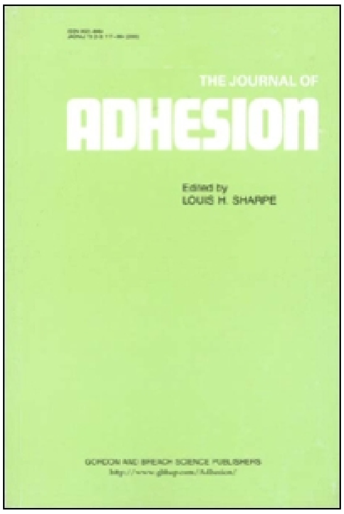

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Influence of the Interphase on Impact Properties of Zirconium Silicate Filled High-Density Polyethylene*

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Yellow zirconium silicate is a promising substitute for cadmium pigments used in plastics. However, the incorporation of zircon pigment in HDPE without loss of impact strength is required. By introducing the untreated pigment in the polymer, the impact strength reduces to 60% of the value for the unfilled polymer. Different types of silane coupling agents were used to regain the impact strength of the composite. Octadecylsilane acted as a wetting agent rather than as a coupling agent. The impact strength hardly improved. A vinyl functional and a methacryloxy functional silane improved the impact strength to 70% relative to the unfilled polymer. The physically bonded, interdiffused network formed by silane and polymer improves the impact strength by the flexible nature of the interphase. An azidosilane improved the impact strength only to 73%: the interphase bonded covalently to the polymer as well as to the filler, in that way improving the impact strength, but behaving as a brittle system. A relatively thick, flexible interphase bonded covalently to filler and polymer was created. This interphase improved the impact strength to the value of the unfilled polymer.

KEYWORDS HDPE; polyethylene; filler; particulates; interphase; impact strength; pigments; silane

INTRODUCTION

Replacing cadmium pigments in plastics is an important and timely item. In the U.S.A. and also in some European countries the use of these pigments has been restricted by governmental laws.[1–3] For example,[4] in The Netherlands the maximum permitted cadmium content for a product is 50 mg/kg. The other countries of the European Community have put the limit for cadmium at 100 mg/kg for plastic products.[4] Products containing higher amounts of cadmium are considered as chemical hazards and they require special waste disposal. In some other countries the use of cadmium pigments is also severely restricted.

Because of the excellent properties of cadmium pigments it is difficult to replace them. Cadmium pigments are heat resistant up to 400°C, have high colouring power,

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high opacity and exhibit good chemical resistance.[5] Moreover, cadmium pigments are generally good UV-stabilisers. At this time no alternatives, acceptable for all applications in plastics, are available. Most of the inorganic alternatives are based on heavy metals (lead, chromium, etc.) and are, therefore, also not acceptable. The drawback of most organic pigments is their low heat resistance. Therefore, they are not stable at typical processing temperatures for plastics.[5]

Yellow zirconium silicate (zircon) is a good alternative for the replacement of yellow cadmium sulphide shades. This zircon pigment is a synthetic, processed, mineral silicate which has no known harmful or toxic properties. It is heat resistant to temperatures as high as 800°C and has a colour resembling that of cadmium yellow. It is already known as a colorant for the use in ceramics, but the use in plastics is new. The chemical resistance is also excellent. The only acid able to attack zircon is concentrated hydrofluoric acid. At low temperatures zircon is also not attacked by basic materials[6].

SCOPE

The main object of this study was to develop a yellow coloured, high-density polyethylene suitable for the production of bottle crates. One of the most important properties of materials used for bottle crates is the impact resistance, because of the rough treatment during transportation. It is well known that, by incorporation of a mineral filler in a polymer, the impact strength in general decreases considerably.[7] Hence, filling HDPE with zircon pigment with a minimal loss of impact strength was the most important object of this work.

