Polymer–filler interactions in poly(vinyl chloride) filled with glass beads: effect of grafted poly(methyl methacrylate)

Gert Boven, Rudy Folkersma, Ger Challa and Arend Jan Schouten*
Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

and Martin Bosma
Akzo Research Laboratories Arnhem, Corporate Research, Physical Chemistry Department, Velperweg 76, PO Box 9300, 6800 SB Arnhem, The Netherlands
(Received 30 July 1990; accepted 28 January 1991)

Adhesion between filler and matrix has been studied using a model system composed of glass bead filled poly(vinyl chloride) (PVC). Stress–strain and volume–strain tests and scanning electron microscopy revealed that adhesion is improved by grafting poly(methyl methacrylate) (PMMA), which is known to be miscible with the PVC matrix, upon the surface of the glass beads. The best results were obtained when large amounts of grafted PMMA were used, leading to maximum stress of the composite, nearly as high as that of pure PVC.

(Keywords: adhesion; glass bead; grafted poly(methyl methacrylate); poly(vinyl chloride); stress–strain; volume–strain)

INTRODUCTION

The adhesion between filler and matrix is an important factor in determining the mechanical properties of a composite. According to Hull[1] the adhesion depends on: (i) wetting of the filler surface by the matrix; (ii) interactions or (iii) chemical bonds between filler and matrix; (iv) interdiffusion of the matrix with compounds on the filler; and (v) filler surface roughness.

Combining points (iii) and (iv), grafting the matrix polymer upon the filler improves the adhesion, as reported for various systems[1–5]. This grafting of polymers to the filler can be done easily for thermoset matrices during the curing reactions[1,2] by making a chemical bond with a surface active group, that can be attached to the filler surface by a silane coupling agent. This is of course not possible for thermoplastics, although transesterification and transamidation reactions of polyester and polyamide matrices[3], respectively, can occur during processing of the composite. In most cases the polymer has to be grafted in a separate step, before the composite is made[4,5].

Although fibre-filled plastics are interesting for industrial applications due to the reinforcing capacities of the fibres, spherical-filled plastics are often used for model studies because of the isotropicity of these composites. The stresses around a spherical inclusion are well understood[6], allowing for model calculations. Brittle and tough matrices filled with good and poorly adhering glass beads have been studied by stress–strain and volume–strain measurements, microscopy and scanning electron microscopy (SEM)[3,6,7]. Grafting of polymers onto glass beads can lead to better adhesion[5], to a weak boundary layer at the grafted polymer–matrix interface[8] or to immiscibility between grafted and matrix polymers[4], as previously described theoretically by de Gennes[9].

A composite, composed of a matrix and a filler with grafted polymers, has two interfaces. The strength of the first, the filler–grafted polymer interface, depends on the number and strength of the covalent bonds. The strength of the second, the grafted polymer–matrix polymer interface, depends on the fracture energy G of the interphase:

$$\sigma \propto G^{1/2}$$

where σ is the fracture bond strength. According to Wu *et al.*[10]:

$$G = n\varepsilon d$$

where n is the number of bonds crossing the original interface, ε is the attractive energy per unit length and d is the thickness of the interphase, resulting in:

$$\sigma \propto (n\varepsilon d)^{1/2}$$

Our aim is to create a strong interphase, which should be achieved by high n, ε and d. This can be done by grafting PMMA with a high graft density (n) and a high molecular weight (d), resulting in a thick interphase with a high number of chains crossing the original interface after mixing the grafted and matrix polymer. Moreover ε will increase if we take PVC as a matrix polymer because these polymers are known to have specific interactions. The interphase between PMMA and PVC is known to have better mechanical properties than either of the components[11], as follows from the facts that the mechanical properties of the homogeneous blends are superior to those of the pure components over a large composition range and that cohesive failure takes place after a long interdiffusion time of PMMA and PVC.

