperatures. An other problem of this often used technique is, that for this kinematically forced experiments the conditions at the interface matrix/domain are not exactly defined. It is expected that discontinuities occur in the interface region. Due to the fact that two-phase blends tend to such interfacial effects it is reasonable to carry out the dynamic forced creep experiment. For this reason in this work it shall be examined if creep measurements are able to overcome these problems.

Experimental

Materials

The two polymers which have been used to manufacture the blends are: Moplen D 50 G (Himont) polypropylene (hereafter denoted PP) and Sniamid ASN 27/33 (Snia) polyamide-6 (PA). As compatibilizing agent Exxelor PO 15 (Exxon) (PPMA) was used. It is a maleic anhydride grafted polypropylene. Some physico-chemical properties of all polymers used are reported in table 1.

Table 1: Physico-chemical properties of the polymers used.

Polymer	M_n^* [g/mole]	M_w^* [g/mole]	$U = M_w/M_n - 1$
PP	100.000	800.000	7
PA	31.630 **	-	-
PPMA	67.000 *	157.000 *	1.34

* GPC-Analysis by the DKI in Darmstadt (standard: Polystyrene)

** Titration of the amine end groups

Blending

Blends containing 30% by weight of the polyamide, different amounts of the maleic anhydride grafted polypropylene, and polypropylene were prepared on a Haake Bucher Rheomix. The PPMA and the PP component make in different compositions 70% by weight of the blend. The mixing was made in two steps (Fig. 1). In the first step the PA was mixed with the PPMA (a). After this step the PA forms the continuous phase, the PPMA is dispersed. In the second step (b) PP is added to the mixture. A phase inversion occurs during which the unreacted maleic anhydride groups which were inside the PPMA particles can react. Hereafter the PP forms the matrix-phase and the PA-phase is dispersed. The Molau-Test performed in a qualitative form showed that almost all anhydride groups did react.

The pure polymers used for the measurements were treated in the same conditions, so that the effects of thermal and mechanical degradation which were found to be very small, could be neglected.

Morphology

For the determination of the morphology before the measurements, the blends were contrasted with OsO_4 and samples for the TEM were prepared under liquid nitrogen. The morphology of the sheared samples was determined by SEM microscopy. The measured and rapidly cooled down platelets (the procedure is described in detail below) were broken in

tangential direction under liquid nitrogen. The PA was dissolved from the surface with concentrated formic acid and the sample was sputtered with gold. In both cases the particle size was determined by measuring and counting the particles of the pictures taken.

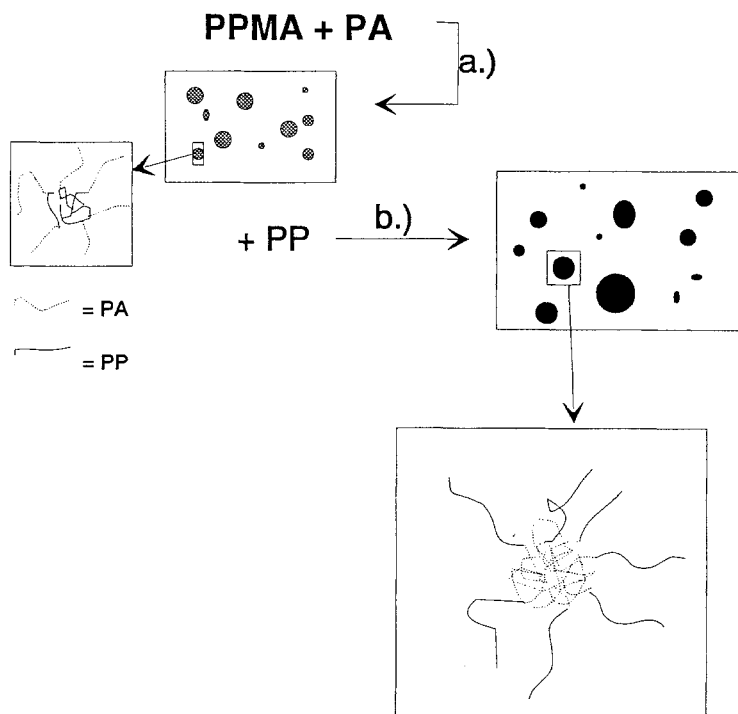


Figure 1: Schematic description of the mixing process

Creep measurements

The measurements have been carried out on a Rheometrics Stress Rheometer with a cone and plate geometry (cone angle 0,1 rad; diameter 12,5 mm). Continuous N₂ purging of the environmental chamber was necessary to avoid degradation. Different stresses were applied to find the region of stress independent (linear viscoelastic) behavior. The measurements were performed at 240° C. At the end of the measurement the samples were immediately cooled down by showering liquid nitrogen into the opened environmental chamber and especially on the sample. According to the procedure with water cooled tools used by Muller et al. [7] one can suppose that the morphology can by this procedure be frozen within at least 3 seconds.