In order to improve the mechanical properties of mineral filled polymers, it is in general essential to modify the surface of the filler. Much research has been done in this field, but the subject of impact strength was scarcely studied. In most cases the influence on tensile strength and tensile modulus was studied. Only a few authors reported the influence of differences in treated and untreated mineral fillers on impact properties of composites; in many cases the improvement was minimal or even a decrease was measured.[8,9]

Often, silane coupling agents are used for the modification of mineral surfaces. Application of these chemicals is well known. Two excellent books on this group of surface modifiers have been published.[10,11] Modification of silicate surfaces with silanes is widely used. For this reason, modification of the surface of the zirconium silicate pigment should not be a problem.

In this work the influence of some selected silanes, differing in organofunctional group, on the impact strength of zircon filled HDPE was investigated. Each type of silane results in a different type of interphase between filler and polymer. The results of impact strength studies should lead to insight into the relationship between the structure of the interphase and the impact resistance of the filled polymer.

EXPERIMENTAL

The yellow zircon used has an average particle size of about 4 μm. The silanes used are shown in Table I, with full chemical name and abbreviation. 3-MPS and VTMS were

TABLE I
Abbreviation and chemical name of silanes used

Abbreviation	Chemical name	Purchased from
3-MPS	3-methacryloxypropyl trimethoxysilane	Taurss Cur Chimica, The Netherlands
VTMS	Vinyl trimethoxysilane	Taurss Cur Chimica, The Netherlands
ODS	Octadecyl trimethoxysilane	Fluka Chimica, Switzerland
Azidosilane	Ethylphenylsulfonylazide trimethoxysilane	Petrarch Systems Inc., U.S.A.

used because of the recommendation in combination with HDPE in a product sheet of Union Carbide.[12] Both these silanes are capable of forming a thick layer on the particle surface. ODS was chosen because of the chemical structure, resembling that of polyethylene. The long C-18 chain might interact with the matrix polymer and improve compatibility between filler and matrix. Azidosilanes are a group of silanes developed especially for the formation of covalent bonds between fillers and polyolefins. The silane part of the molecule is capable of bonding to the filler surface, while the azide group is capable of reacting with polyethylene molecules.[8]

The silanes were deposited at the surface of the zircon pigment by pretreatment from an appropriate solvent. 3-MPS and VTMS were deposited from a 1 vol-% solution in a mixture of ethanol and water (1/1 v/v) at pH ≈ 4. Both these silanes are soluble in the ethanol-water mixture. After allowing 500 ml of this solution to stand for 10 minutes in order to make sure the silanes are hydrolysed, 500 g of zircon were added. The zircon slurry was stirred for 15 minutes. During this period the silanes will absorb at the zircon surface. The zircon was separated from the solvent by centrifuging. Finally the zircon was dried at 70°C in air for 24 hours.

ODS is deposited out of water, but is not soluble in this solvent. Therefore, it was necessary to make a dispersion of ODS droplets in water at pH ≈ 4. This was done by stirring vigorously 10 ml of ODS with 500 ml water for 10 minutes. To this dispersion 150 g of zircon was added. Because of the bad contact between ODS and the zircon surface, the solution was stirred for 2.5 hours in order to get sufficient adsorption of ODS. Again, the zircon and solvent were separated by centrifuging. The zircon was dried at 70°C for 24 hours. The treatment with ODS was done three times in order to modify a total of 450 g of zircon.

The azidosilane was deposited at the surface of the zircon particles from a 1 vol-% solution in methylene chloride. A total of 500 g of zircon was treated from 500 ml of solution for 30 minutes. After the treatment the zircon was separated from the solvent by centrifuging. In this case the zircon was dried for 24 hours at room temperature to prevent breakdown of the azide functionality.

All treated zircons were studied with DRIFT (Diffuse Reflectance Fourier Transform Infrared spectroscopy) to investigate the surface. From this technique it was clear that all treatments were successful. The treated fillers were also extracted with a solvent (THF for 3-MPS, VTMS and ODS, methylene chloride for the azidosilane) to prove that there was chemical bonding between silane and filler surface. It appeared that after extraction silane molecules were still present at the filler surface. This means that all silanes were bonded covalently to the filler surface.

