Nanostructured Polymer Films based on Core-Shell Latexes: Preparation and Characterization

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SUMMARY: We describe the preparation and characterization of core-shell structured latexes, consisting of different methacrylate cores, covered with a shell of a cross-linked rubber poly(*n*-butyl acrylate). The structured latexes were prepared via a two-stage emulsion polymerization process under kinetically controlled conditions by use of reaction calorimetry. Transmission electron microscopy (TEM) confirms the quality of the structural uniformity of the latex particles. The particles maintain their structure during film formation. After drying these structured latexes form nanostructured polymer films. Beside preparation and characterization, first results of investigations of mechanical properties (dynamic mechanical analysis (DMA) and stress-strain experiments) of such nanostructured polymer films are reported.

Introduction

The synthesis of structured latexes, such as core-shell particles, is simple by concept but quite difficult in practice particularly, if one is interested in well-defined and homogeneous dispersions of particles of a distinct type. It has been demonstrated that both thermodynamic and kinetic factors dictate the particle morphology[1,2)]. The influence of many process parameters controlling the particle morphology was recently summarized[3)].

The preparation of core-shell polymer dispersions is usually a two-stage emulsion polymerization via seed latexes with a clear separation between the two preparation steps. For the second stage polymerization different addition modes as batch (swelling method) and the continuous addition process (drop-wise method) are reported[4)]. The structured latexes in this paper were prepared via a first stage batch polymerization and a semi-batch second stage polymerization in the same reactor under controlled kinetic conditions. The polymerization was observed and optimized by use of a reaction calorimeter[5, 6)].

For structural investigations of polymeric composites like core-shell latex particles or heterogeneously structured polymer films transmission electron microscopy (TEM) is widely used. In addition to TEM dynamic mechanical analysis (DMA) leads to valuable information

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about mechanical and morphological features of multiphase polymeric systems[7)]. DMA was used to determine the glass transition temperatures T_g for the polymer composites.

There are a number of studies concerning the mechanical properties of latex films as well as several excellent reviews on the mechanical properties of coatings in general[8, 9)]. Film formation of polymer dispersions with a well-defined particle morphology leads to nanostructured films (see Figure 1). These films possess a controlled particle structure and a network superstructure which can be adjusted by the size, the chemical composition and the architecture of the original latex particles. It is noteworthy, that films prepared of heterogeneous, nanosized structured particles are perfect systems for investigating material properties of polymer blends.

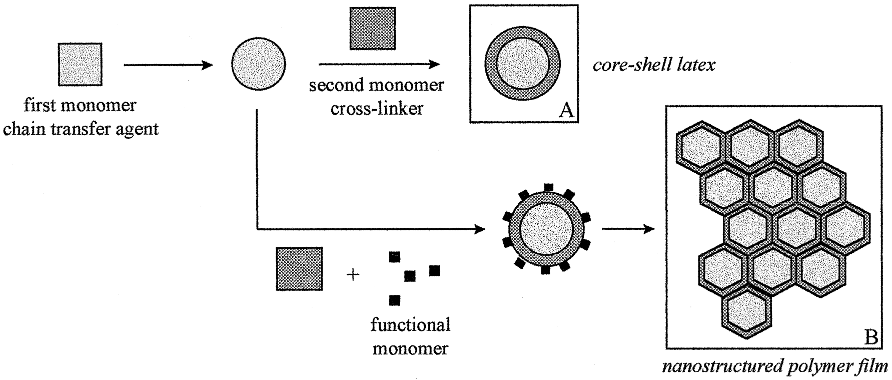

Figure 1: Preparation strategy for core-shell latexes and nanostructured polymer films.

The present work reports on the preparation of such particles (Fig. 1, A) by emulsion polymerization, the characterization of their morphology as well as first results of investigations of mechanical properties of films casted from such dispersions (Fig 1, B).

Results and Discussion

The latexes were prepared using a one-pot two-stage emulsion polymerization technique carried out in a reaction calorimeter made of a glass jacket and a stainless steel bottom (ChemiSens RM2-S, Lund, Sweden)[10)]. The emulsion polymerizations were performed as a semi-batch process with a continuous addition of the second stage monomer (*n*-butyl acrylate(BA)) with a defined amount of cross-linker (allyl methacrylate (AMA)) and functional monomer (*N*-methylol methacrylamide (NMMA)). In the first stage either 2-

ethylhexyl methacrylate (EtHMA) with addition of 1 mol% CBr_4 as chain transfer agent or styrene (STY) and *n*-butyl methacrylate (BMA) (1:3 weight ratio) were polymerized batchwise (Table 1).

