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The Compatibility of the Polystyrene/Acrylonitrile-Butadiene-Styrene Grafted Copolymer System

2. Concentrated Solutions and Solid State

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Summary

The study of polystyrene (PS)/acrylonitrile-butadiene-styrene (ABS) grafted copolymer/cyclohexanone or methylene chloride system compatibility both in concentrated solutions and solid state has been carried out by phase separation, viscosimetrical measurements and thermal behaviour.

Having in view the obtained data it has been ascertained that the systems present different degrees of compatibility depending on the mixtures composition. At higher temperatures, the compatibility of the components is changed.

Introduction

The acrylonitrile copolymers with various comonomers have large use for the commodity and industrial applications.

In order to obtain the desired complex properties corresponding to each domaine of use, on resort either to the multiple copolymerization, or to the one another blending of different copolymers or to the blending with the corresponding homopolymers.

Owing to the great practical importance of these, the compatibility of the binary copolymers acrylonitrile (AN) with different polymers was studied (1-3). Generally, these mixtures are incompatible. There are known few studies concerning with the behaviour of the ABS copolymer/PS system (4,5). Such mixtures appear either during styrene copolymerization or as wastes obtained in the synthesis reactions or from the worn-out industrial and consumer's goods products. Afterwards these wastes can be subjected to an undestructive (by reprocessing) or destructive recovery (pyrolysis, chemical modification, etc). The product qualities resulted from copolymerization or after the wastes recovery process are greatly influenced by the compatibility of the components. That is why, there was necessary to study the compatibility of ABS/PS system in concentrated solutions and solid state as well as the thermal behaviour, the latter being also dependent of the mutual solubility of the components (6,7).

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Experimental

ABS copolymer and PS are those used in the previous paper (8), which were purified by precipitation from methylene chloride solution. Mixtures were prepared with the two components in the following ratios: 90/10, 75/25, 50/50, 25/75 and 10/90, the solutions of 10% concentration being stirred 15-20 min. at 60-70°C. After dissolution, the solvent loss (methylene chloride or cyclohexanone) was added. A part of the solution was precipitated and vacuum dried at 50-60°C for 48h. The other part was kept in ground glass stopper cylinders, watching on the phase separation, and it was determined the dynamical viscosity by means of a Brookfield viscometer using adequate cylinders and spin velocity.

The microscopical examination was carried out in phase contrast, 600 x, with the aid of a MC-1 microscope IOR-Bucharest.

The thermal behaviour has been studied by thermogravimetrical method, pyrolysis and pyrolysis-gas chromatography and different methods of the analysis of the thermal degradation products.

The TG curves were recorded using a MOM-Derivatograph, Paulik-Paulik-Erdey type, on powdered polymer samples with a granulation of 0.1 -0.5 mm, in mixture with freshly calcined Al_2O_3 (20% sample) at 1100°C, working in the following conditions: sample weight 20 mg, heating rate 12.4°C/min. The activation energies were estimated by COATS-REDFERN (9) (global values E_{CR}) and REICH-LEVI (10) methods. By the second method it was obtained the variation of the activation energy with the conversion degree (α) resulting two characteristic values: E_{LR-I} for α=0 -0.1 and E_{LR-II} for α =0.1 -0.6.

The gas chromatographic pyrolysis was carried out at 570°C for 10 sec. by means of a filament type unit coupled with a SIEMENS L-400 gas chromatograph provided with a flame ionization detector and working under following operational conditions: sample weight 0.4mg, the stainless steel column (2m x 4mm i.d.) was packed with Chromosorb W (60-80 mesh) coated with 15% free fatty acid phase (FFAP) washed with acid and silanizated; the column temperature being programmed between 60 to 200°C at a rate of 4.5°C/min. The identification of the pyrolysis products was made by using the relative retention times of various pure substances and relative quantities of each component were determined from the corresponding surfaces. The same conditions were also used to establish the relative differences in the composition of the liquid fraction resulted from the thermal decomposition of the PS, ABS and their mixtures in a autoclave reactor which was previously described (11), at 400-470°C in an inert atmosphere. As a consequence of the pyrolysis process, gases, liquid and solids were obtained in quantities which were presented in the table 1. A quantity of 5-3% gas fraction; 88-96% liquid fraction and 7.3-0.8% solid residue, was obtained for ABS, mixtures and PS respectively.

The density of the gas fraction was measured by pycnometer method and the HCN content was established by CHELLE-REGNIER colorimetrical method (12). For the liquid fraction were determined: density, dynamical and kinematical viscosity (by means of a Höppler viscometer). The composition was analysed by gas-chromatography and NMR spectroscopy. The NMR spectra were recorded with a JEOL C-60 HL spectrometer at 60MHz, the samples being dissolved in CCl_4. From these spectra a styrene index was calculated (I_S) as the ratio of the protons integral, corresponding to the vinyl group of the styrene monomer and the whole integral. The solid residue of the decomposition was characterized by elemental analysis.