Results

Morphology

The domains show an almost spherical shape. A decrease of the particle size with increasing amount of the compatibilizing agent can be observed. The determined data are given in table 2. During the measurements no changes occur except very large particles which deviate strongly from the medium particle size. These big particles (> 10 nm) which were observed in a part of the pictures were deformed to ellipsoidal shape during the measurements.

Table 2: Morphological data determined by electron-microscopy.

Sample	ϕ PPMA**	ϕ PA**	ϕ PP**	$n(\text{PPMA})/n(\text{PA})^*$	Average domain-radius [μm]
1	0	0,30	0,70	-	fibrous
4	0,025	0,30	0,675	0,18	5
3	0,05	0,30	0,65	0,35	2
4	0,1	0,3	0,6	0,71	1
5	0,2	0,3	0,5	1,41	0,5

* $n(\text{PPMA})/n(\text{PA})$ = number ratio of compatibilizer and polyamide [mol/mol].

** ϕ = volume fraction

Creep measurements

The results listed in table 3 were taken from the measurements at 600 Pa because there the optimum range of the applied torque with the smallest errors was reached. The zero shear rate viscosity, the equilibrium compliance and the terminal relaxation- and retardation-times were determined as follows.

Table 3: Data obtained from the creep measurements. Further explanations are given in the text.

Sample	η_0 [$\text{Pa}\cdot\text{s}$] $\cdot 10^4$	J_e^0 [Pa^{-1}] $\cdot 10^{-4}$	λ_1 [s]	λ_2 [s]	t_2 [s]	α
PP	5.3	2.08	11	53	40	0.43
PA	0.06	14.8	0.85	-	-	-
PPMSA	0.008	-	-	-	-	-
1	3.8	3.3	13	26	19	0.38
2	7.2	2.88	21	54	40	0.39
3	8	4.47	36	75	55	0.39
4	9	4.01	36	110	80	0.37
5	12	5.57	67	148	112	0.43

Determination of the zero shear rate viscosity, η_0

The viscosity graph is very noisy in the terminal flow region as can be seen from figure 2. Therefore the viscosity in that zone was determined as arithmetic average value. The average value is available with the help of the program RECAP II. (Rheometrics)

Determination of the equilibrium compliance, J_e^0

To get the value of the zero shear compliance J_e^0 the flow part must be subtracted from the total deformation. This can also be done with the help of the program RECAP II. The flow region is approached by a tangent in the linear plot of the data. This tangent is then subtracted from the total curve in the whole range of the measurement. The remaining data show the pure elastic deformation with the limiting value of J_e^0 in the terminal zone. As can be seen from the viscosity data, even in the logarithmic plot, the data are very noisy. Therefore the procedure was repeated in different regions of the flow zone to obtain reliable curves for the determination of the plateau value J_e^0 and the terminal retardation time.

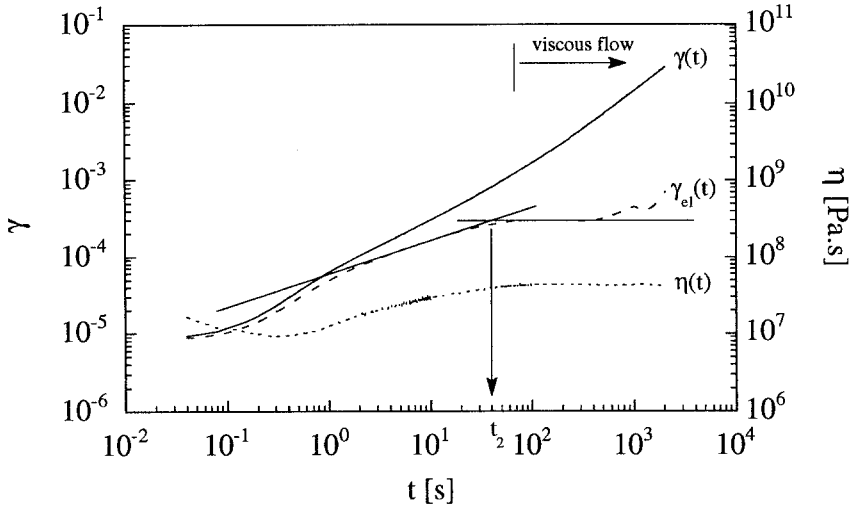


Figure 2: Schematic description of the evaluation of the characteristic rheological quantities from the creep measurement. As an example the creep measurement of sample 2 is shown. (The values of $\gamma(t)$ and $J(t)$ are connected by the relation $\gamma(t) = J(t)/\tau$; τ = applied shear tension = 600 Pa) The corresponding curves $\gamma(t)$ and $J(t)$ can therefore be used adequately.