The treated filler was compounded into a masterbatch in HDPE (40 wt-%) on a two-roll mill at 160°C. The HDPE used was Stamylan 9089U (DSM; $M_w = 6 * 10^4$, MFI = 8 dg/min.), a linear polyethylene developed especially for the production of bottle crates. Then the granulated masterbatch was mixed with virgin HDPE in a Brabender twin-screw extruder, at temperatures of 110, 170, 170 and 140°C for the four heating zones. The composites obtained contained only 2 wt-% of zircon. This amount is needed to get the same colour as with cadmium yellow. The filler content was checked by thermal gravimetric analysis and was found to be 1.98 ± 0.02 wt-%. The mixtures were injection moulded into Izod impact bars (6.4 × 12.7 × 63.5 mm) at 270°C using an Arburg injection moulding machine.

The impact bars were notched, the notch being 45° with a top radius of 0.25 mm (0.01 inch) and 2.5 mm deep. The notched samples were tested on a pendulum impact tester with an energy of 1 Joule. The reported impact strengths are the mean values of measurements on 10 test specimens of each sample. The impact strength is reported as the value relative to the unfilled polymer. Many researchers report the value relative to the polymer with untreated filler. However, this does not tell anything about the decrease in impact strength of the polymer due to the untreated filler. An improvement of 10% relative to the composite with untreated filler can still mean a decrease of more than 40% relative to the virgin polymer.

To obtain further evidence of the interphase structure or behaviour, the fracture surfaces of some tested impact bars were studied with a Philips XL-20 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

An overview of surface treatments and relative impact strengths is given in Table II. The composites with zircon without any coating showed a decrease in impact strength to about 60% of the value for the virgin polymer, even with a filler percentage as low as 2 wt-%. As might be expected, there is no adhesion between filler and matrix polymer. This is shown in Figure 1. It is also clear that filler aggregates are formed. Both the lack of adhesion and the formation of filler clusters are responsible for the dramatic loss of impact strength.

Treatment of zircon with ODS gave only a slight improvement in impact strength to 63%. The interactions at the interphase are weak, although the structure of the long aliphatic organic group resembles the chemical structure of polyethylene. Obviously,

TABLE II
Relative impact strength of 2 wt-% zircon/HDPE-systems with different surface treatments

Surface treatment	Impact strength relative to HDPE (%)
None	60 ± 4
ODS	63 ± 2
3-MPS	70 ± 3
VTMS	70 ± 4
Azidosilane	73 ± 3
Thick, rubbery interphase	95 ± 5

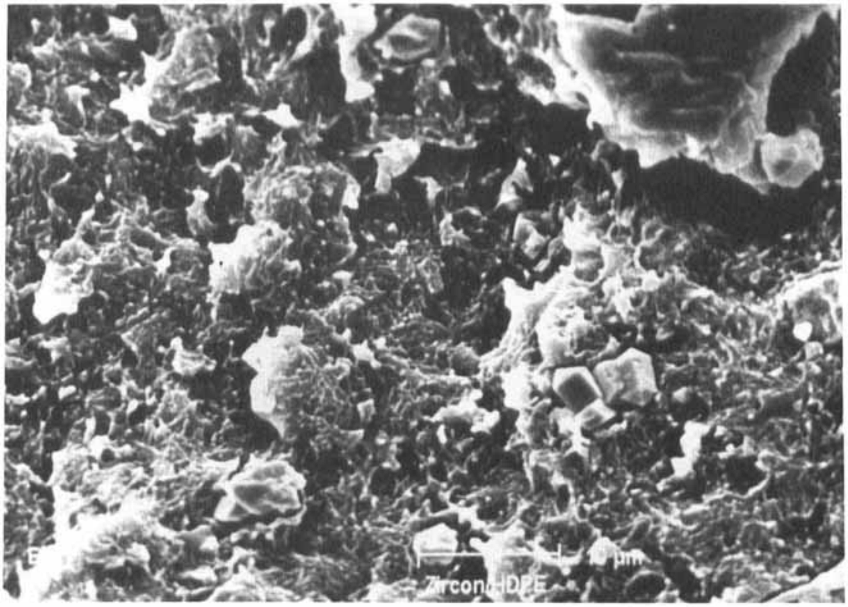

FIGURE 1 SEM-photograph of the fracture surface of a composite of 2 wt-% untreated zircon pigment in HDPE.

