Thermo Fisher
S C I E N T I F I C

Characterizing the miscibility of polymer blend systems by Dynamic Mechanical Thermal Analysis

Author

Philipp Beutler
Thermo Fisher Scientific, Karlsruhe, Germany

Keywords

HAAKE MARS iQ Air Rheometer, DMTA, glass transition, polymer blend systems

Introduction

Polymers are widely used in everyday objects as well as in many industrial applications and their uses are increasing rapidly. However, development and commercialization of new polymers are usually time and cost consuming. To fulfill the increasing requirements towards certain mechanical properties, thermal stability, processability or chemical resistance, blending of two or more polymers has proven to be an easy and cost-effective approach for tailor-made material properties for applications ranging from household plastic products to automotive as well as aerospace components.[1]

Depending on the thermodynamic properties of their chemically dissimilar components, polymer blends are characterized regarding their phase structure on a molecular level either to be miscible (homogenous, single phase) or fully immiscible (heterogeneous, phase separation). Some blend systems are only entirely miscible in a limited concentration, temperature and pressure range and may separate if those conditions are not met. Then, heterogenous as well as homogenous components are present, and it is considered partially miscible.[2]

As polymer blends are categorized by their phase structure, most of the characterization techniques for such systems are related to their glass transition. Single-phase, miscible blends will exhibit a single glass transition temperature $T_{g,blend}$, which is generally located between the glass transition temperatures of the blend components.[3] For amorphous blends, this relationship can be described by the Fox equation (1).[4]

$$\frac{1}{T_{g,blend}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \tag{1}$$

In this equation, w_1 and w_2 correspond to the weight fractions and $T_{g,1}$ and $T_{g,2}$ relate to the glass transition temperatures of the individual components. The existence of a single T_g for polymer blend systems by itself does not fulfill the thermodynamic criteria for miscibility. However, the observation of a single T_g for miscible polymer blends is well-documented in literature.[1–3]

Polycarbonate (PC), for example, is an amorphous thermoplastic polymer, which has excellent impact and heat resistance as well as transparency, among other properties. Scratch sensitivity as well as its low chemical resistance are the main technical shortcomings of this polymer. Blending PC with polymethyl methacrylate (PMMA) is believed to improve these shortcomings. Although, due to the immiscibility of commercially available transparent PC and PMMA grades at most blend ratios, opacity is usually observed as an undesired material property.[5]

Melt mixing using twin-screw compounders is a common technique for polymer blend preparation.[3] Depending on the amount of sample and throughput needed, different laboratory devices like the Thermo Scientific™ HAAKE™ MiniLab 3 Micro-Compounder or small-scale twin-screw extruders like the Process 11 Parallel Twin-screw Extruder are available for blend system development.

thermo scientific

Dynamic Mechanical Thermal Analysis (DMTA) offers much higher sensitivity for the determination of glass transitions of polymers compared to other thermal analysis methods like Differential Scanning Calorimetry (DSC) or Thermo-Mechanical Analysis (TMA).[6] Hence, in this application note, the influence of different component ratios of binary PC/PMMA blend systems on the resulting glass transitions obtained by means of DMTA is evaluated, to get insight into the phase structure that is present. Please note that this application note focuses on physical mixtures only, chemical mixtures of polymers such as copolymers are not in scope.

Materials and methods

Subjects of this investigation were commercially available PC and PMMA grades used for 3D printing applications. Various blend ratios of these materials were prepared according to Table 1.

Blend #	PC / wt%	PMMA / wt%
1	60	40
2	50	50
3	40	60

Table 1: Ratios of PC:PMMA blend systems used for this study.

In the following, the blend ratio of the neat component PC in X wt% to the neat component PMMA in Y wt% will be abbreviated as X:Y.

To ensure a homogenous blend of both components, the prepared systems were mixed in a two-step process. First, mechanically using a blending machine. Second, 10 g of each polymer blend was filled into the barrel of a HAAKE MiniLab 3 Micro-Compounder. Melt mixing was done at a temperature of 260 °C and with a rotating speed of the screws of 50 rpm. The micro-compounder was equipped with two pressure sensors as well as a bypass valve. To ensure homogenous melt mixing, the polymer blend melts were continuously mixed using a backflow capillary with a closed bypass valve. Residence time for each blend system was adjusted according to the pressure difference.

As soon as the difference was constant or a residence time of 5 min was reached, the bypass valve was opened, and the melt was transferred into an electrically heated injection cylinder of a HAAKE MiniJet Pro Injection Molding Machine. Subsequently, 50 mm x 2 mm x 10 mm (length x width x thickness) bars were molded. Neat component PC and PMMA reference samples

were injection molded without any additional extrusion steps. Table 2 shows the temperatures of both the cylinder and the mold, as well as the injection and holding pressures and their respective times.