Two problems may arise in creating the interphase

* To whom correspondence should be addressed

0032-3861/92/010083-06

Table 1 Composite materials

Sample no.	Filler coating	Polymer load (mg PMMA g^{-1} glass)	M_n (10^3 g mol^{-1})	M_w (10^3 g mol^{-1})	Surface area per coil (Å^2)
1	unfilled	–	–	–	–
2	none	–	–	–	–
3	AAPS	–	–	–	–
4	PMMA	1.2	1200	2100	6300
5	PMMA	1.7	1900	2700	7100
6	PMMA	2.0	420	1100	1300

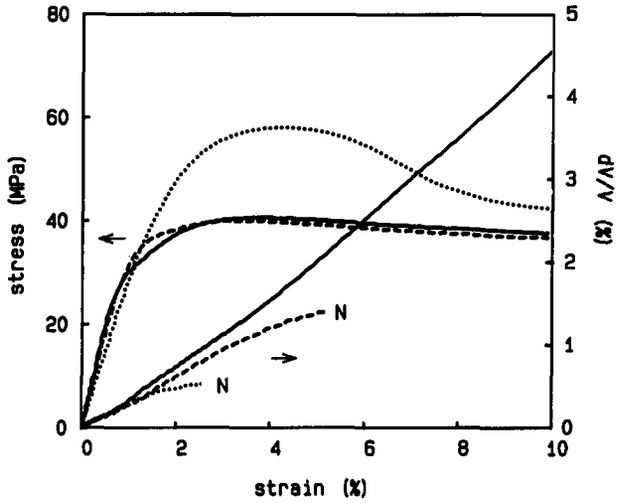

Figure 1 Stress–strain and volume–strain curves of unfilled PVC (·····, sample 1), filled with clean glass beads (—, sample 2) and with AAPS-treated glass beads (----, sample 3). N indicates necking at the position of one of the extensometers

as described above, first the graft density might become too high to retain miscibility with free polymer[4,9] and second the molecular weights might become too high, leading to long interdiffusion times. Prolonged heating times would cause severe degradation of the matrix polymer.

EXPERIMENTAL

Materials

Poly(vinyl chloride) was obtained from Péchiney et St Gobain (Lucovyl RB8010, $M_n = 30 \times 10^3$ g mol^{-1}, $M_w = 55 \times 10^3$ g mol^{-1}). Glass beads with an average diameter of 52 μm were obtained from Potters Ballotini. The low molecular weight organic coating (*N*-acetylaminophenylsilane, AAPS) was attached to the beads by a two-step procedure in which the beads were first coated with aminophenyltrimethoxysilane as described previously[12] and subsequently treated with acetyl chloride under the same conditions as for the synthesis of the immobilized initiator. PMMA grafted glass beads were prepared as described previously[12]. Composites were prepared by mixing 26 wt%(16 vol%) glass beads with PVC, stabilized with 1.2 wt% di-n-octyltin-5,5′-bis(iso-octylmercaptoacetate), on a two roll mill for 8 min at 180°C, after which tensile bars (ASTM D-638) were pressed for 3 min at 4.05 MPa and 180°C. Some samples were annealed for several hours at 0.25 MPa and 150 or 160°C. Unfilled PVC was prepared in exactly the same way as for the filled samples. Details of the samples used are given in *Table 1*.

Mechanical tests

Stress–strain and volume–strain experiments were performed on a Zwick 1474 tensile tester at a constant strain rate of 5% min^{-1}. The volume changes were measured by continuous determination of all three dimensions of the tensile bar by three extensometers[3].

The SEM pictures were taken on an ISI DS-130 scanning electron microscope after gold deposition on the surfaces to prevent degradation of the polymers.

RESULTS

Figure 1 shows the stress–strain and volume–strain curves of unfilled PVC (sample 1), PVC filled with untreated glass beads (sample 2) and filled with AAPS-treated glass beads (sample 3). *Figure 2* shows the stress–strain and volume–strain curves of PVC filled with glass beads having a grafted PMMA coating (samples 4–6). All materials show a volume increase at low strains. For isotropic materials, the volume change at low strains (ε_x) can be approximated by:

$$\Delta V / V_0 = (1 - 2\nu_m)\varepsilon_x$$

As the volume change at low strains is a function of Poisson's ratio of the matrix polymer (ν_m) only, the same initial slope is measured in the volume–strain curve for all materials in *Figures 1* and *2*. For samples 2 and 3 in *Figure 1*, an increased slope in the volume–strain curve is measured at strains above 0.7 and 0.9%, respectively. This extra volume increase is due to debonding of the filler particles, resulting in the formation of voids at the poles of the debonded particles. As a consequence the slope of the stress–strain curve starts to decrease at the debonding point. This results from the fact that debonded glass beads do not carry any load. These stress–strain and volume–strain curves closely resemble some literature experiments describing poorly adhering glass bead filled thermoplastics[3,6]. Above a few per cent elongation, samples 1, 4, 5 and 6 start to shear yield. As expected for a deformation mechanism dominated by

