

Figure 7 gives the results with respect to AN-AA grafting onto polyester fibers. In general, the dye uptake values are very low, specially in case of acid dye as both AN and AA grafts or their mixtures adsorb very low amounts of this anionic dye. The AN graft adsorbs a certain amount of cationic dye, and it can be seen that the maximum amount of dye uptake is by the sample grafted from 80:20 AN:AA in the grafting bath, thus showing the synergistic influence for AN component during its grafting in presence of AA monomer onto polyester fibers. It is also interesting to note that a minimum in the curve is obtained in the case of grafting from binary mixtures of AN:AA 20:80 composition. These results confirm that the above mixture exhibits the highest amount of negative synergism in case of AA graft add-on in the binary mixture.

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Enhancement of Adhesion between Filler and Polymer in Alumina-Filled Rigid Polyurethane Foams

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Synopsis

The balance of the reinforcement and flame retardancy of rigid polyurethane foams (PUR) may be envisaged by controlling the dispersion and adhesion of the filler. Encouraging results are reported by grafting onto the filler surface a polymer miscible and reactive with the foam-forming ingredients. It appears that polyethers may do for PUR foams what the silanes do for glass fiber reinforced plastics.

INTRODUCTION

Rigid polyurethane foam (PUR) is recognized as an outstanding material for insulation applications. It exhibits many desirable properties, such as a low thermal conductivity, an excellent dimensional stability, resistance to compression, a low moisture permeability and a reduced water absorption.¹ The flammability of PUR and the smoke evolved when burning may be a drawback in building applications, which are governed by ever-increasingly stringent fire regulations. This has prompted active efforts in achieving better flame retardancy. Phosphorus and halogen-modified glycols and polyols that are compatible with polyurethane chemistry have been evaluated as reactive fire retardants.^{2,3} A large number of additives consisting mainly in halogen, nitrogen, antimony, and phosphorus compounds have been mixed within the foam-forming mixture and physically dispersed into the final material.^{2,4} The modification in chemical structure of PUR resulting in carbodiimide and isocyanurate units has been considered as a means of improving fire resistance.^{3,5}

Inorganic fillers can also impart a highly efficient flame retardancy when they are well-chosen and suitably added to the polymer, as evidenced in the following examples. Post-treatment of flexible polyurethane foam with alumina trihydrate dispersed in a latex of a flexible halogenated film forming polymer offers a remarkable flame-retardant effect.⁶ Through polymerization of ethylene onto catalytically activated mineral surfaces, Du Pont de Nemours & Company has developed homogeneous composites which combine reinforcement and impact toughness. Composites based on alumina trihydrate (75%) are, furthermore, flame-resistant, and they develop a very little smoke when they do burn under forced conditions.⁷ That remarkable behavior undoubtedly results from the high level of a fine and well-adherent filler which decomposes endothermally with evolution of water vapor upon strong heating. It is therefore attractive to extend such an approach to rigid polyurethane foams in order to achieve the best balance between reinforcement and flame resistance. This paper describes the

control of the dispersion and adhesion of alumina into PUR, and it reports a preliminary investigation of the morphology of these filled polyurethane foams.

EXPERIMENTAL

Materials

Rigid polyurethane foams were prepared from proprietary formulations of PRB-Recticel, Polyurethane Foam Division (Wetteren, Belgium) and containing polyol (40 wt % of propylene oxide), crude diphenylmethane-4,4'-diisocyanate (31.5 wt % of NCO), a silicone surfactant, a phosphonate cosurfactant, a tertiary amine as catalyst and monofluorotrichloroethane as blowing agent.

Aluminum hydroxide (FRF 30 from Baco Chem. and dried aluminum hydroxide gel from Merck) were heated overnight under reduced pressure (10^{-3} mm Hg) at 180°C and converted into alumina with a 85% yield. Diethylene glycol (Aldrich) and polyols were previously dissolved in toluene and dried by refluxing the solvent in a Soxhlet apparatus, the thimble of which contained calcium hydride.

Phenylisocyanate (Aldrich) was distilled before use, whereas toluylene diisocyanate (TDI, Bayer) was used as received. Triisobutylaluminum (TIBA, Fluka) was used in solution, in toluene previously dried by refluxing over calcium hydride under nitrogen.

Polyether Grafting onto Alumina

The grafting reactions were carried out with carefully dried reagents, under nitrogen.

First Approach. A solution of 0.098 mol of phenylisocyanate in 50 mL of dry toluene was mixed to 0.098 mol of α,ω -dihydroxylpolyether (1000 MW) in 300 mL of the same solvent. After refluxing for a few hours, the isocyanate was completely reacted as assessed by IR analysis. 0.098 mol of TDI were then added to the reaction mixture, and the titration of the isocyanate with dibutylamine agreed with the consumption of half the added NCO groups. The mixture was finally poured into a slurry of alumina (40 g) in dry toluene, and after refluxing (24 h) the solvent was removed under reduced pressure. The alumina was prepared from the dried aluminum hydroxide gel from Merck.

