Macromol. Symp. ***179,*** *305–314 (2002)*

Polystyrene/Poly(butyl acrylate) Dispersions Having *N*-Methylol Groups.

A Spectroscopic Study

*Ľudmila Černáková, Viera Chrástová, Petra Volfová, Anna Zahoranová**

Faculty of Chemical and Food Technology, Slovak University of Technology, Department of Plastic and Rubber, Radlinskeho 9, 812 37 Bratislava, Slovak Republic

*Faculty of Physics, Mathematics and Informatics, Comenius University, Mlynská Dolina, F2, 842 48 Bratislava, Slovak Republic

Summary: Polystyrene/poly(butyl acrylate) dispersion with N-methylol groups were prepared through two - steps semi continuous emulsion polymerization, where N-methylol acrylamide (NMA) was used as a functional monomer. A high content of insoluble portions depending on the NMA dosing during polymerization was found in films casted from such dispersions. The crosslinking reactions between methylol groups during polymerization were assumed. Attenuated total reflectance Fourier transform infrared spectroscopy was used to study changes in films prepared from the functionalized and unfunctionalized dispersions. Comparison of the spectra of as-dried films and heat- treated films suggests the occurrence of post-polymerization crosslinking.

Introduction

In the coating industry, there is an increasing number of applications where functionalized polymer dispersions are used as binders in film forming formulations. Particularly, a need exists for waterborne polymer compositions, which undergo crosslinking upon film formation imparting one or more desired properties to the resulting coatings. In the waterborne composition functional groups help to increase the colloid stability and polarity, and to improve adhesion.

One of the best known series of compounds by which cure is effected often without an external addition, and which may occur at ambient temperature, are the reactive derivates of acrylamide[1,2].Three monomers are commonly used to incorporate methylol functional groups into latex particles: N-methylol acrylamide (NMA), N-methylol metacrylamide (NMMA), and N-(iso-butoxymethyl) acrylamide (IBMA). In this way crosslinking sites are introduced into

CCC 1022-1360/00/$ 17.50+.50/0

latex particles. The pendent methylol groups can react with other methylol groups present on the surface of adjacent latex particles during film formation process and form covalent bonds at elevated temperatures, typically in the 120-150°C range. Covalent bonds may also be formed with carboxyl, hydroxyl and epoxy groups at elevated temperatures, usually under acid catalysed conditions. Both NMA and NMMA can also undergo room temperature crosslinking reactions via hydrogen bond formation.

Polystyrene (PS)/ Poly (n-butyl acrylate (BA)/ amide type functional monomer) latex particles were prepared by Hidalgo et al. [3] through two stage emulsion polymerization in the presence of NMA, NMMA and IBMA. It has been shown that different hydrophilicity of monomers leads to different distributions of the functional groups in the final latexes. The functional groups location has effected the thermomechanical properties of films cast from the latexes. Due to high hydrophilicity of NMA important proportions of the total amount of functional groups are found in the aqueous phase either in the form of functional homopolymer or in the form of a copolymer rich in functional groups. The rest of functional groups can be found in the latex particles in a functional monomer-rich layer of the surface [3].

Šňupárek et al.[4,5] synthetised self - crosslinkable butyl acrylate copolymers, which contain besides hydroxyl groups also N-alkoxy methyl groups incorporated by copolymerization with different amounts of IBMA. A decreasing extend of swelling in trichlorethylene observed with increased content of IBMA has indicated the effective crosslinking even at ambient temperature. In the films samples without IBMA the crosslinking proceeded only by heating film at elevated temperatures. It was proved, that the trans-esterification of OH groups and butyl ester groups of the butyl acrylate copolymer proceeds at elevated temperatures.

Our previous work was focused on the study of the synthesis conditions of polystyrene/poly(butyl acrylate) (PS/PBA) dispersions [6]. Further work was oriented on the synthesis and properties of PS/PBA dispersions with „core-shell“ structure by two-step semicontinuous emulsion polymerization[7].