Results and discussion

The phase separation study of the two polymer mixtures in cyclohexanone or methylene chloride concentrated solutions, show that the solutions rich in ABS (100-75%ABS/0-25%PS) are opaque, their aspect is unchangeable during a month,while those rich in PS (50-10%ABS/ 50-90%PS) are separated in two phases after a day. The volume of separated phases is approximately equal to that of the solutions used in the mixture preparation and after five days it is unchanged. Of course, the PS solution is clear und unchanged.

The dynamic viscosities of the two polymer mixtures in solution are inferior to those additively calculated (figure 1a) proving that the components incompatibility is due to the repulsive interactions; the deviations keep unchanged in time,but the values increase owing to the crowded particles in ABS rich solutions (figure 1b). It must be emphasized the great influence of the concentration, in this case. In diluted solutions, the deviations from additivity were positive (see bibl. 8), consequently attractive interactions between components are dominating. The solvent nature is less important for the compatibility of these components.

In the figure 2 it is presented the variation versus composition of the initial degradation temperature (T_i) and the temperature corresponding to the maximum decomposition rate (T_m). The variation of the apparent activation energies (E_{CR}) or those for different conversion degrees (E_{LR-I} and E_{LR-II}) is shown in figure 3. It is observed the more advanced incompatibility of the systems rich in PS, but only for the first stages of degradation.

At higher temperatures, the curves aspect changes, the temperatures corresponding to the maximum decomposition rate are much higher although the activation energies remain inferior than that of pure components and to those additively calculated; they present different deviations which are greater for systems rich in PS.

These data evidenced that the behaviour and compatibility of the PS/ABS systems are dependent on time and change at higher temperatures. This conclusion results from figures 4 and 5 where it is presented the microscopical aspect of the films: (a) immediately after

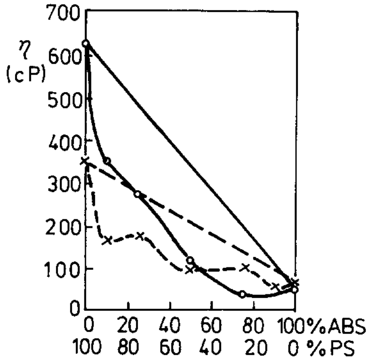

Fig.1a. The variation of the dynamical viscosity with composition for ABS/PS system (---) initial and (——) after four months of preparation

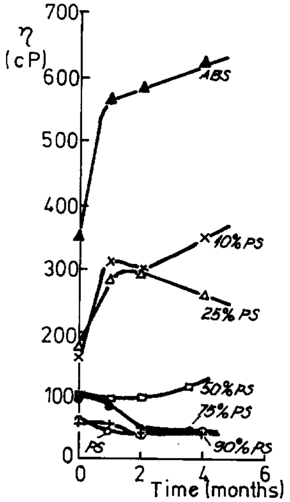

Fig.1b. The variation with time of the dynamical viscosity for ABS/PS system

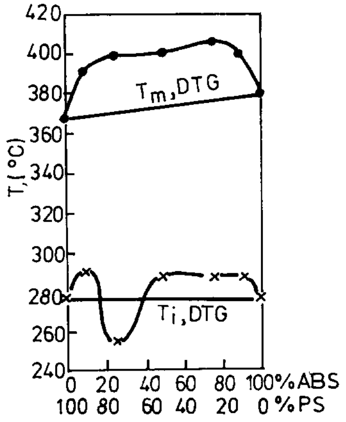

Fig.2. The variation of the T_i and T_m (evaluated from DTG curves) with ABS/PS mixtures composition

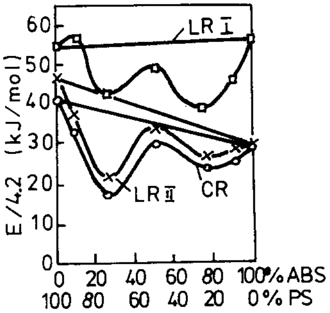

Fig.3. The variation of activation energies versus ABS/PS mixtures composition

preparation; (b) after a lapse of a year and (c) thermal treated for an hour at 160°C.

The initial aspect of the film (a) depends on the mixture composition. After a year, usually, it appears same homogenization (b), which becomes more obvious after heating (c).

