Properties of Polystyrene/Poly(butyl acrylate) Core/Shell Polymers Modified with *N*-Methylol Acrylamide

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Summary: Polystyrene/poly(butyl acrylate) PS/PBA polymer dispersions with core/shell particles functionalized by N-methylol acrylamide (N-MA) were prepared through two-steps emulsion polymerization. The influence of N-MA situated in shell and/or in core/shell of particles on the crosslinking reaction was studied to relate its mechanical properties and organic solvent resistance of films cast from basic and modified PS/PBA latexes. The changes in the phase arrangement of functionalized and unfunctionalized films after treatment with solvent and annealing were monitored. It was found that at the presence of N-MA the crosslinking reaction occurred already during the polymerization. Films from functionalized dispersions exhibit improved tensile strength and higher resistance against organic solvent.

Introduction

In recent years the commercial interest in multiphase polymer systems combining positive properties of individual components markedly increased. One of the way to prepare multiphase polymer systems is mixing different polymer types[1,2)]. Another possibility is two-steps seeded emulsion polymerization. In the course of emulsion polymerization simple microgels as well as multilayer latex particles of core/shell type from one or several types of polymers can be prepared[3-5)]. Core and shell parts of latex particles containing suitable functional groups can be crosslinked[6,7)]. Polymer latexes with core/shell morphology are good materials to prepare films for various applications[5)].

The present work deals with preparation of the polystyrene/poly(butyl acrylate) PS/PBA polymer dispersion with core/shell particles, which comprise methylol groups. These functional groups from N-methylol acrylamide N-MA enter into either only the shell of particles or both the core and shell of particles during the two-step emulsion

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polymerization. The influence of functional monomer N-MA content on crosslinking reactions and on mechanical properties of films prepared from functionalized core/shell polymers was investigated. Changes of morphology of functionalized material after treatment by organic solvent and annealing via the method of scanning electron microscopy were studied.

Experimental Part

Polymerization procedure. The seeded two-steps emulsion polymerization was carried out in glass reactor at 40°C. The recipe of polymerization is given in Table 1. In the first step, styrene (S) or its mixture with functional monomer *N*-methylol acrylamide (N-MA) was added dropwise to the emulsion containing aqueous solutions of emulsifiers (Slovasol 2430 0.145 mol/dm^3 and dodecyl sodium sulfate DDHS 0.146 mol/dm^3), initiator (potassium peroxodisulfate $K_2S_2O_8$ 0.092 mol/dm^3) and activator (sodium dithionite $Na_2S_2O_4$ 0.1139 mol/dm^3). After the end of the first step, additional initiator and activator solutions were charged and during the second step butyl acrylate (BA) or its mixture with N-MA was continuously added. The polymerization was followed at selected time interval by taking of the latex samples. After precipitation of polymers from the emulsion in cold methanol, the samples were dried and conversion of polymer was calculated in wt.% of the monomer feed.

Preparation of films. The layer of dispersion with a thickness of about 50 μm on glass support was applied and dried over three days at 25°C. Consequently the samples were heat treated at standard conditions for 6 hours at 60°C and/or for 1 hour at 100°C.

Sol-gel analysis. The polymer samples were immersed in ethylmetylketone (EMK) for 48 hours at 25°C. The content of insoluble portions was determined gravimetrically.

Tensile strength of films. The tensile strength on the film specimens of standard dimension was measured by using an Instron. The tensile strengths of films were determined from the force at break.

Scanning electron microscopy. The phase arrangement of films was examined by the scanning electron microscope Tesla BS-340. The specimens after cooling in liquid nitrogen were broken, covered with gold and introduced to the SEM chamber at room temperature and the fracture surface was examined.

Table 1. The recipe of two-steps seeded emulsion polymerization

1st step / PS seed		2nd step / BA	
Ingredients	m / g	Ingredients	m / g
Slovasol 2430	1.74		
DDHS	0.43		
$K_2S_2O_8$	0.19	$K_2S_2O_8$	0.19
$Na_2S_2O_4$	0.06	$Na_2S_2O_4$	0.06
S	19.13	BA	19.17
N-MA	0.025-0.15[a) c)]	N-MA	0.025-0.15[a) c)]
			0-3.0[a) b)]

[a)]weight % in monomers mixture
[b)]volume of N-MA was charged only in the 2nd step of polymerization; designation of samples PS/P(BA/N-MA).
[c)]N-MA was divided equally in both 1st and 2nd step; designation of samples P(S/N-MA)/P(BA/N-MA).