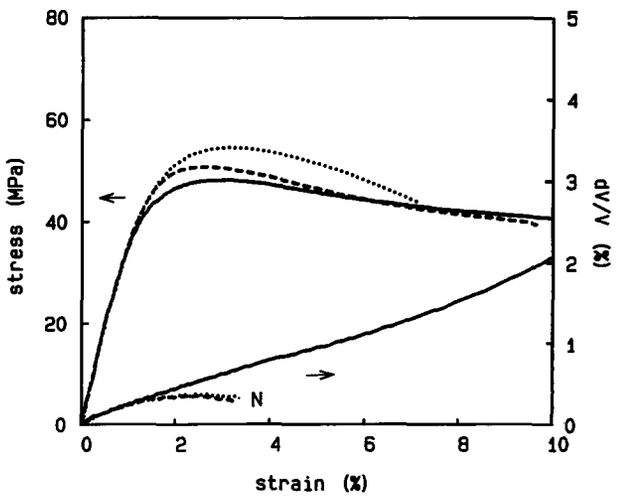

Figure 2 Stress–strain and volume–strain curves of PVC filled with glass beads having a PMMA coating (—, sample 4; ----, sample 5; ·····, sample 6). N as in *Figure 1*

Table 2 Mechanical properties of PVC samples after milling and pressing at 180°C

Sample no.	Filler coating	Polymer load (mg PMMA g^{-1} glass)	E_{mod} (GPa)	σ_{yield} (MPa)	ε_{yield} (%)
1	Unfilled	–	2.94	58.3	4.4
2	None	–	3.95	40.5	3.7
3	AAPS	–	3.99	41.8	3.5
4	PMMA	1.2	3.93	47.9	2.9
5	PMMA	1.7	3.99	50.6	2.5
6	PMMA	2.0	3.91	55.0	3.1

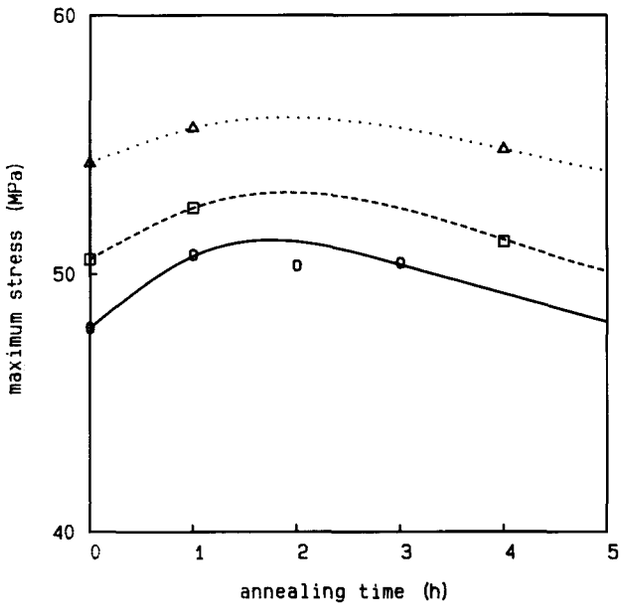

Figure 3 Maximum stress *versus* annealing time (○, sample 4 at 160°C; □, sample 5 and △, sample 6 at 150°C)

shear yielding, the volume hardly changes in this stage. At higher strains, most samples begin to neck. If one of the extensometers is located in the necking region, this non-uniform deformation mechanism causes a sharp decrease in the measured (apparent) volume. The volume–strain curves of samples 5 and 6 do not show any sign of debonding. For these composites a higher stress level is measured, compared with the composites with untreated or AAPS-treated glass beads. From *Figures 1* and *2* it can be seen that the level of adhesion between filler and polymer matrix in samples 4 and 5 is intermediate between good adhesion (sample 6) and poor adhesion (sample 2 and 3).