the alkyl chains of ODS are still too short to entangle with the polymer. This is in agreement with a minimum chain length of 200–300, that is needed for entanglement.[13] Although some good adhesion exists after extrusion of the composites, this adhesion was probably destroyed during injection moulding of test specimens. The interphase presumably cannot cope with the high shear rates during injection moulding. The absence of adhesion between the interphase and the matrix polymer is clearly shown by SEM (Figure 2). Most likely ODS is forming only one effective monomolecular layer at the interphase. This is shown schematically in Figure 3. A second layer of this silane would probably deposit with the alkyl chains oriented towards the filler surface. The interaction with the first layer will be very weak, because there are only relatively weak Van der Waals interactions between the alkyl chains. This will not give a stronger interphase. Upright deposition with the silanol groups towards the surface is almost impossible because of sterical hindrance of the long alkyl groups. The absence of polar groups in the organofunctional part of the silane makes it impossible to form a network at the interphase.

Presumably, the only improvement achieved by the use of ODS is the better dispersion of filler particles, resulting in the absence of aggregates. This would mean that ODS is acting more as a wetting agent than as a a coupling agent, thus providing a better dispersion of filler particles in the polymer, rather than improving adhesion between filler and polymer. Hence, the improved dispersion of particles in the polymer is the origin of the slight improvement in impact strength.

VTMS and 3-MPS both gave a reasonable improvement in impact strength. The impact strength rose to about 70% of the unfilled polymer. Obviously, these modifiers

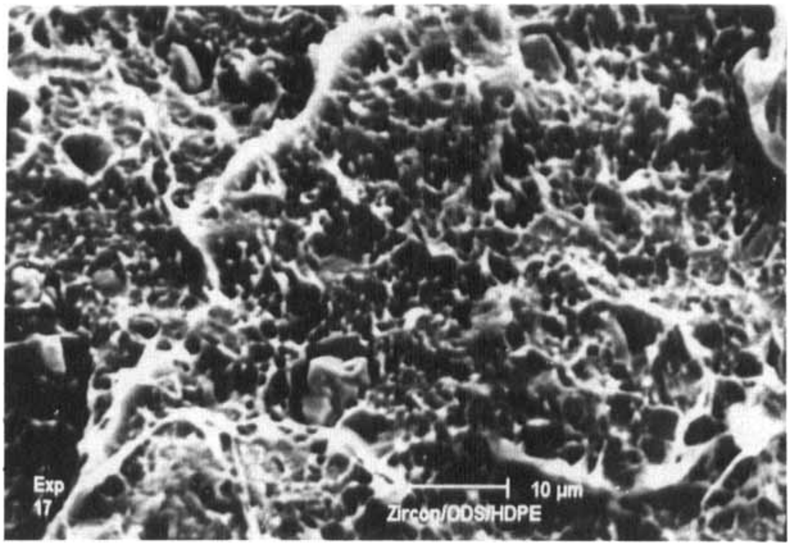

FIGURE 2 SEM-photograph of the fracture surface of a composite of 2 wt-% ODS treated zircon pigment in HDPE.

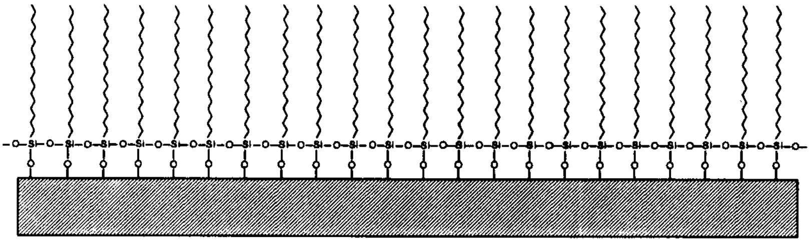

FIGURE 3 Simple schematic representation of the layer formed on an inorganic surface by ODS.

did improve the adhesion between filler and polymer. This might be expected, taking into consideration the publications by Jones[14] and Plueddemann[15] on the structure of the interphase formed by 3-MPS. They both presented figures that clearly illustrate a diffuse interphase of silane and polymer molecules interacting through physical bonds.