Dynamic Mechanical Thermal Analysis was conducted using a HAAKE MARS™ iQ Air Rheometer equipped with a TM-CR-O450 temperature module. All thermo-mechanical measurements were performed using a solids clamping fixture. Figure 1 shows the temperature module in combination with the clamping fixture.
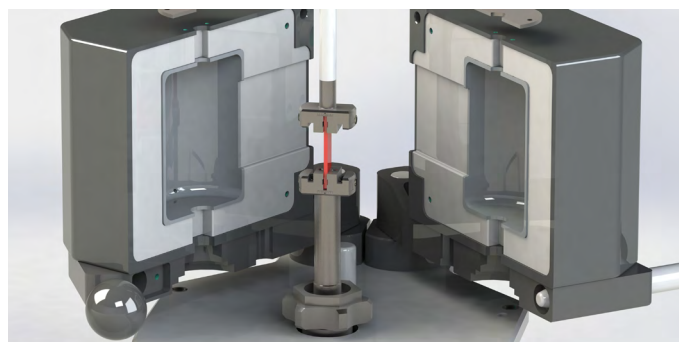

Figure 1: Temperature module TM-CR-O450 in combination with solids clamping fixture.

An oscillation deformation amplitude γ_0 of 0.04 %, which is within the viscoelastic range of the blend systems and their neat components, as well as a frequency f of 1 Hz were selected as test parameters. The temperature ramp ranged from 30 °C to 200 °C with a heating rate of 2 K/min. To compensate for thermal expansion, the normal force control of the rheometer was activated and set to maintain a constant value of 0 N. The measurement routine of the HAAKE RheoWin™ Rheometer Control Software is shown in Figure 1.
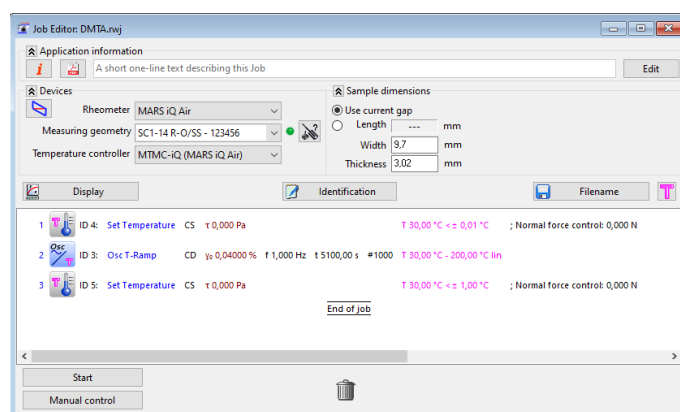

Figure 2: Measurement routine in HAAKE RheoWin Software.

PC:PMMA / wt%	Cylinder temperature / °C	Mold temperature / °C	Injection pressure / bar	Injection time / s	Holding pressure / bar	Holding time / s
100:0	260	80	600	5	150	5
60:40	260	70	600	5	150	5
50:50	260	70	600	5	150	5
40:60	260	70	600	5	150	5
0:100	230	60	600	5	150	5

Table 2: Injection molding parameters for PC, PMMA and PC:PMMA blends.

Results and discussion

Assessing the thermo-mechanical properties over a broad temperature range

Thermo-mechanical properties of a material can be assessed by applying a sinusoidal force or deflection to a solid sample while simultaneously varying the experiment temperature. Figure 3 illustrates the various distinct physical states that an amorphous polymer undergoes with increasing temperature obtained by torsional DMTA.

Polymer chains become increasingly mobile as the free volume expands with increasing temperature.

Beyond a certain temperature, polymeric materials show a phase transition from a rigid and inflexible glassy state into a more flexible rubbery state before entering liquid flow. An opportunity to characterize the various physical states a polymer passes is by monitoring the storage modulus G' as a function of temperature. Starting from a fairly constant storage modulus of ~10^9 Pa in the glassy state, the polymer becomes leatherier as it enters its glass transition. Above the glass transition temperature, in the range of ~10^6 Pa, an amorphous polymer enters its rubbery plateau region and exhibits elastic behavior that can be compared to an elastomer. At even higher temperatures, the polymer still exhibits rubbery properties but shows a tendency to flow. Hence, it enters its rubbery flow regime. Beyond this physical state, the polymer flows like a liquid.[7]

Depending on the components present in the tested material, different mechanical properties become apparent. Figure 4 illustrates the dependency of the storage modulus on the blend ratio PC:PMMA.