The mechanical properties of unfilled and glass bead filled PVC are given in *Table 2* as a function of the glass bead coating. The Young's modulus is determined from the initial slope of the stress–strain curve, where all the glass beads are well bonded (even for the composite with untreated glass beads). The Young's modulus seems to be unaffected by the type of coating on the glass beads. On the other hand the coating has a pronounced effect on the maximum stress, which increased in the sequence going from samples 2–6 almost attaining the maximum stress of unfilled PVC. The increasing maximum stress is due to an increased adhesion between filler and matrix, as was found for nylon 6, polystyrene and polycarbonate matrices[3,6].

Annealing the test bars should promote interdiffusion of grafted PMMA and PVC[13] but it did not result in significantly higher maximum stresses (*Figure 3*). The small increase in the first hour could be attributed to better adhesion but also to some degradation (and stiffening) of the PVC matrix. The latter could also account for the lightly increased modulus and darkening of the matrix. Further annealing led to severe degradation and lowering of the observed Young's moduli and maximum stresses.

Some conclusions can be drawn from macroscopic examinations of the test bars. As shown in *Figure 4a*, shear bands can clearly be observed after deformation of clean glass bead filled PVC (sample 2). These bands can only be observed very close to the fracture surface for composites with PMMA grafted beads (sample 6, *Figure 4b*). Unfilled PVC does not show any shear bands.

Scanning electron microscopy micrographs of the fracture surfaces clearly show the effect of the glass coating on the extent of adhesion. *Figures 5* and *6* are SEM micrographs of the fracture surface of samples 2 and 3, respectively. The large voids around the beads and the lack of any matrix polymer attached to the filler is indicative of poor adhesion between filler and matrix. Upon grafting PMMA on the filler surface, adhesion is improved, as can be clearly seen from the SEM micrograph of the fracture surface of sample

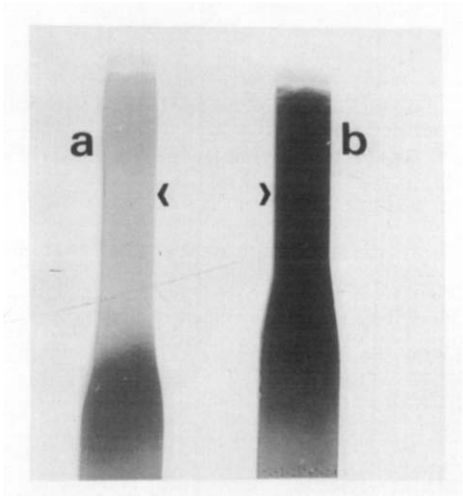

Figure 4 Tensile bars after fracture: (a) sample 2; (b) sample 6. Scale bar = 25 μm

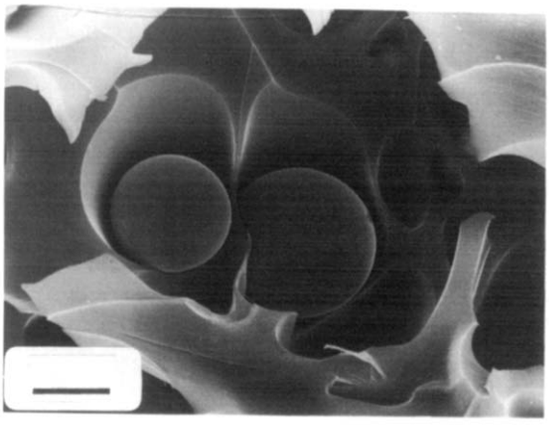

Figure 5 SEM micrograph of the fracture surface of sample 2, after annealing at 150°C for 1 h. Scale bar = 25 μm

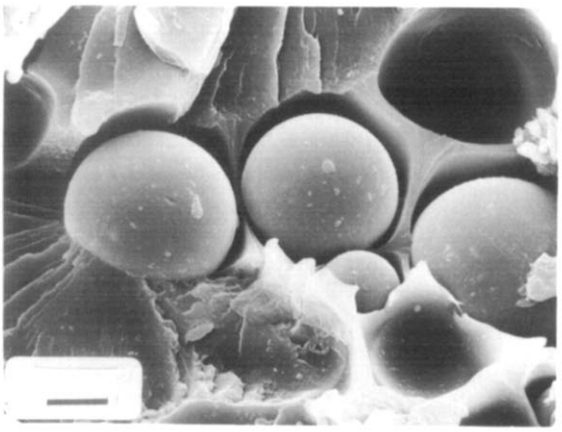

Figure 6 SEM micrograph of the fracture surface of sample 3, after annealing at 150°C for 1 h. Scale bar = 25 μm