Second Approach. A known volume of the TIBA solution in toluene (1 mL^{-1}) was mixed to the vigorously stirred slurry of alumina (prepared from FRF30) in dry toluene. The amount of TIBA was adjusted to values ranging from 1 to 5 wt % compared to alumina. The resulting mixture was then poured into the dried polyol solution, and the solvent was finally removed under reduced pressure.

Scanning Electron Microscopy (SEM)

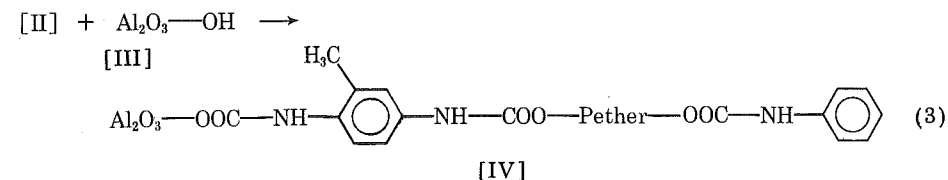
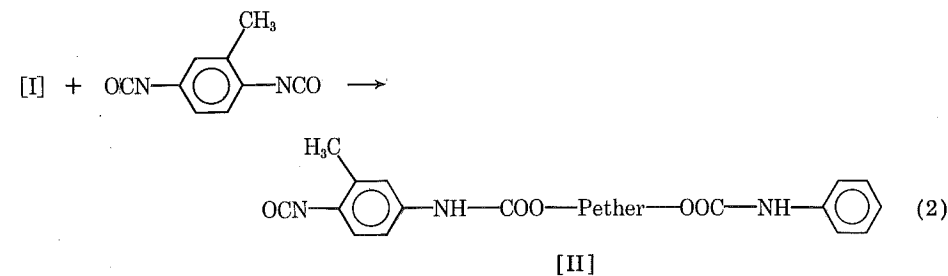
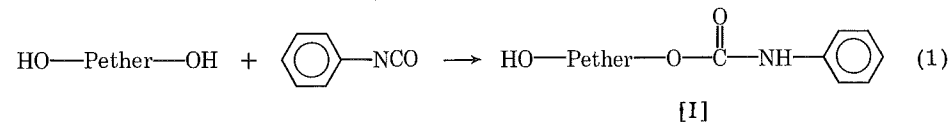
The samples to be investigated were cut out inside the foamed materials with a razor blade and mounted onto the object slide. They were gold metalated by ion sputtering and analyzed with the Philips PSEM 501-B Microscope.

RESULTS AND DISCUSSION

The obtention of a fine and stable dispersion of alumina in PUR foam requires a molecular bridge between the filler and the organic polymer which is compatible with the foam-forming formulation.

First Approach

It consists in grafting a polyether unreactive towards the foam-forming agents onto alumina. The reaction of tolylene diisocyanate with a monohydroxyl polyether in a 1:1 molar ratio leads to an isocyanate-terminated polymer [I, eq. (2)], which easily reacts with the hydroxyl groups of the filler [eq. (3)]:



The monofunctional polyether may be prepared by adding a α,ω -dihydroxyl polyether with a stoichiometric amount of phenylisocyanate ($\text{OH}/\text{NCO} = 1$) [eq. (1)]. The mode of addition has a critical importance in eqs. (1) and (2). The monofunctional compound ($\text{C}_6\text{H}_5\text{-NCO}$ or [I]) is to be added dropwise into the difunctional reagent under vigorous stirring to obtain [I] and [II] in high yields. Furthermore, the formation of [II] is favored by the unequal reactivity of the isocyanate groups of TDI.⁸

The α,ω -dihydroxyl polyether to be grafted to the alumina is selected for its miscibility with the PUR formulation: it makes the filler compatible with the polyurethane foam, as surfactants behave in water/oil emulsions. It is clear that the treated alumina is chemically inert to foam-forming ingredients and that it is unable to combine with the polyurethane during the foaming process. The polyether grafted onto alumina improves the wettability and adhesion properties of the filler, and makes its dispersion easier and more stable. Industrial PUR foams have been loaded with 10 wt % of untreated [III] and surface-modified [IV] alumina, respectively. The morphology of the filled foams have been investigated by scanning electron microscopy (SEM) and compared to that of the unloaded foam. Figure 1 shows a cross section of an inner cell wall of the reference

