

Novel Coupling Agents for Mineral-Reinforced Polyamides

INTRODUCTION

The addition of particulate mineral fillers to thermoplastics, while improving some properties such as stiffness and thermal conductivity, almost always leads to attrition of other desirable properties such as tensile strength, impact strength, and ductility.¹ Recent work² relating to the incorporation of glass spheres into thermoplastics has indicated that this attrition is caused by "dewetting" of the filler under conditions of stress. This "dewetting" can be avoided by chemically coupling the filler to the thermoplastic matrix, and the organosilanes have been used almost exclusively for this purpose. The mechanism of the coupling reaction for organosilanes is believed to consist of a silanol group (formed by hydrolysis of the organosilane) condensing with a reactive hydroxyl group on the filler surface to form a filler—O—Si bond. A suitable organic substituent on the organosilane residue then interacts with the polymer matrix to couple it to the filler.^{3,4}

In the present work, this mechanism has been extended to enable the prediction of a wide range of types of organic compounds which will act as coupling agents and impart reinforcing properties to mineral fillers in polyamide composites. The extension of the theory depends upon the fact that some fillers, such as silica, contain hydroxyl groups which will take part in reactions in the manner very similar to the hydroxyl groups in aliphatic alcohols. Silica, for example, is readily chlorinated with thionyl chloride⁵ and esterified with lactic acid,⁶ and forms ethers with glycerol.⁷ It was therefore expected that organic compounds containing reactive groups such as carboxyl or primary alcohol groups would condense with silica on heating to form esters and ethers, respectively, the elimination of water being catalyzed by the acidic surface of the silica. By choosing suitable polyfunctional compounds containing not only groups capable of reacting with the silica but also groups capable of interacting with the polyamide, it was considered that it would be possible to predict organic materials capable of coupling polyamides to silica, thereby promoting reinforcement by the filler.

EXPERIMENTAL AND DISCUSSION

A selection of polyfunctional compounds was made on the basis of the above theory. In order to ensure facile reaction with the silica, groups such as aromatic hydroxymethylene or carboxyl groups were chosen for the functionalities desired for condensation with the silica. Similarly, the other groups in the coupling agent were chosen to maximize interaction with the polyamide and were typically aromatic amino and phenolic hydroxyl groups which could form strong hydrogen bonds with the amide linkages of the polyamide.

The coupling agents were used at a concentration of 0.7% by weight (based on the filler). Novacite silica was used as the filler, and the coupling agent was applied as a solution in just enough acetone to permit uniform wetting of the silica. After removal of the acetone, the coated silica was heated to 170°C for 45 min to promote condensation of the coupling agent with the silica. After cooling, the treated silica was mixed with nylon 6 in a 40:60 weight ratio. The mixture was then extruded at 265°C in a 1.5-in. Sterling extruder using a single stage screw of 30:1 *L:D* ratio. After granulation and injection molding, tensile testing was carried out on dry as-molded tensile test bars according to ASTM D-638-61T. Typical results obtained are shown in Table I.

In the absence of a coupling agent, the incorporation of 40% silica into nylon 6 caused a 22.5% loss of tensile strength compared to that of pure nylon. The effectiveness of the coupling agents is shown by the tensile strength of the composites treated with coupling agents. Thus, even 2-naphthoic acid which, while coupling well to the silica by ester formation, probably interacts primarily with the nylon only through Van der Waals forces still reduced this loss to only 9%. As the coupling capability with the nylon improved, the tensile strength improved as exemplified by *o*-hydroxybenzyl alcohol

TABLE I
Effect of the Use of Coupling Agents on Tensile Strength of Nylon 6
Containing 40% by Weight Novacite Silica

Coupling agent applied to filler	Tensile strength, psi	Tensile strength of composite as % of tensile strength of unfilled nylon 6
Nylon 6 unfilled	11,400	—
None	8,835	77.5
2-Naphthoic acid	10,400	91
<i>p</i> -Aminobenzyl alcohol	11,300	99
<i>p</i> -Aminobenzoic acid	11,400	100
<i>p</i> -Hydroxybenzoic acid	11,630	102
<i>o</i> -Hydroxybenzyl alcohol	11,970	105
γ -Aminopropyltriethoxysilane	11,856	104

which can form powerful hydrogen bonds with the nylon through its phenolic hydroxyl group and which led to a composite with a tensile strength in excess of that of the pure nylon. A control experiment using γ -aminotriethoxysilane confirmed that the new coupling agents described here are capable of promoting coupling as effectively as the organosilanes.

Confirmation that these new coupling agents formed actual compounds with the silica was obtained from the following facts: (a) Coupling agents could be extracted from the silica surface with methyl ethyl ketone prior to heating the mixture to 170°C but not afterward. (b) Organic material on the silica surface was confirmed by observation of a weight loss on ashing at 540°C, positive carbon and hydrogen analyses, and predicted fragments found in mass-spectrometric analysis of pyrolysis gases. (c) The necessity of having active hydroxyl groups on the filler surface was confirmed by treating calcined aluminum silicate, calcium carbonate, and graphite with *o*-hydroxybenzyl alcohol as the coupling agent. As predicted, no coupling occurred, the tensile strengths of the composites showing 43%, 35%, and 22% losses compared to the tensile strengths of the unfilled nylon.

In future work, we plan to use suitable polyfunctional low molecular weight polymeric compounds such as epoxy resins and resols where low vapor pressures will simplify the coating procedure as well as providing a multiplicity of coupling sites per molecule.

References

1. R. Barnet and J. Cuevas, Proc. 21st Ann. Tech. Conf., S.P.I., Reinforced Plastics Division, Sect. 13F, Chicago, 1966.
2. K. Yagii, C. K. Lim, M. Ikuyama, and N. W. Tschoegl, Abstracts 167th ACS National Meeting, Los Angeles, March 31–April 5, 1974. Division of Industrial and Engineering Chemistry, Paper 114.
3. P. E. Cassidy and B. J. Yager, *J. Macromol. Sci. Rev., Polym. Technol.*, **D1**(1), 1, 1971.
4. P. A. Tierney, U.S. Pat. 3,328,339 (1967).
5. G. Jander and H. Schlapman, *Z. Anorg. Chem.*, **254** 255 (1968).
6. A. A. Chuiko, G. E. Pavlik, A. B. Kondratenko, L. V. Manchenko, N. V. Khaber, and E. I. Neimark, *Izobret. Prom. Obraztsy, Tovarnye Znaki*, **45**(1), 37, 1968; *Chem. Abstr.*, **69**, 76654m (1968).
7. K. R. Lange, *Chem. Ind. (London)*, **14**, 441 (1968).

JOHN NEWBOULD

Polymers Department
GM Research Laboratories
Warren, Michigan 48090

Received August 8, 1974