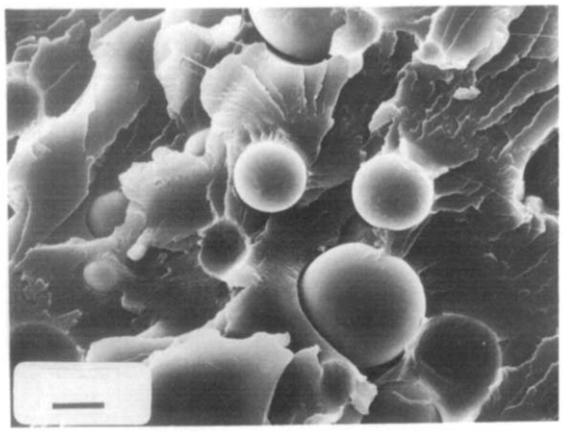

Figure 7 SEM micrograph of the fracture surface of sample 6, after annealing at 150°C for 1 h. Scale bar = 25 μm

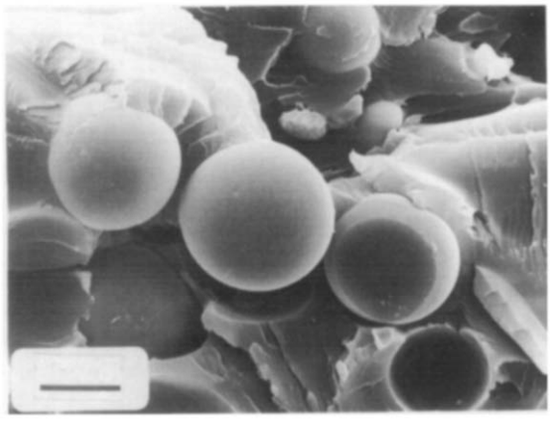

Figure 8 SEM micrograph of the fracture surface of sample 4, after annealing at 160°C for 1 h. Scale bar = 25 μm

6 (*Figure 7*). There is still some debonding observed but the adhesion of matrix polymer to the filler is improved compared with the former cases. Samples 4 and 5 have matrix–filler adhesion levels intermediate between samples 2 and 6, as can be seen from the SEM micrographs of the fracture surfaces (*Figures 8* and *9*, respectively). The voids around the glass spheres decrease in size and the amount of matrix polymer bonded to the filler increases upon going from sample 3 to samples 4, 5 and 6, indicating that adhesion improves in that order.

The fracture surface of sample 6, after annealing for 4 h at 150°C (*Figure 10*), seems to be similar to that in *Figure 7*, indicating that annealing of the tensile bar does not seem to promote adhesion, as previously concluded from mechanical tests (*Figure 3*). We examined the tensile bars at the point indicated by the arrow heads in *Figure 4*, and shear bands were observed in the case of poor adhesion but were absent in the case of good adhesion. The bars were broken at liquid nitrogen temperature to avoid additional debonding of the filler particles. The differences between samples 2 and 6 are clear, as can be seen from the SEM micrographs of the surfaces in *Figures 11* and *12*, respectively. The filler particles of sample 2 are completely debonded whereas the adhesion in sample 6 is very good.

DISCUSSION

The Young's modulus increases by the introduction of glass spheres, irrespective of the surface modification of the filler. The modulus of PVC filled with 16 vol% glass beads is 4.18 GPa, calculated from the Chow model[14] and 4.20 GPa using the modified Kerner[15] model, both assuming perfect adhesion between filler and matrix. The mechanical properties (tensile moduli E_f, E_m and Poisson's ratio ν_m) used in these calculations are: $E_f = 70$ GPa, $E_m = 2.94$ GPa and $\nu_m = 0.38$. The measured moduli are all very close to the calculated ones

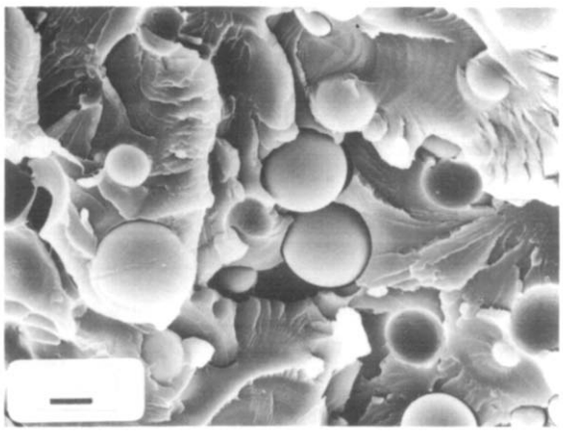

Figure 9 SEM micrograph of the fracture surface of sample 5, after annealing at 150°C for 1 h. Scale bar = 25 μm