All materials tested exhibit a storage modulus in the range of ~10^9 at 80 °C indicating that they are in their glass region.

At around 115 °C, PC starts to soften and enters its glass transition. For blends with decreasing PC content, the onset of glass transition shifts significantly towards lower temperatures. In general, reducing the PC content below 60 wt% will weaken the strength of the resulting blend in the glassy region. However, adding PMMA to PC broadens the transition range for all blend systems. Depending on the final application of a blend, this effect must be taken into consideration. Additionally, the 40:60 as well as the 50:50 blend system show a less steady transition indicating a partial miscibility that can be analyzed more conveniently using the loss modulus G'' or the loss factor tan (δ).

Besides this, at temperatures above 130 °C, both blend systems show a similar rubbery plateau/flow regime like neat PMMA, whereas a 60:40 composition gets closer to the properties of PC in its rubbery state.

Characterizing miscibility of polymer blends by their glass transition

A glass transition of polymers does not occur at a single temperature, but over a certain temperature range. Hence, several evaluation methods like the maximum of G'' or tan (δ) can be used to obtain a single reference value (T_g) as an indicator for the glass transition. More information regarding the evaluation of DMTA measurements can be found in [7]. For this study, the glass transition evaluation method of the maximum of tan (δ) was chosen.
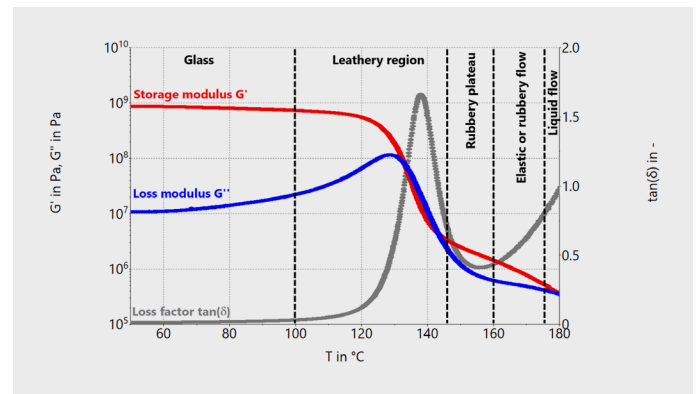

Figure 3: Thermogram of an amorphous polymer and its various physical states with increasing temperature according to.[7]
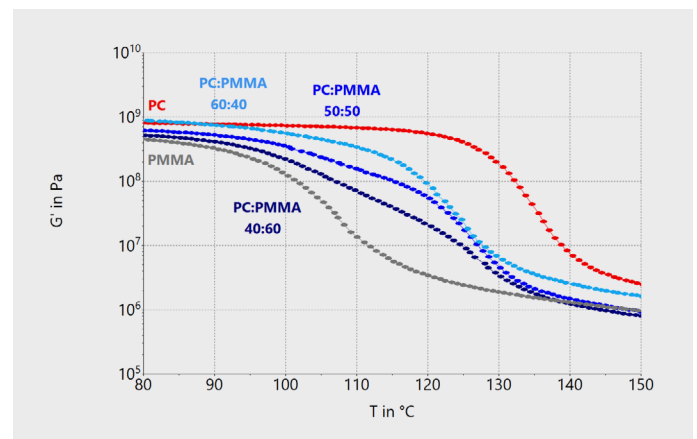

Figure 4: Storage modulus G' of PC:PMMA blend systems with blend rations 60:40, 50:50 and 40:60 as well as their neat components.
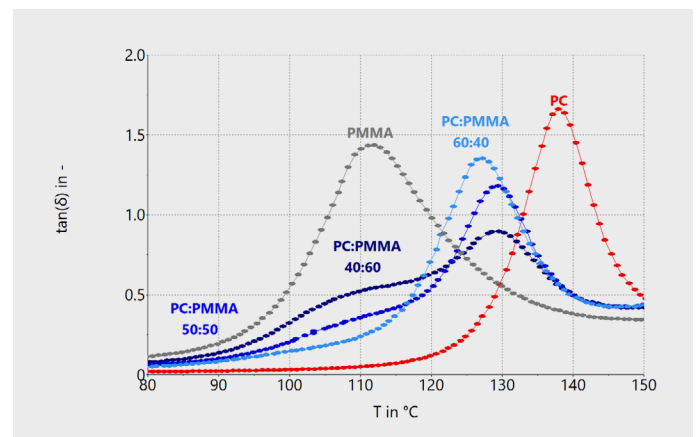

Figure 5: Loss factor tan (δ) of PC:PMMA blend systems with blend rations 60:40, 50:50 and 40:60 as well as their neat components.

