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Phase behavior of poly(methylmethacrylate) and poly(α-methylstyrene-co-acrylonitrile)-PMMA/MSAN-Blends

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Summary

Phase equilibrium curves of blends of PMMA and MSAN have been determined by means of laser light scattering. In dependence of the copolymer composition blends exhibit immiscibility and miscibility and LCST behavior. A window of miscibility can be designed in the temperature-copolymer composition plane.

Introduction

Blends of PMMA/MSAN are known to exhibit lower critical solution temperature (LCST) behavior if the AN content of the copolymer is 30 wt% (1). One expects for the system PMMA/MSAN a similar behavior as it can be observed for blends of PMMA and poly(styrene-co-acrylonitrile) (SAN). In these systems miscibility is found in the range of copolymer compositions from 9 up to 26.5 wt% of AN in the SAN (2), but for a given system only up to a certain temperature at which phase separation occurs (LCST behavior) (3). As a result in the temperature-copolymer composition plane a miscibility window is obtained. The window of miscibility seems to be a general phenomenon for a certain class of homopolymer/random copolymer blends (4,5,6).

The aim of the present report is to check the phase behavior of PMMA/MSAN blends within a wide range of copolymer compositions.

Experimental

The MSAN was prepared at 75°C in ethylbenzene with 0.04 mol/l AIBN and a monomer concentration of 8 mol/l. The maximum degree of conversion was about 6 p.c.. The copolymer composition was determined by Kjeldahl method. Fig. 1 shows the copolymerization diagram. The molecular weights estimated by g.p.c. are listed in Tab. 1. The polymerization of PMMA (M_w = 43000, M_w/M_n = 1,72), the blend preparation and phase diagram determination were made by using equipment and methods detailed in a previous paper (7).

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A Perkin-Elmer DSC-4 was used for the Tg measurements. The sample weight was about 10 mg and the heating rate 10 K/min.

Tab.1: Molecular weights of MSAN samples estimated by g.p.c.

MSAN wt% AN	M_w g/mol	M_w/M_n
0	136000	1.19
18.5	5900	2.68
30.5	16000	2.23
31.3	18700	1.75
33.1	19800	2.05
34.8	19800	1.94
41.3	17300	2.50
44.3	15600	2.78
53.4	16000	2.64

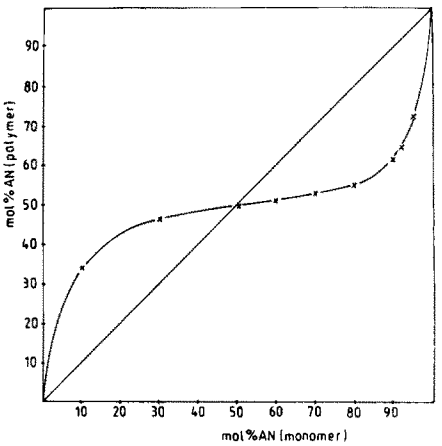

Fig.1: Copolymerization diagram of MSAN

Results and Discussion

To design the window of miscibility the phase behavior of PMMA/MSAN blends was studied for different copolymer compositions. The binodals determined by laser light scattering are summarized in Fig.2.

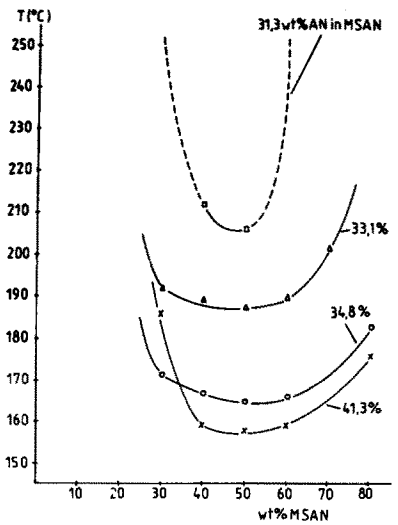

Fig.2: Binodals for blends of PMMA with MSAN containing different AN amounts

According to Fig.1 it is impossible to prepare high molecular weight MSAN copolymers with low AN contents by free radical copolymerization. As the lower limit we could get a copolymer with an AN content of 18.5 wt%. Due to the fact,

however, that all of the three involved segmental interactional parameters are positive one expects a window of miscibility in the temperature-copolymer composition plane (6). To estimate the miscibility window at low AN contents a 40/60 blend of poly(α-methylstyrene) anionically prepared and PMMA was investigated. The results are presented in Fig.3.

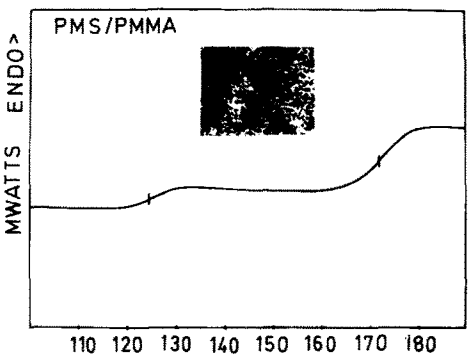

Fig.3: DSC trace of PMS/PMMA/40/60 blend and the phase morphology observed by light microscopy

As expected the DSC trace displays two glass transition temperatures. The immiscibility is also evidenced by the two phase morphology.

All of the experimental results used to design the miscibility window are listed in Tab. 2. The miscibility window is depicted in Fig.4.

Tab.2: Values for the determination of miscibility window

wt% AN in MSAN	cloud point for 60/40 blends / °C
0	cloud
18.5	clear up to the decomposition
30.5	clear up to the decomposition
31.3	212
33.1	190
34.8	167
41.3	159
44.3	cloud
53.4	cloud

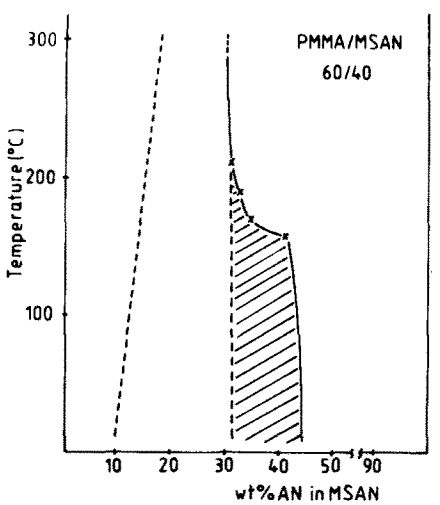

Fig.4: Miscibility window of PMMA/MSAN/60/40 blends

The hatched area represents the range of copolymer composition in which PMMA/MSAN/60/40 blends display LCST behavior. For blends with an AN content in the range from 30.5 wt% up to a probably very low content of AN in the MSAN copolymer

the LCST exceeds the decomposition temperature. Finally, blends containing MSAN with an AN content above 44.3 wt% are cloud at room temperature.

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