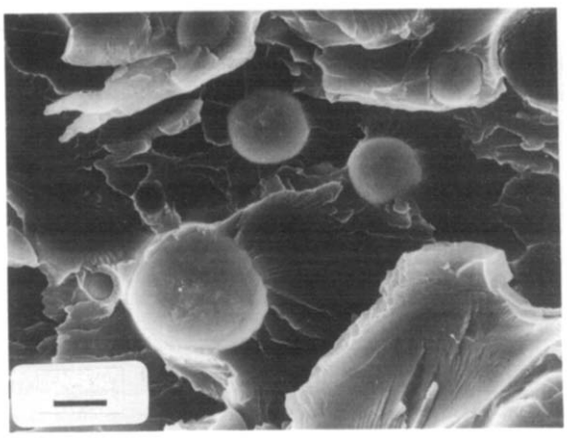

Figure 10 SEM micrograph of the fracture surface of sample 6, after annealing at 150°C for 4 h. Scale bar = 25 μm

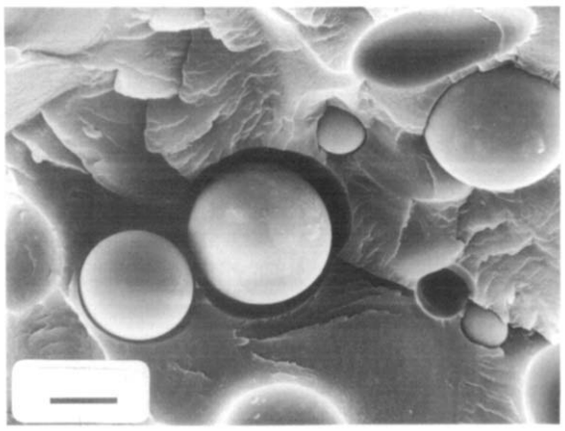

Figure 11 SEM micrograph of the surface at the height of the arrow head in *Figure 4*, after breaking sample 2 at liquid nitrogen temperature. Scale bar = 25 μm

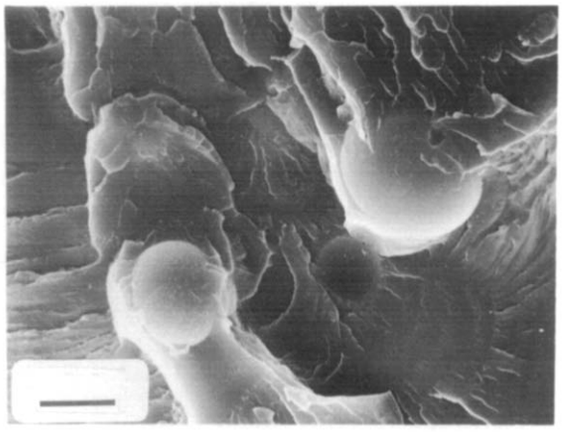

Figure 12 SEM picture of the surface at the height of the arrow head in *Figure 4*, after breaking sample 6 at liquid nitrogen temperature. Scale bar = 25 μm

(*Table 2*), indicating that adhesion between filler and matrix is perfect at low strains. This is confirmed by tensile tests, where we observe a bend in the stress–strain and volume–strain curves of samples 2 and 3 (*Figures 1* and *2*), indicating that debonding starts at an elongation of 0.7 and 0.9% for samples 2 and 3, respectively. Samples 4–6 do not show any clear bends, due to debonding before the yield point.