Table 1: Characterization of the core-shell latexes (DIPB - 1,3-Diisopropenylbenzene).

latex	**core materials**	**T_g(core)**	**shell materials**	**interfacial crosslinking**
L 1	EtHMA / CBr_4	0 °C	BA / AMA	no
L 1b	EtHMA / CBr_4	0 °C	BA / DIPB	no
L 2	EtHMA / CBr_4	0 °C	BA / AMA / NMMA	yes
L2b	EtHMA / CBr_4	0 °C	BA / DIPB / NMMA	yes
L 3	STY / BMA (1:3)	20 °C	BA / AMA / NMMA	yes

Knowing the reaction rate profile (RRP), the addition of the second stage monomer mixture is started after 80-90 % conversion of the first monomer. For simplicity, only symmetric systems were examined, which means that the weight ratio of first stage monomer to second stage monomer was always 1:1. The detailed description of monomer purification from inhibitors and more comments on preparation of the heterogen structured latexes is given elsewhere[11, 12)]. To avoid the cross-linking reaction of NMMA during the polymerization the initiator system was changed from potassium peroxodisulfate (KPS) to a redox system (ammonium peroxodisulfate, ferrous (II) sulfate heptahydrate and sodiumsulfite) which allows a polymerization temperature of 35 °C instead of 70 °C.

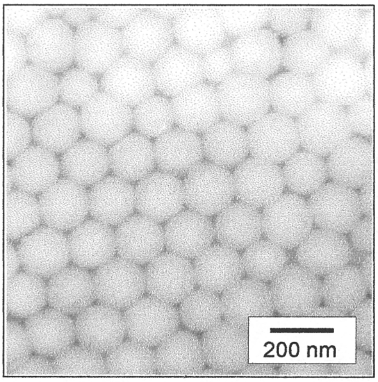

Figure 2a: TEM of a diluted core-shell latex (L2b) without further staining.

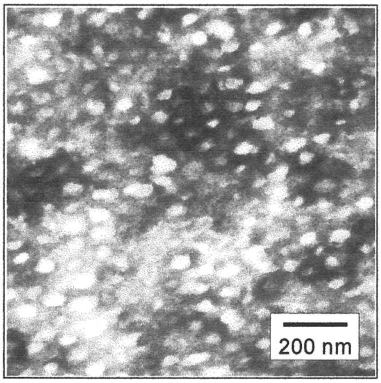

Figure 2b: TEM of a ultrathin section of the polymer film (L2b) stained with RuO_4.

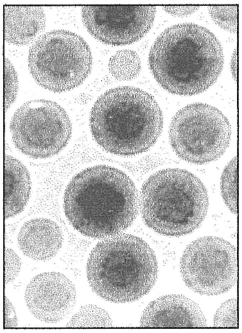

Figure 3: Cryo-TEM of a diluted latex (L1b).

To obtain the TEM picture shown in Figure 2a the diluted dispersion were brought onto the carbon grid and water was allowed to evaporate from the film at ambient temperatures[13]. It is clear to see that the film consists to a wide extent of a almost ideal hexagonal pattern of deformed particles. To get insight into the morphology of the latex particles, the corresponding polymer film of the original undiluted core-shell latex (casted at 60 °C) was also characterized with TEM (Figure 2b) after staining with RuO_4; a detailed description about the TEM preparation technique is given elsewhere[11]. The core-shell morphology is clearly resolved: the cross-linked shell is darker than the core because of the staining of the cross-linker molecules[14]. The close contact package of the particles leads to a position of particles at different depths of the sample. In addition the picture made by cryo-TEM (Fig. 3) confirms the structural uniformity of the original latexes. It is interesting to note that in this particular case, the core becomes visible even without further staining; the chain tranfer agent CBr_4 leads to an increased electron density of the core polymer.

The molecular weights (number average M_n) of the core polymer (L1, L1b, L2, L2b), as determined by size exclusion chromatoraphy (SEC), were about 16000 g/mol, what implies that the chain transfer agent, applied to obtain low molecular weight core polymer, worked well. Without chain transfer agent, we obtained a molecular weight of around 70000 g/mol. It should be noted, that the shell polymer cannot be characterized by SEC because it is highly cross-linked. The fact that we can still analyze the core polymer even for core-shell particles proves that the short linear chains forming the core can penetrate through the shell. Peak integration of SEC traces shows that almost the complete core polymer is detected and hence no grafting between core and shell polymer is observed.

To investigate the influence of the particle structure and composition of macroscopic film properties, mechanical investigations were carried out. The film formation process was carried out at 60-70 °C on a teflon coated aluminium foil. To ensure the cross-linking of the NMMA the films were annealed at 120 °C for 2 hours. The dynamic mechanical behavior of polymer films based on latex L3 as a function of temperature is shown in Figure 4. The magnitude of the storage tensile modulus (E`) and the tangent of the phase angle (tan δ) were recorded. The straight lines indicate the two transitions caused by the composite nature of the polymer films for the storage tensile modulus. In the case of tan δ, one peak (core polymer) with a shoulder (shell polymer) is observed. The broad peak is due to the molecular weight distribution of the core polymer and probably due to a small amount of copolymer. It can be concluded, that the results of the DMA prove the SEC results that almost exclusively the core-shell particles consist of two separate polymer phases.