Terminal relaxation time λ_1

The specific time constant λ_1 is determined according to the equation

$$\lambda_1 = \eta_0 \cdot J_e^0$$

which is known from linear polymers, and which is supposed to work also at the example of polymer blends. It merely gives an expression for the terminal relaxation time.

The values are listed in table 3.

Terminal retardation time λ_2

The two regions in the graph showing the pure elastic deformation and a plateau zone were fitted by tangents. The time constant t_2 was taken at the point of intersection of the tangents (figure 3). From the time constant t_2 the terminal retardation time λ_2 can be calculated using the Maxwell model with fractional derivatives derived by Friedrich and Braun /12/. This leads to an expression for λ_2 in the form:

$$\lambda_2 = \frac{t_2}{\Gamma[\alpha+1]^{1/\alpha}}$$

where $\Gamma(a+1)$ denotes the Gamma-function.

The retardation function of the normal generalized Maxwell model $(1 - e^{-t^2/\lambda_2})$ is less suitable because the slope of the starting zone in the double logarithmic plot should be equal to one according to this model. This is not true for the graphs we obtained for our materials. The resulting values for α , t_2 , and λ_2 are given in table 3.

Discussion

Dynamic measurements have the disadvantage that in the case of polymer blends and generally in materials which are characterized by large time constants, the according processes can't be measured within the experimentally accessible range. The creep measurements were up to the present not used for the characterization of these materials because of the large macroscopic deformations which come along with this method. These deformations were thought to change the morphology so that no information about the genuine material could be obtained by this method. Our basic idea was to apply low enough shear stresses so that changes of the morphology could not occur during the measurement. As can be seen from SEM pictures of the sheared and rapidly frozen samples it is possible to perform creep experiments to large deformations without disturbing the morphology of the sample. Slight deformations occurred only in the case of domains which deviate strongly from the average particle size. From that slightly deformed domains it is possible to estimate roughly the interfacial tension between the polymers using equation /11/

$$\sigma = \tau/2r_D$$

where σ denotes the interface tension, τ the applied shear tension and r_D the equilibrium domain radius at which slight deformations begin to occur. The calculated value of $4,2 \cdot 10^{-3}$ N/m is in good accordance with the value calculated by Muller et al. /7/. This demonstrates clearly that it is possible to make measurements at low stress levels. This observation is in accordance with the fact that linear viscoelastic behavior is observed during the measurements. This can be concluded from the tension independence of the creep compliance $J(t)$. The characteristic data J_e^0 , η_0 , λ_1 , and λ_2 are accessible from the creep experiment. With the help of these data it is possible to compare the different blends quantitatively in terms of emulsion models and to calculate further characteristic parameters of the system such as interface tension. This will be done in a forthcoming paper.

References

1. Wu S (1982) Polymer Interface and Adhesion Marcel Dekker Inc. p 360
2. Creton C, Kramer EJ, Hadziioannou G (1992) Macromolecules 24: 1846
3. Dai KH, Kramer EJ (1992) Macromolecules 25: 220
4. Creton C, Kramer EJ (1992) Macromolecules 25: 3075
5. Ide F, Hasegawa A (1974) J. Appl. Polym. Sci. 18: 963
6. Scholz P, Froelich D, Muller R (1989) J. Rheol. 33(3): 481
7. Graebbling D, Muller R (1990) J. Rheol. 34(2): 193
8. Graebbling D, Froelich D, Muller R (1989) J. Rheol. 33(8): 1283
9. Valenza A, La Mantia FP, Demma GB, Romano V, Acierno D (1991) Polym. Networks Blends 1(2): 71
10. Utracki LA, Sammut P (1992) Polym. Networks Blends, 2: 23
11. Utracki LA, Walsh DJ, Weiss RA (1989) in Multiphase Polymers: Blends and Ionomers Eds. Utracki LA, Weiss RA Am. Chem. Soc. Washington DC, Chapter 1
12. Friedrich CHR, Braun H (1992) Rheol. Acta 31: 309
13. Braun H, Rudolf B, Cantow H-J (1993) " Diblock Copolymers With Blocks Interacting With Immiscible Polymer Blend Components -Interfacial Properties-" Die Makromolekulare Chemie, Theory and Simulations, submitted