As the maximum in tan (δ) of the PMMA component in the 40:60 as well as 50:50 ratio cannot be identified sufficiently, the inflection point was used as an approximation of this maximum. Table 3 shows the obtained values for T_g.

PC:PMMA / wt%	$T_{g,PC}$ / °C	$T_{g,PMMA}$ / °C
100:0	138	—
60:40	127	
50:50	129	110
40:60	128	110
0:100	—	112

Table 3: Obtained glass transition temperatures for the neat PC and neat PMMA component as well as their respective blend systems.

When mixing two polymers to obtain a binary blend, miscibility depends on the solubility of the dispersed phase in the matrix component.[2] Hence, a good solubility and, therefore, a possible miscibility of both components can be identified by a single glass transition temperature, which will be located in between the glass transition temperatures of the neat components. If a binary blend shows the occurrence of two glass transition temperatures identical to those of the neat components, it can be considered immiscible. If the glass transition temperatures are shifting towards each other, but do not fully merge into one single temperature, the components are soluble to a certain extent and the blend system can be characterized as partially miscible. In the case of the PC:PMMA blend systems discussed here, the glass transition temperature of the PMMA component for the 40:60 and 50:50 blend ratios cannot be identified as a clear maximum, but as a shoulder in the range of the T_g of the neat PMMA, whereas, the T_g of the PC:PMMA blend component can be identified for all ratios. With decreasing PMMA content from 60 wt% to 50 wt%, this shoulder gets less prominent, but the inflection point as a measure of T_g remains around 110 °C, which is characteristic of immiscibility.

Nevertheless, a PC:PMMA blend ratio of 60:40 shows only one maximum in tan (δ) and hence appears to be fully miscible. A possible explanation for this might be that the PMMA within the PC:PMMA blend systems is only miscible up to a certain saturation concentration.

As already mentioned, miscible polymer blends obey the Fox equation as described in equation (1). For the 60:40 blend system, the theoretical glass transition temperature is 126 °C which is quite close to the experimentally observed 127 °C. For a final proof of miscibility, for example, a microscopic analysis by means of Transmission Electron Microscopy (TEM) could be utilized.

Miscibility is not always a desired property of polymer blends. In fact, in an immiscible phase structure, all the characteristic properties of the blend components remain, whereas a miscible blend is characterized with properties intermediate of the neat components. However, immiscible structures tend to be weak at the interfacial boundaries between the polymer components. Hence, certain properties like the mechanical strength can be severely limited. Compatibilization or reactive extrusion can be used to improve the interfacial strength of blend systems by creating chemical or physical interphase connections between the blend partners.[2]

Besides improving mechanical properties, also optical properties can be improved, among other things. In the case of PC:PMMA blend systems, the opacity observed for commercially available transparent PC and PMMA grades at most blend ratios can be overcome by utilizing reactive extrusion.[5]

Conclusion

In this application note, the concept of miscibility of polymer blend systems was introduced and DMTA as a thermo-mechanical technique to scan for miscibility was presented. To mimic industry standards, PC:PMMA blends with varying blend ratios were compounded by means of melt mixing and specimen needed for thermo-mechanical analysis were generated using injection molding. The storage modulus G' was discussed to identify the different physical states a polymer undergoes with increasing temperature. Besides this, the maximum and shape of the loss factor tan (δ) curve was presented as an evaluation method for a characteristic glass transition temperature to characterize miscibility. Finally, the Fox equation was used to prove miscibility for a 60:40 PC:PMMA blend ratio.

References
1. Thomas, S., Grohens, Y., Jyotishkumar, P. – Characterization of Polymer Blends: Miscibility, Morphology, and Interfaces – 1st Edition (2015)
2. Utracki, L. A., Wilkie, C. A. – Polymer Blends Handbook – 2nd Edition (2014)
3. Robeson, L.M. – Polymer Blends – 1st Edition (2008)
4. Fox, T., G. – Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Polymer System – Bull. Am. Phys. Soc. 1, 123 (1956)
5. Bubmann, T., et al. – Transparent PC/PMMA Blends with Enhanced Mechanical Properties via Reactive Compounding of Functionalized Polymers – Polymers, 14, 73 (2022)
6. Menard, K. – Dynamic Mechanical Analysis – A practical introduction – 2nd Edition (2008)
7. Menczel, J., D, Prime, R., B. – Thermal Analysis of Polymers - Fundamentals and Applications – 1st Edition (2009)
8. Beutler, P. – V301 - Impact of irradiation time on reaction kinetics and thermo-mechanical properties of an UV light sensitive adhesive (2022)

Learn more at **thermofisher.com/rheometers**

thermo scientific