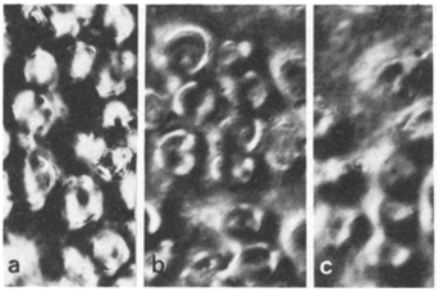

Fig.4. Microscopical aspects of the 50ABS/50PS mixture film

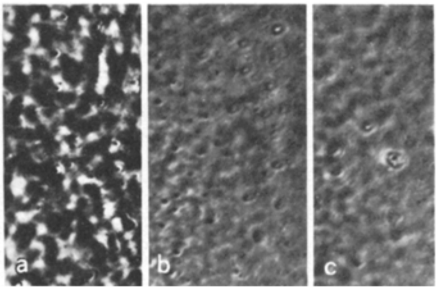

Fig.5. Microscopical aspects of the 75ABS/25PS mixture film

Greater deviations occur in the thermal decomposition products characteristics resulted at 450°C (autoclave reactor) and 570°C (pyrolysis-gas chromatography), as it results from the data listed in tables 1 and 2 respectively; the majority of experimental data are in a large extent different from those calculated considering the additivity of the corresponding values to the pure components.

The greatest differences are to be found in gaseous and liquid fractions composition, for instance, the experimental data for HCN, toluene, m- and p-xylene, styrene and α-methylstyrene are inferior to those calculated and the values corresponding to the unidentified components are simultaneously increasing. The nature of these components is peculiar to each mixture, as it results from the chromatograms of the liquid products presented in figure 6 ; these are similar in a large extent to the mixture pyrogramms resulting from the data comparison in tables 1 and 2 (excepting the fact that in the pyrogramms are evidenced the butadiene and C_1-C_4 hydrocarbons that are presented in the gaseous fraction obtained from decomposition using both procedures.).

The unidentified components may by dimers or trimers that originate in different comonomers, as it was established in the thermal decomposition of some S/AN binary copolymers (13). Along with these products , an other compounds could results as well because of the chemical intercations which appear by heating of the systems containing ABS copolymers. These intercations have been evidenced in another papars, too (14).

On comparing all the results, appears clearly that the mixtures rich in PS have a greater difference in their behaviour and the modification of compatibility degree by thermal treatment is more evident.

The presented data showed that the new components apparition at the thermal decomposition was influenced by the mixture composition and compatibility of the components.

Table 1

The reaction products characteristics resulting from thermal decomposition of ABS/PS systems, at 400 - 450°C

Property	ABS	90 ABS 10 PS		75 ABS 25 PS		50 ABS 50 PS		25 ABS 75 PS		10 ABS 90 PS		PS
		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	
				Gaseous fraction (5-3 %)								
Density (g/l)	1.13	1.14	1.14	1.14	1.17	1.18	1.19	1.27	1.25	1.28	1.28	1.29
HCN(mg/100g s.)	91.83	18.28	82.65	11.64	68.87	8.95	45.92	7.34	22.96	2.41	9.18	-
				Liquid fraction (88-96 %)								
Density (g/cm^3)	0.94	0.94	0.94	0.95	0.94	0.94	0.93	0.94	0.93	0.93	0.93	0.92
Dynamical viscosity (cP)	3.23	2.55	3.07	2.59	0.82	2.05	1.77	3.15	2.01	2.12	1.77	1.61
Kinematical viscosity(cSt)	3.42	2.69	3.28	2.74	2.99	2.18	2.57	3.37	2.16	2.23	1.90	1.73
Composition(%)												
Acrylonitrile	2.51	2.28	2.25	2.26	1.89	2.96	1.25	2.24	0.75	1.07	0.25	-
Toluene	10.06	9.82	10.27	9.89	10.59	7.84	11.13	10.73	11.66	9.38	11.98	12.20
m- ,p-xylene	11.36	10.48	11.39	10.68	11.45	9.06	11.54	9.14	11.63	9.11	11.68	11.72
o-xylene	2.83	2.06	2.64	2.12	2.15	1.97	1.92	1.57	1.26	1.03	1.16	1.00
Styrene	45.29	41.46	46.26	41.35	47.72	43.01	50.15	42.50	52.51	46.83	54.04	55.01
I_S(NMR)	38.98	39.22	41.13	40.20	44.37	40.13	49.76	46.38	55.15	53.89	58.39	60.55
α -methyl styrene	11.49	11.22	11.82	11.26	12.30	12.48	13.12	13.86	13.73	12.32	14.42	14.74
Unidentified Compounds	16.05	24.21	14.96	22.30	13.32	20.95	10.59	19.81	8.79	20.01	7.39	5.12
				Solid residue of decomposition (7.3 - 1 %)								
C(%)	69.28			66.86	66.24			57.15	66.17			66.60
H(%)	3.39			3.34	3.27			2.93	3.05			3.00
N(%)	4.15			3.65	3.49			1.52	1.03			0.00
Noncombustible residue (%)	17.43			24.16	22.66			38.39	22.17			30.40

Table 2
The amount of the main products obtained on the pyrolysis of ABS, PS and ABS/PS mixtures