In Figure 4 the model of a silane layer as proposed by Jones[14] is shown. The silane (3-MPS) forms a thick gradient layer at the interphase, going from bonded covalently through siloxane bonds at the filler surface to bonded to one another through hydrogen bonds in the outer layers. The more loosely bonded silane molecules in the outerlayers of the interphase are able to form a network with polymer molecules by interdiffusion. This concept is shown in Figure 5.[15]

3-MPS and VTMS are both capable of forming an interdiffused network with the matrix polymer. Most likely, this also occurs in the zircon/HDPE-system. The interaction between the polymer and the silane is physical, no chemical bonds between

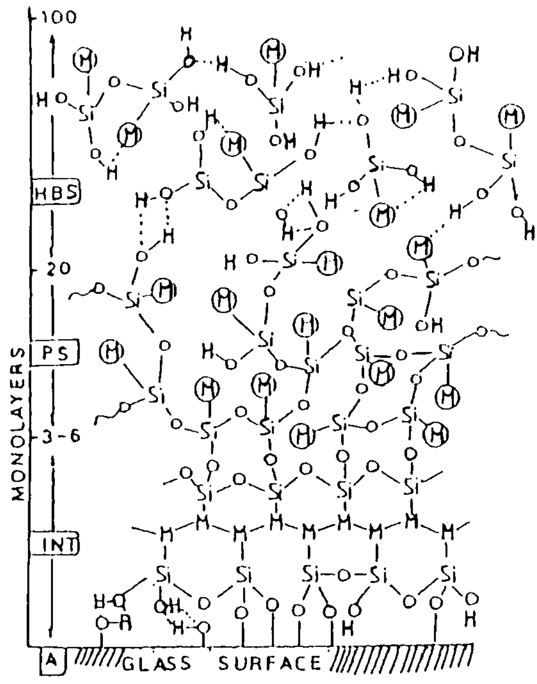

FIGURE 4 Schematic representation of the multilayer formed by 3-MPS on an inorganic surface as was presented by Jones.[14] INT = silane-filler interface. PS = polysiloxane region. HBS = layer of hydrogen bonded oligomeric siloxanes.

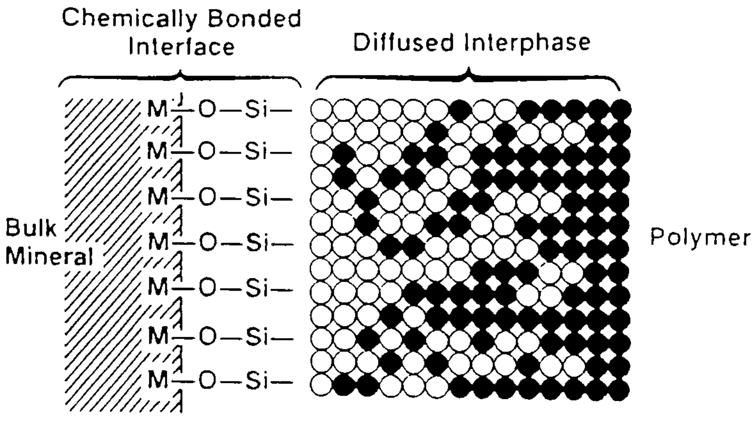

FIGURE 5 Model of the formation of an interdiffused network of silane and polymer molecules as was presented by Plueddemann.[15] (○ regions of silane; ● regions of polymer)

silane and polymer can be formed. The interphase is capable of absorbing part of the energy applied during impact measurements, because of its flexible nature. The adhesion between interphase and polymer is confirmed by SEM measurements (Figure 6). The SEM-photograph shows adhesion across the interphase, but the

FIGURE 6 SEM-photograph of the fracture surface of a composite of 2 wt-% 3-MPS treated zircon pigment in HDPE.

pigment particles are clearly visible. This means that failure of the composite during impact measurements most likely takes place at the interphase. Apparently, the physically bonded network at the interphase is torn apart. The adhesion between polymer and silane is obviously not strong enough to withstand the high forces applied during an impact measurement.