PS/PBA dispersions functionalized with N-methylol groups were prepared when N-methylol acrylamide (NMA) was used as the functional comonomer. NMA was added in the first stage of polymerization together with styrene or in the second stage together with butyl acrylate. The mechanical properties and organic solvent resistance of films cast from these latexes were studied [8].

We expected that after introducing the NMA functional groups to the polymer, the post-polymerization crosslinking reactions could occure . A series of our experiments have shown that crosslinking in which methylol groups took part proceeded already in the course of polymerization[8].

The object of this work is to study in more detail the crosslinking reactions, which can proceed in the course of PS/PBA/NMA dispersion synthesis and can continue also during their film formation or temperature treatment of films. The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to specify the crosslinking mechanism. This technique is a rather new tool for monitoring the consumption of functional groups during the latex film formation process[9] and has also been used to study surfactant migration behaviour during latex film formation[10].

Experimental Part

Polymerization procedure. The functionalized polymer dispersions were prepared by two-steps emulsion polymerization as described in detail in the previous paper[8] .The polymerization system is inscribed in the Table 1. In the first step, styrene (S) or its mixture with N-methylol acrylamide was added dropwise to the emulsion containing aqueous solutions of emulsifiers, iniciator and activator. After the end of the first step, additional activator and iniciator solutions were charged and during the second step butyl acrylate (BA) or its mixture with NMA was added continuously.

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

The insoluble parts determination. The film samples were put in the Soxlet extractor at temperature 80 °C for 6 hour. Methyl ethyl ketone was used as the extraction solvent. The insoluble parts were calculated from the weight difference of films before and after the extraction.

Spectroscopic measurements by ATR FTIR spectroscopy. The spectra were taken from the films samples by a Bruker SPECTRA 22 spectrometer, using a ZnSe crystal, with a 45°incidence angle. 20 scans were co-added for all samples to reduce noise-to-signal ratio. The resolution was 2cm^{-1}.

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

I. step PS seed		II. 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
NMA	0.4 - 1.2*	NMA	0,4 - 1.2*

*calculated at monomer mixture which is adequate 1% - 3% NMA
The volume of NMA was charged in the I. step of polymerization-designation of samples P(S/NMA)/PBA or in the II. step of polymerization-designation of samples PS/P(BA/NMA)

Results and Discussion

Polystyrene/poly(butyl acrylate) dispersions with core-shell particles functionalized with N-methylol acrylamide were prepared with the aim to study their crosslinking properties. N-methylol acrylamide was added in the first stage of polymerization together with styrene (core) or in the second stage of polymerization together with butyl acrylate (shell). From NMA functionalized dispersions were casted films in which insoluble parts in methyl ethyl ketone were determined. The films were analysed as obtained after drying at 25°C and an additional heat treatment at 100°C.

The high content of insoluble parts was determined already in the as-dried films. Depending on the way of NMA dosing, the different content of insoluble parts was determined. As shown in Fig.1A, a surprisingly high content of insoluble parts was determined in the samples, where NMA was added in the first stage of polymerization together with styrene.

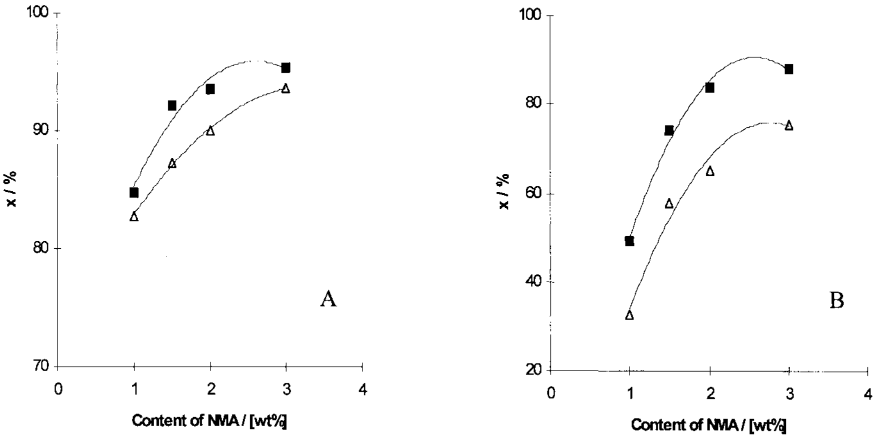


Fig.1: Insoluble parts x in P(S-NMA)/PBA films prepared from dispersions where NMA was added in the first stage of polymerization (A) and PS/P(BA-NMA) films prepared from dispersions where NMA was added in the second stage of polymerization (B) with various NMA content during polymerization.
△ as dried films, ■ films heated at 100 °C