The apparent good adhesion between filler and matrix in samples 2 and 3 at low strains is caused by thermal shrinkage stresses around the glass spheres. These stresses arise from the different thermal expansion coefficients of filler and matrix, causing the matrix to shrink more than the filler upon cooling the composite after moulding. According to the theory of Fowkes *et al.*[16] PVC may be considered as a Lewis acid which has little interaction with the acidic surface of clean glass whereas the surface of AAPS-treated glass is more basic and might have a specific interaction with PVC, through the carbonyl group of AAPS and the CHCl group of PVC, leading to a better interaction between filler and matrix. The slightly better adhesion in sample 3 compared with sample 2 was indicated by the higher debonding strain of the former. Samples 4–6 have better adhesion between filler and matrix, due to specific interactions between PVC and PMMA[17] which can lead to interdiffusion and formation of entanglements between grafted PMMA and PVC.

Taking the maximum stress as a measure of the level of adhesion, we see that the adhesion improves going from samples 4 to 5 to 6. Sample 6, with the highest polymer load, the lowest molecular weight and the smallest surface per coil of grafted PMMA, has clearly the highest level of adhesion, but more experiments are needed to reveal which of the above properties is the most important for good adhesion.

Annealing the tensile bars at 150 or 160°C for several hours does not improve adhesion significantly (*Figure 3*). The slightly higher maximum stresses are accompanied by slightly higher moduli, indicating that the matrix stiffens upon heating, probably resulting from some degradation. In order to improve adhesion by interdiffusion of PVC and grafted PMMA, annealing times should exceed 4 h as we have shown that, using high molecular grafted and free PMMA, interdiffusion over a few tenths of a micrometre takes many hours[13]. However, as annealing deteriorates the mechanical properties of PVC, due to thermal degradation, at longer annealing times such degradation would mask the effects of an eventually improved adhesion.

The polydispersity of grafted PMMA allows the ends of the longest chains to stretch further away from the glass surface than the ends of the shorter chains, so in a relatively short time, some interdiffusion between these long chain ends and PVC might lead to a mixture with entanglements that improve the strength of the interphase.

There exists some controversy in the literature about the fracture mechanism of PVC; one author could not find any evidence for crazing[18], whereas others found craze initiation at places of increased stress like surface flaws[19] or notches[20], or observed combined crazing and shear deformation[21]. In glass bead filled PVC we found no evidence of craze formation, and observed that before fracture shear bands are formed in PVC with poorly adhering glass beads. These bands are formed much less in PVC with good adhering glass beads. The shear band formation needs some explanation. Dekkers and Heikens[6] studied glass bead filled polycarbonate and interpreted the fracture mechanism by analysing the stress around a glass sphere. With excellently adhering spheres, shear bands were formed at 45° from the poles, which is the place of maximum shear stress (τ_1) and distortion strain energy density (W_d). With poorly adhering spheres, debonding proceeded until the interfacial crack was at an angle of 60° from the pole and shear bands formed at the interfacial crack tip. Debonding and shear band formation resulted in a macroscopically observable shear band pattern which is characteristic of a ductile polymer filled with poorly adhering glass beads.

The shear band pattern observed in clean glass bead filled PVC (*Figure 4a*) indicates that adhesion between filler and matrix is poor. The presence of these bands only close to the fracture surface in sample 6(*Figure 4b*) confirms the results discussed above, that the adhesion between PMMA grafted glass and PVC is superior to the adhesion between clean glass beads and PVC. The fact that shear bands are formed close to the fracture surface can be attributed to increased stresses resulting from necking prior to fracture. Shear bands are also observed in sample 3, and with decreasing intensity in

samples 4, 5 (not shown) and 6, indicating poor adhesion between AAPS-treated glass and an improved adhesion between PVC and PMMA grafted glass with increasing PMMA content (*Table 2*).

The SEM study confirms the observations discussed above and gives additional information. Comparing the fracture surfaces of samples 2–6 (*Figures 5, 6, 8, 9* and *7*, respectively), we see that the adhesion between filler and matrix in samples 2 and 3 is very poor, resulting in smooth glass bead surfaces and the large voids between filler and matrix. There is hardly any improvement in adhesion between filler and matrix in sample 4, having PMMA grafted upon glass with the smallest polymer load, compared with sample 3(AAPS-treated glass), and in sample 5 again little improvement is achieved. The best adhesion is found in sample 6(*Figure 7*), although some debonding can be observed, resulting in some smooth areas at the surface of the glass beads and the voids between filler and matrix. Annealing of sample 6 does not improve the mechanical properties of the composite. Moreover, hardly any further improvement in adhesion could be found from SEM (*Figure 10*).