The azidosilane improved the impact strength of the filled polyethylene to approximately 73% of that of the virgin polymer. The improvement is somewhat better than with the use of 3-MPS and VTMS. SEM shows good adhesion between filler and polymer (Figure 7). This is not surprising, because azidosilanes are developed to form a covalent bond with polyolefins. Hence, the interphase is bonded chemically to the filler by siloxane bonds and to the polymer through reaction of the azido-group. However, the improvement in impact strength to only 73% shows that the interphase is not strong enough to absorb fully the energy applied during an impact measurement. SEM also shows that the filler particles are again clearly visible at the fracture surface of the composite. So, with the use of azidosilane the failure is still in the interphase.

The azidosilane is probably forming only a thin layer at the surface of the particle. This is common for silanes deposited from an organic solvent.[10] Due to the absence of large amounts of water, the silanes can only hydrolyse (and bond) in the presence of water at the surface of the filler. Therefore, only a thin interphase between particle and matrix polymer will be formed. However, the number of covalent bonds is high. The silane is bonded strongly to the filler as well as to the polymer. In this way a thin layer with many strong bonds is formed. As is known from the work of Plueddemann[10,15] thin interphases with many strong bonds may lead to brittle failure. So, with the use of

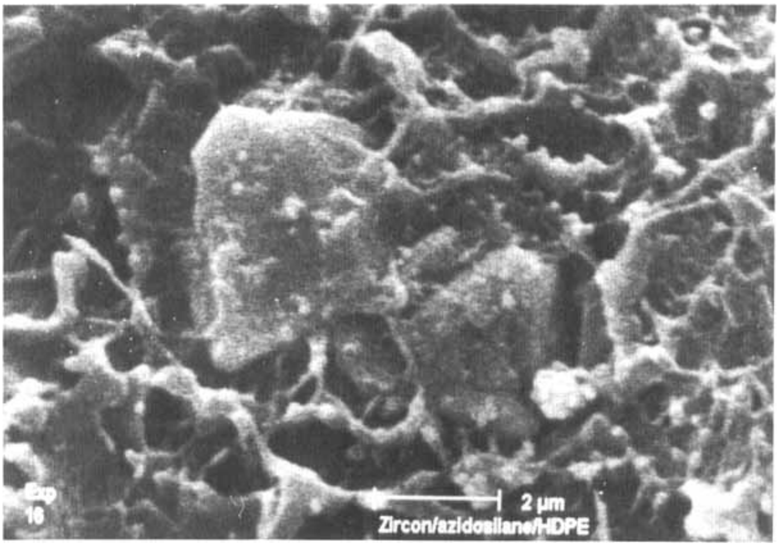

FIGURE 7 SEM-photograph of the fracture surface of a composite of 2 wt-% azidosilane treated zircon pigment in HDPE.

azidosilane, brittle failure across the interphase is the most likely cause of failure of the composite. Probably, due to the stronger covalent bonds the impact strength is somewhat higher than in the case of the physically bonded network formed by 3-MPS and VTMS.

Knowing that a relatively thick silane layer with only physical interaction with the polymer improved the impact strength to 70% and that a covalently bonded, thin azidosilane interphase improved it to 73%, it was decided to create a relatively thick, rubbery and covalently bonded interphase. This was achieved by using a standard commercially available silane, which is capable of forming an interdiffused network with the matrix polymer, in combination with an agent that is able to bond the silane to polyethylene. By this method a thick, flexible network, which is bonded covalently to the filler as well as to the polymer, is created. The structure of this interphase can again be represented by Figure 5.[15] The only difference between the 3-MPS or VTMS interphase and the thick rubbery interphase is the type of bond between the "white" and "black" circles. With the use of 3-MPS and VTMS the bonds are physical in nature, while in the case of the thick, rubbery interphase the bonds are chemical.