As indicated by Fig.1B, when NMA together with butyl acrylate were added in the second stage of polymerization, the content of insoluble parts was lower, arising from 30% up to 75% with increasing content of NMA. Heating of films at 100°C led in both cases to a further increase of insoluble parts (Fig.1A,B).

To find out if the crosslinking begins already in the course of dispersions synthesis, the development of insoluble parts as a function of polymerization time was investigated To verified this, when NMA was added in the first stage together with styrene, the insoluble parts were determined in polymer samples during both the first and second stage of polymerization, The results summarized in Fig.2 indicate that already in the first stage of polymerization (Fig.2-I) the crosslinking between N-methylol groups began and continued in the second stage (Fig.2-II.) even though no NMA was added with butyl acrylate. At the end of the first stage of synthesis the polymer samples contained about 40% of insoluble parts, and in the second stage the amount of insolubles arised up to 70% . The similar results we obtained in our previous work[8], where we analysed the isoluble parts development during the polymerization, adding

NMA together with butyl acrylate in the second stage of polymerization. The polymer samples from the first stage was completely soluble in methyl ethyl ketone. In the polymer samples from the second stage the rising content of insoluble parts with polymerization time was observed.

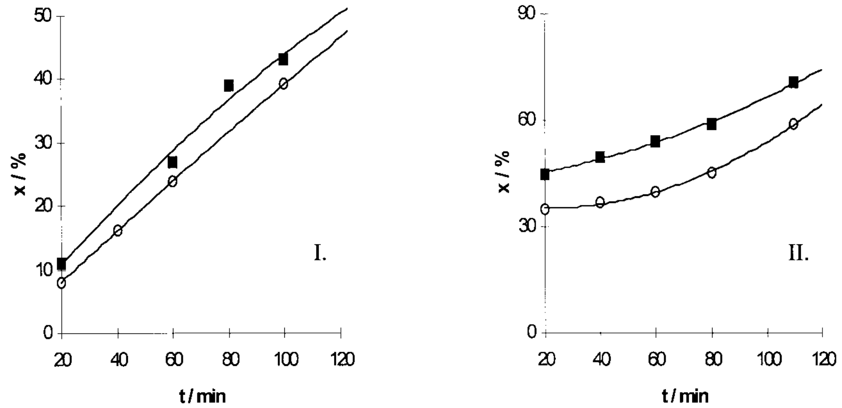
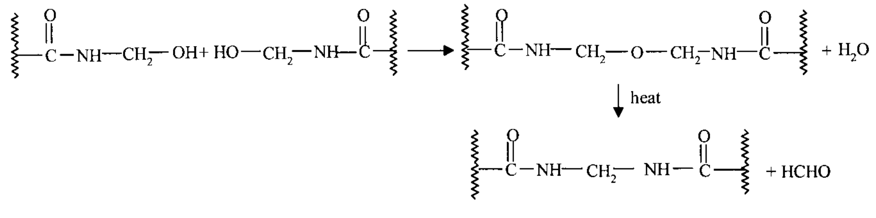


Fig. 2. Development of gel content in polymer samples P(S/NMA)/PBA during both stage of polymerization (I.stage, II.stage) as a function of polymerization time. NMA was added only in the first stage of polymerization ○ 1%NMA, ■ 3% NMA

In our opinion the above discussed results show that the majority of the insoluble parts, indicated crosslinking reactions, are created already during the polymerization. In a much less extent the post polymerization crosslinking takes place.