Results and Discussion

Fig. 1 shows the conversion curves of first and second stage of PS/PBA dispersion synthesis at the presence of functional monomer in the core and shell of latex particles. It can be seen that individual conversion curves are essentially the same for the used concentration of N-MA. The similar conversion curves were obtained also by another synthesis, where N-MA was present only in the second stage of polymerization.

We expected that after introducing the N-MA functional groups to the polymer, the post-polymerization crosslinking reactions could occur. According to the literature[9)], these reactions can proceed after addition of crosslinker to the system and improve mainly the mechanical properties of prepared materials.

The tensile strength measurements of N-MA functionalized PS/PBA films without any treatment are shown in Fig. 2. It is evident that even when no post-polymerization crosslinking has been carried out, the functionalized films exhibit a higher tensile strength than the unfunctionalized ones.

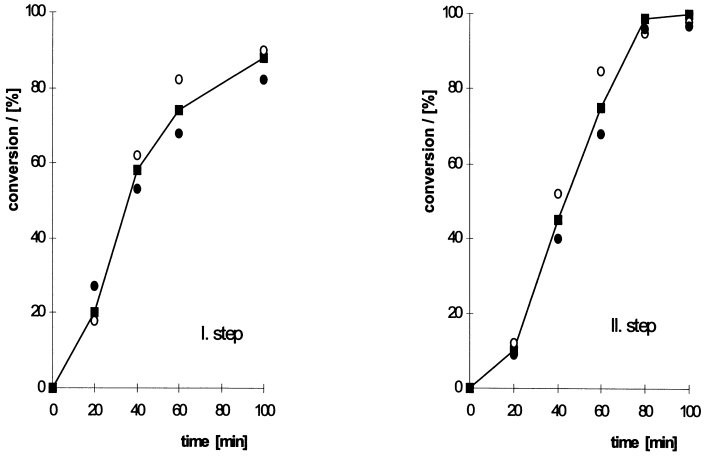


Fig. 1: Conversion curves for the 1st step (S/N-MA) and 2nd step (BA/N-MA) polymerization with various concentration of N-MA, 1st step/2nd step (wt.%): ■ 0.5/0.5, O 1/1, ● 1.5/1.5

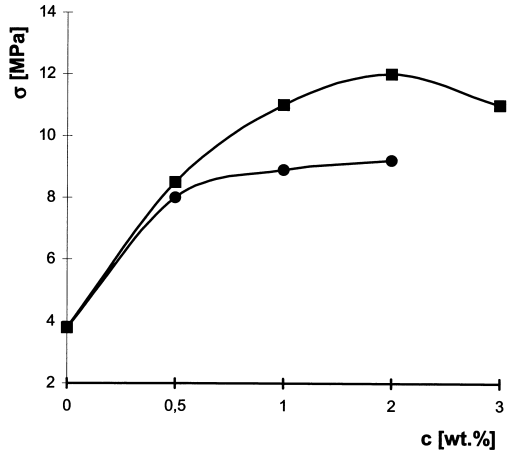


Fig. 2: Tensile strength σ of unfunctionalized PS/PBA film and functionalized films as a function of N-MA concentration c used at the synthesis of polymers, ■ P(S/N-MA)/P(BA/N-MA), ● PS/P(BA/N-MA)

The sol-gel analysis of functionalized PS/P(BA/N-MA) films prepared from final dispersion was done directly at the end of polymerization. The results in Table 2 indicate

that these samples contain a very high volume of EMK insoluble portions. Unfunctionalized PS/PBA in EMK are completely soluble.

Table 2. The effect of concentration *c* of N-MA at the synthesis of polymers PS/P(BA/N-MA) on content of insoluble portions *x* in solid final samples

c / wt.%	1	1.5	2	3
x / %	62.6	64.9	64.5	75.0

Therefore, the presence of insoluble portions was verified by monitoring of gel during the 2nd step of PS/P(BA/N-MA) synthesis (Fig. 3). It has been observed that already after a short time of the 2nd stage the content of insoluble portions in material is relatively high and increases with polymerization time. Similar results of the sol-gel analysis of P(S/N-MA)/P(BA/N-MA) core/shell polymers were obtained.