The impact strength of composites with this type of interphase is nearly equal to that of the unfilled polymer (95%). The fracture surface is shown in Figure 8a. This picture is taken at the same conditions as the other SEM photographs. Most important is the energy of the electron beam, the applied voltage being 12 kV; in this case no particles are visible at the fracture surface, indicating that the particles are still covered by polymer after fracture of the composite. In order to make the particles perceptible at the fracture surface, the energy of the electron beam was increased by raising the voltage to 30 kV. At this energy it is possible to look more deeply into the composite. In fact, it is possible to look directly underneath the surface of the sample. A photograph of the

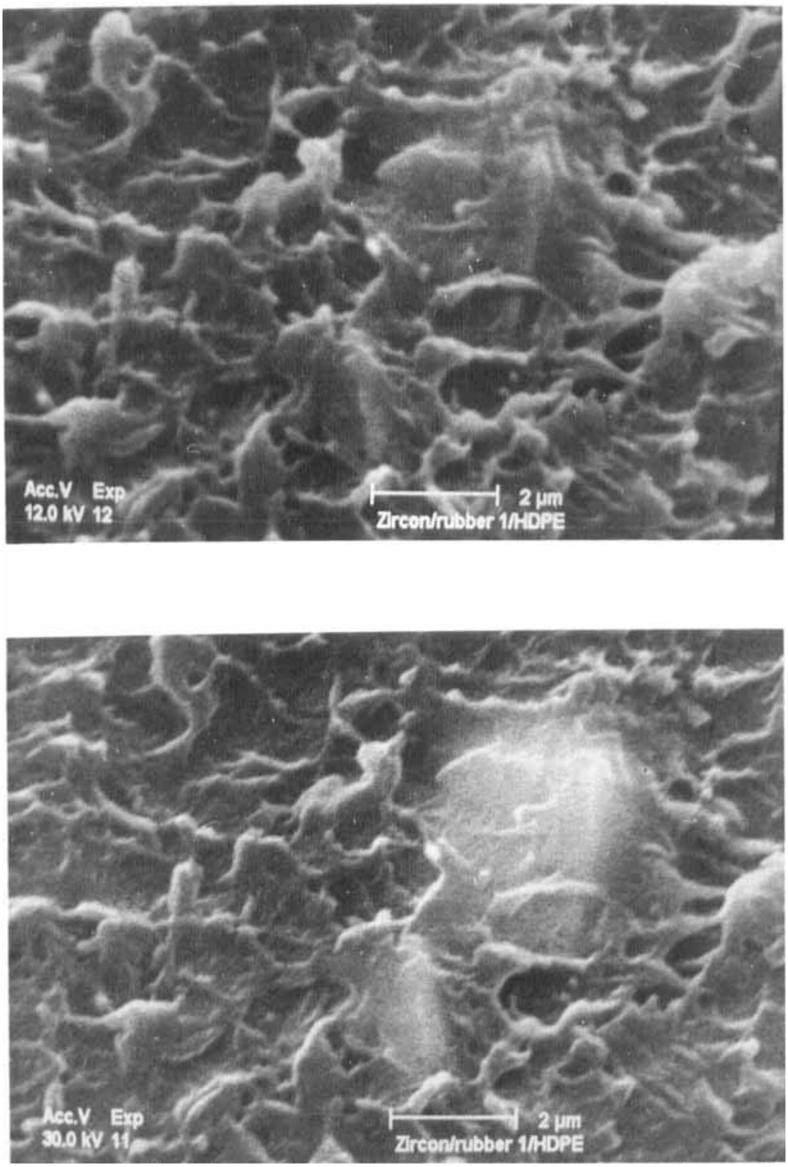

FIGURE 8 SEM-photographs of the fracture surface of a composite of 2 wt-% zircon in HDPE with a rubbery interphase between pigment and polymer. (a) energy of electron beam is 12 kV. (top) (b) energy of electron beam is 30 kV. (bottom).

same part of the fracture surface scanned at 30 kV is shown in Figure 8b. The (bright) particles are now clearly visible.