In the presence of NMA in polymerization system the following crosslinking reactions are assumed:

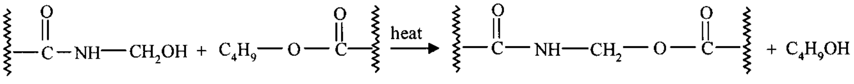
a) the reactions between methylol groups



$$\sim\overset{\overset{O}{\|}}{C}-NH-CH_2-OH + HO-CH_2-NH-\overset{\overset{O}{\|}}{C}\sim \longrightarrow \sim\overset{\overset{O}{\|}}{C}-NH-CH_2-O-CH_2-NH-\overset{\overset{O}{\|}}{C}\sim + H_2O$$

$$\xrightarrow{\text{heat}} \sim\overset{\overset{O}{\|}}{C}-NH-CH_2-NH-\overset{\overset{O}{\|}}{C}\sim + HCHO$$

b) the reactions of methylol groups with butylester groups of the butyl acrylate



$$\sim\overset{\underset{\|}{O}}{C}-NH-CH_2OH + C_4H_9-O-\overset{\underset{\|}{O}}{C}\sim \xrightarrow{heat} \sim\overset{\underset{\|}{O}}{C}-NH-CH_2-O-\overset{\underset{\|}{O}}{C}\sim + C_4H_9OH$$

To support the above considerations the changes in the absorption bands of functionalized and unfunctionalized latex films, prepared at 25°C, were analysed by the ATR-FTIR spectroscopy. The comparison of functionalized P(S/NMA)/PBA and unfunctionalized PS/PBA films spectra shown in Fig.3 demonstrates differences in the 3100-3500 cm^{-1} region corresponding to the vibrations of N-H bonds. This indicates the presence of N-H bonds from NMA in the functionalized films.

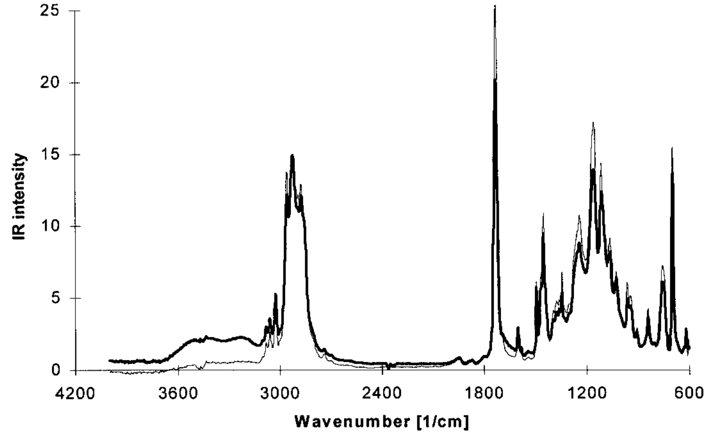


Fig.3: ATR FTIR spectra of film casted from unfunctionalized PS/PBA dispersion and films cast from dispersions with 3%NMA added in the first stage of polymerization.
——— PS/PBA, ━━━ P(S-NMA)/PBA

Next we analysed the films casted from dispersions PS/P(BA/NMA) with the functional groups in the shell. From the comparison of the films dried at 25°C with the heat treated films at 100 °C the differences are evident in 1100-1200 cm^{-1}region, where the strong bands of esters group from BA can be seen due to C-O-C vibrations[10]. It is apparent that the absorption band at 1113 cm^{-1} increased, respectively, the proportions between bands at 1158 and 1113 cm^{-1} were changed. The crosslinking reaction according to the mechanism (b) led to a different substituent on the carbon atom adjacent to the oxygen, i.e., C-C-O bonds in butyl ester group changed to N-C-O bonds in crosslinked films, which usually leads to different splitting of the absorption bands.[11] The changes observed in this absorption region suggest that during an additional heating of the functionalized films the butyl ester groups can react with unreacted N-methylol groups.