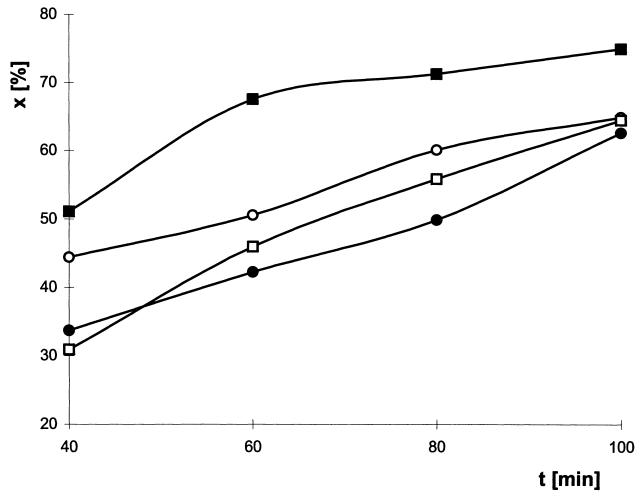


Fig. 3: Content of insoluble portions *x* in PS/P(BA/N-MA) polymers with various N-MA concentration as a function of polymerization time *t*, ■ 3%N-MA, ○ 2%N-MA, □ 1.5% -MA, ● 1%N-MA

The results indicate the crosslinking reaction between the methylol groups takes place during polymerization. These reactions are promoted by the acidic environment (pH 2-3) as well as the presence of peroxides[8]. Also, the reaction between methylol groups and carboxyl groups cannot be ruled out. The carboxyl groups can originate from the acid hydrolysis of ester bonds in BA under the polymerization condition. Acid hydrolysis of

poly(alkyl acrylate) lattices is catalyzed by strongly acid surface sulfate groups derived from the initiator[5,7].

According to the literature[9] these crosslinking reactions could be described by the following mechanism:

1) mutual reaction of methylol groups:

$$2\ \text{-CO-NH-CH}_2\text{-OH} \longrightarrow \text{-CO-NH-CH}_2\text{-O-CH}_2\text{-NH-CO-} + \text{H}_2\text{O}$$

$$\text{-CO-NH-CH}_2\text{-O-CH}_2\text{-NH-CO-} \xrightarrow{\text{heat}} \text{HCHO} + \text{-CO-NH-CH}_2\text{-NH-CO-}$$

2) reaction of methylol groups with carboxyl groups:

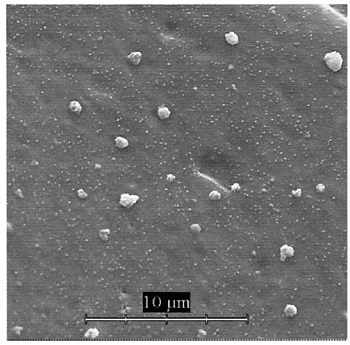
$$\text{-CO-NH-CH}_2\text{-OH} + \text{HO-CO-} \longrightarrow \text{-CO-NH-CH}_2\text{-O-CO-} + \text{H}_2\text{O}$$

For a better verification of the influence of various N-MA concentrations on crosslinking reaction as well as on film properties, the film samples were submitted to annealing at temperatures 60 °C and 100 °C. The results of sol-gel analysis of heated films, which were formed from dispersion with rising N-MA shown in Tab. 3. It is evident that at a constant concentration of N-MA in polymer films, the volume of insoluble portions grows with temperature. This can be explained by crosslinking reactions of the part of functional groups unreacted during synthesis of P(S/N-MA)/P(BA/N-MA) polymers. This crosslinking is evoked by annealing of the prepared films at elevated temperatures.

Table 3. The influence of the film annealing temperature *T* on content of insoluble part of P(S/N-MA)/P(BA/N-MA) films prepared from dispersion with increasing the concentration *c* of N-MA

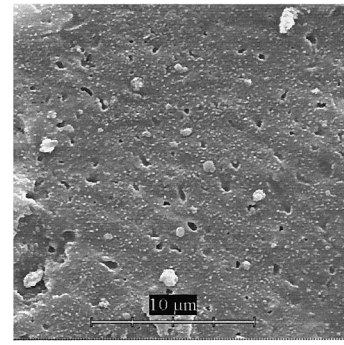
	gel [wt.%]		
c / wt.%	T / °C		
	25	60	100
1	70.2	78.9	81.0
2	86.6	94.5	92.7
3	91.7	92.9	96.6

Since the influence of elevated temperature and organic solvent (EMK) on films from functionalized dispersion was apparent, the fracture surface of so treated films by scanning electron microscopy (SEM) was studied (Fig. 4). The SEM observations were made for core/shell functionalized P(S/N-MA)/P(BA/N-MA) sample with 2% of functional monomer treated by heating and ethylmetylketone at 60 and 100°C. They were compared with the images of PS/PBA films.