Substance	ABS	90 ABS 10 PS		75 ABS 25 PS		50 ABS 50 PS		25 ABS 75 PS		10 ABS 90 PS		PS
		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	
C_1-C_4 hydrocarbons	2.05	0.15	1.82	0.16	1.56	0.10	1.01	0.13	0.67	0.08	0.43	0.21
Butadiene	2.05	1.11	1.84	1.15	1.58	0.80	1.03	0.55	0.51	0.29	0.21	-
Acrylonitrile	11.36	12.38	10.22	8.42	8.52	6.53	5.68	3.40	2.84	0.92	1.14	-
Toluene	4.76	5.39	4.72	4.91	4.67	4.52	4.59	4.71	4.51	4.74	4.45	4.42
m,p-xylene	1.07	1.25	1.06	1.51	1.03	1.10	0.99	1.16	0.96	0.93	0.94	0.92
o-xylene	0.16	0.10	0.14	0.14	0.12	0.27	0.08	0.27	0.04	-	0.01	-
Styrene	66.08	64.18	68.60	68.20	74.25	71.59	78.62	74.65	84.88	77.94	88.12	91.16
α-methyl styrene	2.76	3.15	2.62	3.08	2.42	2.94	2.08	2.67	1.74	1.73	1.54	1.40
Unidentified Compounds	15.18	13.15	13.83	12.40	11.43	12.12	8.43	12.34	3.92	13.76	3.03	1.68

These relative values were established to estimate the diferences in the thermal behaviour of the mixtures as compared to the corresponding homopolymers.

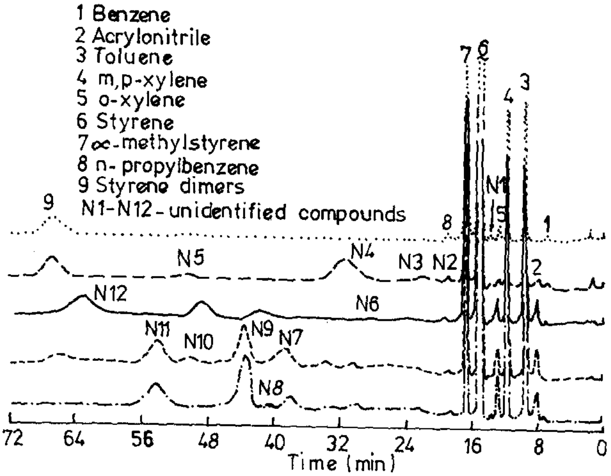

Fig.6. The chromatogramms of the liquid fractions resulted at the thermal decomposition of the PS, ABS and different mixtures at 400-450°C.

References
1. BREUERS W., HILD W. and WOLFF H., Plaste u. Kautschuk, 1, 170 (1954)
2. ZLATKIEVICH L.Yu. and NIKOLSKII V.G., Rubber Chem. Technol., 46, 1210 (1973) ; JORGENSEN A.H., CHANDLER L.A. and COLLINS E.A., Rubber Chem.Technol., 46, 1087 (1973)
3. ENYIEGBULMAN M. and HOURSTON D.J., Polymer, 20, 818 (1979)
4. BELESTRINI A.,"Seminaire sur l'utilization des déchets de hauts polymères" Dresda 18-23 Sept.(1978)
5. GLEZIN I.L., PETROV V.N., BEZMOZGIN E.S., VINOGRADOV A.P. and BRYSKOVSKAIA A.V., Plast. Massy, 5, 59 (1978)
6. VASILE C. and SCHNEIDER I.A., European Polymer J., 10, 381 (1974)
7. VASILE C., SCHNEIDER I.A., AIRINEI A. and CHIRIAC A., European Polymer J., 12, 749 (1976)
8. SABLIOVSCHI M.V., IOAN S. and VASILE C., Polymer Bull. 5, 53 (1981)
9. COATS A.W. and REDFERN J.T., Nature (London) 201, 68 (1964)
10. REICH L. and LEVI D.W., Makromol. Chem., 66, 102 (1963)
11. VASILE C., SCHNEIDER I.A., CASCAVAL C.N., CALUGARU E.M. and SABLIOVSCHI M.V., Romania Patent 74577 (1980)
12. KOHEN-ABREST E., "Precist de Toxicologie" Ed. G. Doint, Paris, 1948, p. 81
13. GRASSIE N. and BAIN D.R., J.Polym. Sci., A-1(8), 2653, 2665, 2679 (1970)
14. DOKUKINA L.F., EGOROVA E.I., EREMINA E.N., SIVOGRAKOVA K.A., USMANOVA N.F., NIKITIN Yu.V., SHAFIR K.F., GOLUBEVA A.V. and BRYSKOVSKAYA A.V., Plast.Massy, 1, 7 (1971)

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