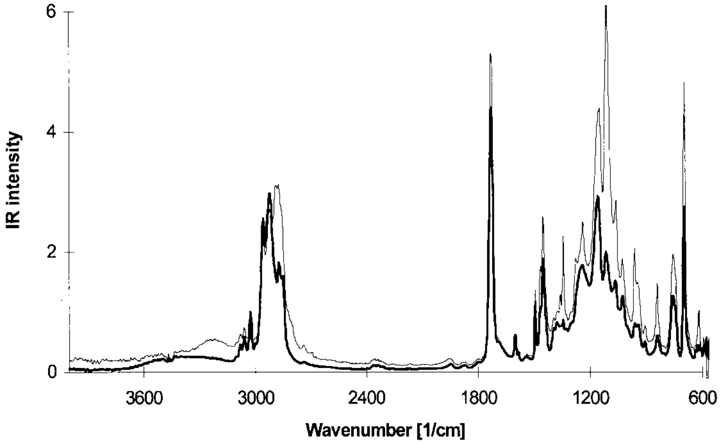


Fig.4: ATR FTIR spectra of films casted from dispersions PS/ P(BA/NMA) with 3%NMA added in the second stage of polymerization ━━━ as dried films, ——— films heated at 100 °C.

Based on the above results and sol-gel analysis one can assume that during the synthesis the methylol groups undergo self reaction (scheme a). These reactions are catalysed by acidic surroundings (pH 2-3) and peroxides in the used polymerization systems[12] . The unreacted methylol groups can react with functional groups of butyl acrylate (scheme b) mainly by heat treatment. According to the location of functional groups in latex particle their intra-particle or inter-particle crosslinking can proceed.

Conclusion

Polystyrene/Poly(butyl acrylate) dispersions with core shell structure, functionalized with N-methylol acrylamide in the first or second stage of synthesis, were prepared with the aim to study their crosslinking properties. The insoluble parts determined in polymers sampled during both stages of polymerization indicate that crossslinking reactions in which NMA can take part proceeded already in the course of polymerization. The high contents of insoluble parts were determined also in the films casted from functionalized dispersions directly after polymerization. Heating of the films led to a further increase of the insolubles, which indicates post-polymerization crosslinking.

While the sol gel analysis revealed the occurence of crosslinking reactions, the results of ATR FTIR spectroscopy indicates the mechanism of these reactions. In the functionalized films, the absorption band in 3100-3500 cm^{-1} region suggests the presence of N-H bond originating from NMA. The qualitative analysis of the functionalized films additionaly heated to 100°C revealed changes in the 1100-1200 cm^{-1} region, where butyl ester groups from butyl acrylate have their characteristic absorption bands. These results demonstrate that unreacted N-methylol groups can react with butyl ester groups at elevated temperatures. According to the location of functional groups in latex particles their intra-particle or inter-particle crosslinking can proceed.

Acknowledgement

This work was made with support of Grant VEGA 1/7338/20, Grant agency of the Slovak Republic.

References

1. P. A. Lovell, M.S.El-Aasser: Emulsion Polymerization and emulsion Polymers, Wiley, England 1997, p.216
2. H.Warson, J.of oil and Colour Chemists Association, JOCCA, **70**, 8, 1987
3. M. Hidalgo, J.Y. Cavaillé, J. Guillot, A. Guyot, J. Perez, R. Vassoille, J. Polym.Sci. Polym.Phys.**33**, 1559 (1995)
4. J.Šňupárek, M. Kaška, G.A.Baghaffar: Plasty a kaučuk, **37**, 164 (2000)
5. J.Šňupárek , L.Mrkvičková, O.Quadrat, Z.Walterová, P.Bradna, Colloid Polym.Sci.,**278**,1205 (2000)
6. V.Chrástová, S.Ďuračková, J.Mrenica, Ľ.Černáková, Chem. Papers **53**, 2, 140 (1999)
7. V.Chrástová, J.Mrenica, Ľ.Černáková, J.Mončeková,Plasty a kaučuk, **35** ,300 (1998)
8. P.Volfová, V.Chrástová, Ľ.Černáková, J.Mrenica, J.Kozánková,Macromol. Symp. **170**, 283 (2001)