Combining the facts that the yield stress of the PVC filled with PMMA grafted glass beads is almost as high as the yield stress of unfilled PVC, that annealing the tensile bars does not improve adhesion and that interdiffusion of grafted PMMA and matrix PVC cannot be complete after the diffusion times used, leads to the conclusion that adhesion is already greatly improved by interdiffusion of PMMA chain ends and the PVC matrix, which is a relatively fast process.

The greatest effect of grafted PMMA on adhesion can be seen in *Figures 11* and *12*, which show the surfaces of the tensile bars (cold) broken at the place indicated by arrow heads in *Figure 4*. As we have already concluded from *Figure 4*, sample 2 (*Figure 11*) has poor adhesion between filler and matrix and sample 6 (*Figure 12*) good adhesion. In *Figure 12* no debonding can be observed, the glass beads are buried in the matrix and the matrix material is bonded well to the spheres, indicating that the adhesion between this filler and PVC is very good. During tensile testing, adhesion between filler and matrix (sample 6) remains good, although some debonding may occur due to necking of the sample.

CONCLUSIONS

In a model composite, consisting of glass bead filled PVC, the adhesion between filler and matrix can be improved by grafting PMMA onto the filler surface. The improved adhesion was concluded from several observations:

- the absence of an additional volume increase, indicative of debonding;
- the increased maximum stress of filled PVC upon grafting PMMA upon the filler, almost reaching the maximum stress of the matrix;
- SEM photography shows better adhesion between filler and matrix when the filler is grafted with PMMA.

The adhesion appears to be improved by grafting higher amounts of PMMA, decreasing the surface area per coil and decreasing the molecular weight of grafted PMMA.

Mixing the chain ends of grafted PMMA with the PVC matrix seems to be sufficient for good adhesion beween the glass beads and matrix.

ACKNOWLEDGEMENTS

We would like to thank Harry Nijland for taking the SEM photographs. The present investigation was supported by the Dutch Ministry of Economic Affairs, Innovation-oriented Research Programme on Polymer Composites and Special Polymers.

REFERENCES

1 Hull, D. 'An Introduction to Composite Materials', Cambridge University Press, Cambridge, 1981
2 Plueddeman, E. P. 'Silane Coupling Agents', Plenum Press, New York, 1982
3 van Hartingsveldt, E. A. A. and van Aartsen, J. J. *Polymer* 1989, **30**, 1984
4 Eastmond, G. C. and Mucciariello, G. *Polymer* 1982, **23**, 164
5 Abate, G. F. and Heikens, D. *Polym. Commun.* 1983, **24**, 342
6 Dekkers, M. E. J. *PhD Thesis* Eindhoven University, 1985
7 Vollenberg, P. H. Th. *PhD Thesis* Eindhoven University, 1987
8 Kendall, K. and Sherliker, F. R. *Br. Polym. J.* 1980, **12**, 85
9 de Gennes, P. G. *Macromolecules* 1980, **13**, 1069
10 Wu, S., Chuang, H.-K. and Han, C. D. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 143
11 Vorenkamp, E. J., van Ruiten, J., Kroesen, F. A., Meyer, J. G., Hoekstra, J. and Challa, G. *Polym. Commun.* 1989, **30**, 116
12 Boven, G., Folkersma, R., Challa, G. and Schouten, A. J. *Polym. Commun.* 1991, **32**, 50
13 Boven, G., Brinkhuis, R. H. G., Vorenkamp, E. J., Challa, G. and Schouten, A. J. *Polymer* in press
14 Chow, T. S. *J. Polym. Sci. Polym. Phys. Edn* 1978, **16**, 959
15 Kerner, E. H. *Proc. Phys. Soc.* 1956, **B69**, 808
16 Fowkes, F. M., Tischler, D. O. and Wolfe, J. A. *Org. Coat. Appl. Polym. Sci. Proc.* 1981, **46**, 1
17 Vorenkamp, E. J. and Challa, G. *Polymer* 1988, **29**, 86
18 Kambour, R. P. *J. Polym. Sci.* 1966, **A2**, 17
19 Wales, J. L. S. *Polymer* 1980, **21**, 684
20 Lee, L. H., Mandell, J. F. and McGarry, F. J. *Polym. Eng. Sci.* 1986, **26**, 626
21 Brown, H. R. and Chin, T. H. *J. Mater. Sci.* 1980, **15**, 677