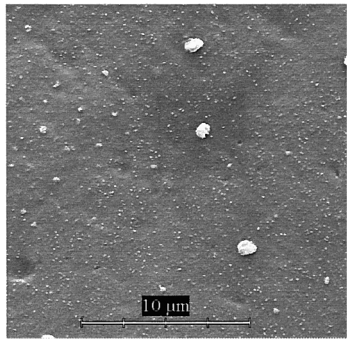
A

The SEM image of the unfunctionalized PS/PBA film conditioned at 25°C



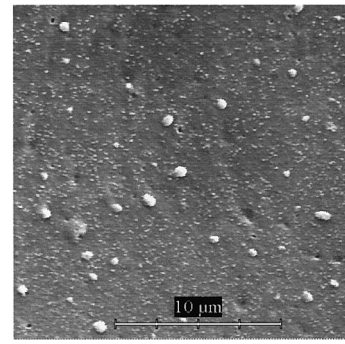
B

The SEM image of the unfunctionalized PS/PBA heated film (100°C)



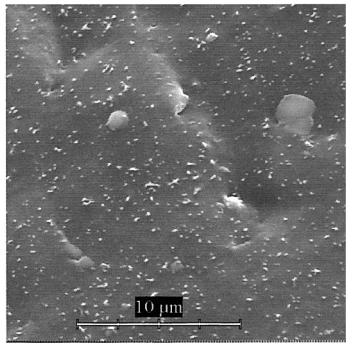
C

The SEM image of the functionalized P(S/N-MA)/P(BA/N-MA) film conditioned at 25°C



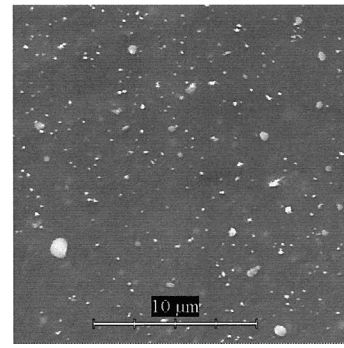
D

The SEM image of the functionalized P(S/N-MA)/P(BA/N-MA) heated film (100°C)



E

The SEM image of the functionalized P(S/N-MA)/P(BA/N-MA) film treated with ethylmetylketone at 25°C



F

The SEM image of the functionalized P(S/N-MA)/P(BA/N-MA) heated film (100°) and treated with EMK at 25°C

Fig. 4: The SEM images of the PS/PBA and P(S/N-MA)/P(BA/N-MA) films

From Fig. 4A and 4B it is evident that heating of unfunctionalized PS/PBA film to 100°C leads to a formation of defects in the PBA matrix (black part) while the PS inclusions (white) remain without changes. SEM image of heated functionalized film (Fig. 4C and 4D) proves that the presence of a small amount of functional N-MA polymer is able to protect the material (mainly the PBA shell) against thermal destruction. The treatment of functionalized PS/PBA films with ethylmetylketone leads to the partial solvation of PS domains seen in both 25°C heated and 100°C heated films (Fig. 4E and 4F). No destruction of N-MA functionalized material by EMK was observed. The unfunctionalized PS/PBA films are soluble in EMK before as well as after the thermal treatments.

Conclusion

The results obtained indicate that methylol functional groups of N-MA incorporated to shell and/or to core/shell of P(S/N-MA)/P(BA/N-MA) particles can take part on crosslinking reaction mainly in the course of synthesis. The crosslinking reactions are supported by high acidity of the system (pH 2-3) in which the synthesis proceeds. The unreacted groups take a part in the crosslinking during heating of the functionalized film. In comparison to films from PS/PBA dispersions, films from functionalized dispersions show improved tensile strength and higher resistance against organic solvent (EMK). From the SEM study of surface fractured films it is evident that functionalized films do not exhibit any destruction changes in materials after thermal (100 °C) and organic solvent (EMK) treatment.

Acknowledgement

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