The impact strength measurements combined with the SEM analysis indicate that the failure of this composite does not take place in the interphase, but in the matrix. Hence, failure of the composite is of a cohesive nature. In theory this is the best situation possible, because only a different matrix polymer could improve the impact strength any further. The slight decrease in impact strength relative to the unfilled polymer is probably caused by imperfect treatment of some particles with silane. SEM studies showed that some interphases between matrix and filler are not strong enough to withstand the forces applied during impact tests. Probably these particles were not treated perfectly with silane. Perhaps, then only perfect treatment of the particles will improve impact strength to 100%.

CONCLUSIONS

It is possible to incorporate a mineral filler in polyethylene without significant loss of impact strength of the polymer. To achieve this it is necessary to create a thick rubbery interphase that is bonded covalently to both filler and matrix polymer.

The influence of the interphase on the impact strength of filled polyethylene can be explained by the structure of the interphase. The interactions between matrix polymer and interphase are too small in the case of ODS. The alkyl chains of ODS are too short to entangle with the polymer molecules. The near monomolecular ODS layer only provides a better dispersion of the filler particles. Hence, ODS is acting as a wetting agent and not as a coupling agent.

By using 3-MPS and VTMS a network is formed by inter diffusion of silane and polymer molecules, but the physical interaction between polymer and interphase is too weak to withstand fully the forces applied during impact strength measurements.

A thinner azidosilane interphase bonded chemically to the matrix polymer results in a reasonable improvement in impact strength. However, also in this case the value of the impact strength of the unfilled polymer was not reached. Most likely this thin, strongly bonded interphase is behaving in a brittle manner.

Combination of covalent bonding and formation of a flexible network at the interphase improves the impact strength to that of the virgin polymer. Obviously, the flexible, rubbery network is capable of resisting the high forces during impact strength measurements. Failure is transferred from adhesive (at the interphase) to cohesive (in the matrix). Hence, creation of this type of interphase is a good method to incorporate a mineral filler in a polymer without loss of impact resistance.

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References

1. D. Balmer, *J. Vinyl Technol.* **12**(2), 78–81 (1990).
2. E. J. Reger, *Ann. Tech. Conf. Soc. Plast. Eng.*, 5–8 (1990).
3. J. L. Heij, *Kunstst. en Rubber* **8**, 21–26 (1992).
4. *Kunststof Magazine*, june, july 1991, p. 60.

5. H. Jani, *Eng. Plast.* 3(5), 351–361 (1990).
6. W. J. Baldwin in *High Temperature Oxides, part II*, A. M. Alper, Ed. (Academic Press, New York, 1970), pp. 167–184.
7. A. Theisen, M. Hess and R. Kosfeld in *Integration of Fundamental Polymer Science and Technology*, 5, P. J. Lemstra and L. A. Kleintjens, Eds. (Elsevier Applied Science Publishers, New York, 1991), pp. 72–76.
8. G. A. McFarren *et al.*, *Polym. Eng. Sci.* 17(1), 47–49 (1977).
9. P. G. Pape and E. P. Plueddemann in *Silanes and Other Coupling Agents*, K. L. Mittal, Ed. (VSP, Utrecht, 1992), pp. 105–116.
10. E. P. Plueddemann, *Silane Coupling Agents*, (Plenum Press, New York, 1982).
11. K. L. Mittal, Ed., *Silanes and Other Coupling Agents*, (VSP, Utrecht, 1992).
12. *Silanes*, Union Carbide product sheet.
13. J. Klein in *Encyclopedia of Polymer Science and Technology*, vol. 9, J. I. Kroschwitz, Ed. (John Wiley & Sons, New York, 1987), p. 207.
14. F. R. Jones in *Interfacial Phenomena in Composite Materials '89*, F. R. Jones, Ed. (Butterworths, London, 1989), pp. 25–32.
15. E. P. Plueddemann in *Interfaces in Polymer, Ceramic and Metal Matrix Composites*, H. Ishida, Ed. (Elsevier Science Publishing Co., New York, 1988), pp. 17–33.