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Glass surface-grafted poly(methylmethacrylate)

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SUMMARY

This thesis deals primarily with the study of a model composite compound, consisting of a filler grafted with a polymer which is compatible with the matrix polymer. Adhesion between filler and matrix should be improved by mixing grafted and matrix polymer. In this study the model composite is glass bead filled polyvinylchloride (PVC), in which the glass bead surface is covered with a layer of grafted poly(methylmethacrylate) (PMMA).

The aims of this thesis are further described in *chapter one*, together with a short survey of the literature dealing with subjects connected with our investigations, e. g. adhesion in composite materials, grafting of polymers on solid surfaces, interdiffusion of polymers and glass bead filled plastics.

To be able to graft PMMA upon glass in a controlled way, this reaction was tested on Aerosil 200 substrates, because the high specific surface area allows us to study the surface modifications in detail. As shown in *chapter two*, PMMA was grafted on glass by initiation of an immobilized radical initiator, which was attached to the glass surface by a two step reaction. Firstly a silane coupling agent (aminophenyltrimethoxysilane) was used to functionalize the glass surface and secondly a diazo-radical initiator (4,4'-azobis(4-cyanopentanoyl chloride)) was linked to the coupling agent by an amide bond, which was confirmed by infrared spectroscopy. The kinetics of the graft-polymerization were largely determined by the Trommsdorff effect, which increased the molecular weights of the polymers and by that also the polymer load on Aerosil. The Trommsdorff effect and polymer load could be influenced by a proper choice of polymerization temperature, initiator and monomer concentration. At low initiator concentrations, oxygen, that is present in very small concentrations in purified nitrogen gas, slowed down the polymerization because it was built in in the propagating chain and the thus formed peroxyde had a very low initiation rate.

The reproducibility of grafting PMMA upon larger substrates as large glass spheres, glass slides and silicon wafers, was hampered by the high unfavourable oxygen/initiator ratio, because the amount of initiator was

very small, due to the small surface area of the substrates. Still some correlations between reaction circumstances and polymer load found in chapter two, e. g. increasing the monomer concentration results in a larger amount of grafted polymer, were also found in this case, as described in *chapter three*. The distance between two grafts on the surface is much smaller than the radius of gyration of the grafted polymer, so the polymers have to adapt a stretched conformation, especially after mixing with other, non-grafted polymers. In some cases we are close to the regime, defined by de Gennes, where grafted and free polymer of the same kind become immiscible.

In *chapter four* interdiffusion of PMMA and PVC was investigated using external reflection infrared spectroscopy. Using s-polarized light, PMMA features in the spectra of a double layer, consisting of a PMMA film on gold and a PVC film on top of PMMA, increased upon annealing which indicated interdiffusion of PMMA and PVC. This phenomenon can be explained as follows: The electrical field intensity increases with distance from the substrate, because the standing wave, created by interference of incoming and reflected s-polarized light, has a node on the gold surface and a ventral region further away from the surface. Because absorption is directly proportional to the square of the electrical field intensity, the PMMA absorptions in the unmixed double layer are small because PMMA is close to the substrate, in the low intensity region, whereas upon annealing the sample, PMMA diffuses away from the surface into the regions of higher electric field intensity, and consequently PMMA absorptions increase. Complete agreement between experimental and simulated spectra was found in case of an unmixed double layer and the completely mixed layer. For low molecular weight PMMA and PVC, diffusion over 0.5 μm is complete in two hours. On glass substrates the optical situation is not as easily understood as on gold substrates, but clear differences were found between the unmixed double layer and the mixed layer when p-polarization was used. In this case, using a double layer of the same thickness as the one on a gold substrate hardly any differences were found after more than 0.5 h. annealing, leading to the conclusion that the gold substrate/s-polarization setup is more sensitive for later stages of interdiffusion and glass substrate/p-polarization more for earlier stages.

This technique together with attenuated total reflection infrared spectroscopy was used for interdiffusion studies of high molecular weight PMMA and grafted PMMA with PVC in *chapter five*. It was shown that the

diffusion rate decreased significantly with higher molecular weights, even when these were well above the molecular weight between two entanglements. This might result from the shift of the spinodal curve to lower temperatures with increasing molecular weights, diminishing the driving force for interdiffusion. It took over 30 h. to complete interdiffusion of high molecular weight PMMA and PVC, whereas 3 h. were sufficient for complete interdiffusion over the same distance for low molecular weight PMMA. Grafted, high molecular weight PMMA and PVC interdiffused at a very low rate, even lower than the interdiffusion rate of high molecular weight PMMA and PVC, but they are still miscible as was expected.

The adhesion between PMMA grafted glass beads and the PVC matrix, presented in *chapter six*, was investigated by using mechanical tests as stress-strain and volume strain experiments and by scanning electron microscopy. Stress-strain and volume-strain curves of clean glass and N-acetylaminophenylsilane (AAPS) treated glass filled PVC, clearly showed bends, indicating debonding. The slightly higher delamination strain of AAPS treated glass compared to clean glass bead filled PVC might be explained by specific interactions between the carbonyl group of AAPS and the CHCl group of PVC. The tensile bars showed clearly shear bands, and SEM pictures of fracture surfaces revealed no interaction between filler and matrix. The bends, indicating debonding, were not found in case of PMMA grafted glass bead filled PVC and the maximum strength of the composite almost reached the maximum strength of unfilled PVC. With increasing amounts of PMMA grafted upon the glass beads, the maximum strength increased. The shear bands in the tensile bars became less pronounced and were, in case of the highest amount of grafted PMMA, only observed very close to the fracture surface. SEM pictures of fracture surfaces showed the same characteristics as mentioned above, adhesion between PVC and glass beads increased upon grafting more PMMA. Annealing the tensile bars did not increase the maximum strength very much nor showed SEM a clearly improved adhesion. The shear bands formed close to the fracture surface indicated that adhesion had improved very much but was not excellent. The fact that annealing did not improve adhesion, combined with the high maximum strength of the composites and the knowledge that interdiffusion between grafted PMMA and PVC was very slow, led us to the conclusion that wetting and some diffusion of the PMMA chain ends, which are short time scale processes, were sufficient for a good adhesion between glass beads and PVC.