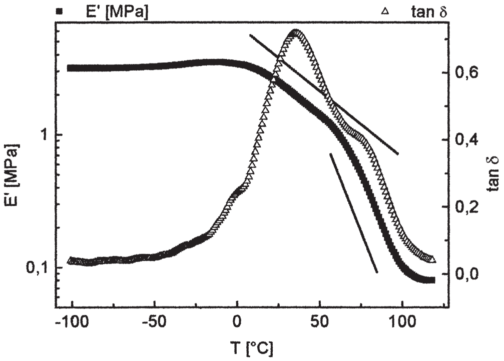

Figure 4: Dynamic mechanical behavior of a polymer film based on core-shell latex L3 (sample: (5×5×2) mm^3; mode of measurement: compression; frequency: 1 Hz; deformation amplitude: ± 30 mm; rate of heating: 3 K/min).

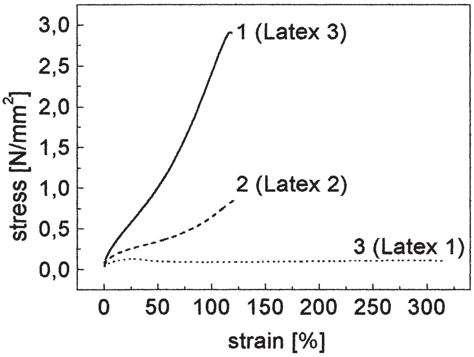

Figure 5: Stress-stain plots for the three different nanostructured latex films (sample: (20×5×1) mm^3; rate of expansion: 10 mm/min; room temperature; average of three measurements).

An overview of the stress-strain plots of three nanostructured polymer films is shown in Figure 5. The different behavior depends on the kind of core material and wether or not an interparticle cross-linking took place. It is clearly to see that interparticle cross-linking reduces the maximum stain from over 300 % (curve 3) down to 120 % (curves 1, 2). In contrast, the higher glass transition temperature of the core material (curve 1 versus curve 2) leads to a steeper slope of the stress-strain plot.

Conclusion

It has been shown that core-shell particles can be synthesized by sequential emulsion polymerization under kinetically controlled conditions. In order to optimize the preparation process the reaction calorimetry was found to be a powerful tool. Monitoring on-line RRP of emulsion polymerizations is very helpful for the preparation of structured latex particles in a one-pot two-stage reaction. The films formed of the core-shell latexes were studied by TEM and it has been shown that the films stay nanostructured after the drying process. They exhibit both a controlled morphology on the scale of particle size as well as a macroscopic network superstructure originating from the characteristics of the original latexes. Both the SEC and the DMA were used to get a further insight into the characteristics of the latexes. These methods confirm that the core-shell particles and the final polymer film consist of two separate polymer phases. In addition to these properties, the stress-strain behavior depends on the kind of core polymer for example. These points lead to a first understanding how to adjust mechanical properties in well-defined nanostructured polymer networks.

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References

1. D. Sundberg, A.P. Casassa, J. Pantazopoulos, M.R. Muscato, *J. App. Polym. Sci.* **41**, 1429 (1990)
2. Y.C. Chen, V.L. Dimonie, M.S. El-Aasser, *Macromolecules* **24**, 3779 (1991)
3. V.L. Dimonie et al. in: *Emulsion Polymerization and Emulsion Polymers*, P.A. Lovell and M.S. El-Aasser (Eds.), J. Wiley & Sons 1997, Chapter 9
4. M. Okubo, A. Yamada, T. Matsumoto, *J. Polym. Sci.: Part A: Polym. Chem.* **18**, 3219 (1980)
5. L. Varela De La Rosa, E.D. Sudol, M.S. El-Aasser, A. Klein, *J. Polym. Sci.: Part A: Polym. Chem.* **34**, 461 (1996)
6. K. Tauer, H. Müller, C. Schellenberg, L. Rosengarten, *Colloid and Surfaces A: Physicochemical and Engineering Aspects* **153**, 143 (1999)

7. A. Zosel, G. Ley, *Macromolecules* **26**, 2222 (1993)
8. A. Zosel, *Prog. Org. Coat.* **8**, 47 (1980)
9. L.W. Hill, K. Kozlowski, *J. Coat. Tech.* **59**, 63 (1988)
10. H. Nilsson, C. Silvegren, B. Tornell, *Angew. Makromol. Chem.* **112**, 125 (1985)
11. C. Schellenberg, S. Akari, M. Regenbrecht, K. Tauer, F.M. Petrat, M. Antonietti, *Langmuir* **15(4)**, 1283 (1999)
12. C. Schellenberg, K. Tauer, M. Antonietti, *DECHEMA Monographs on Polymer Reaction Engineering* **134**, 375 (1998)
13. C. Schellenberg, K. Tauer, M. Antonietti, *J. Disp. Sci. and Techn.* **20**, 177 (1999)
14. We have used in this special case 1,3-diisopropenyl benzene as cross-linker instead of AMA to get the additional ruthenium bound at the aromatic cross-linker molecules.