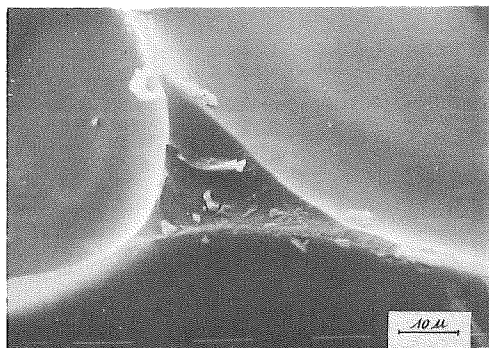
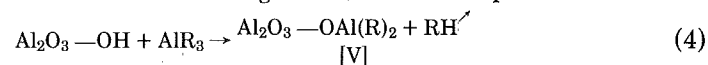


Fig. 1. Scanning electron microscopy of a cross section through a rigid polyurethane foam.

PUR foam. Figure 2 illustrates how the untreated alumina is imbedded in the polymer without any indication of adhesion: the edges of the alumina particles are well defined and not at all blunt by an adherent polyurethane skin. When alumina is coated with chemically attached polyether chains, the situation is deeply modified. The filler aggregate observed on Figure 3 seems to be buried into the cell wall and protected by a strong continuous polymeric film. The adhesion has undoubtedly improved, but is not sufficient to prevent some alumina particles to be drawn out by the blade used in the foam cross-sectioning.

Second Approach

An improvement of the actual situation was inspired by a process patented by DuPont de Nemours and Co. to prepare low viscosity inorganic filler dispersions.⁹ According to that invention, the high viscosity of slurries of finely divided inorganic fillers in hydrocarbon diluents (at least 9 wt/vol %) is avoided by mixing them with an organoaluminum compound (0.01–2 wt % based on the filler). The reported effect is probably due to the inactivation of the surface hydroxyl groups of the filler by their reaction with the organoaluminum compound



R is an alkyl group, for instance, a triisobutylradical. The alkylaluminum coated

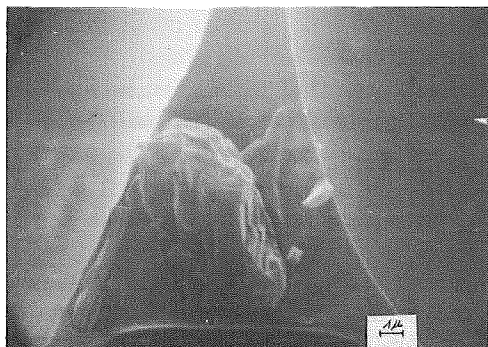


Fig. 2. PUR foam containing 10 wt % of untreated alumina (BACO FRF30).

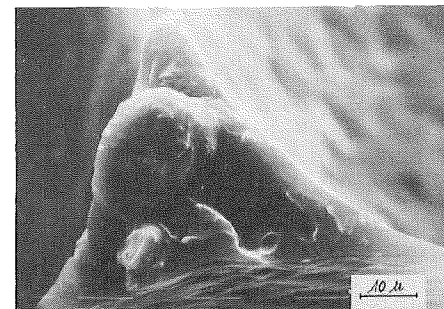
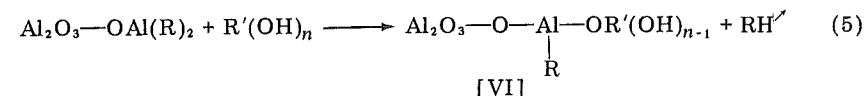


Fig. 3. PUR foam containing 10 wt% of alumina (BACO FRF30) coated with a polyether (1000 MW) unreactive toward isocyanate.

alumina [V] is then poured into an excess of diol or polyol (excess of OH groups compared to reactive alkyl–alumina bonds) to provide the filler a cover of hydroxyl-terminated arms hopefully compatible with the formulation



R' is an alkyl ether, polymeric or not, and $n > 2$. When R' is a polymer, the third R alkyl group carried by Al remains probably unreacted because of steric hindrance, as evidenced elsewhere.¹⁰ Conversely to what happens in the first approach, the alumina is now expected to become a true part of the PUR foam through the mixing of [VI] with the foam-forming agents.

As claimed by Howard,⁹ the viscosity of a slurry of alumina in toluene decreases at the addition of triisobutylaluminum (TIBA). However, the subsequent reaction of the organoaluminum coated filler [V] with an excess of polyol produces just the contrary. It means that the filler reacts with polyol and loses its free-flowing property, because of intermolecular interactions (H bonding) developed at the surface hydroxyl groups of [VI]. When the alumina is reacted with either 1% or 5% of TIBA, the subsequent addition of a liquid polyol leaves, after solvent removal, a viscous liquid or a completely solidified material, respectively. That experiment clearly shows that the attachment of the polyol to the filler surface is quite efficient and easily controlled by the relative amount of the organoaluminum used. 1% of TIBA vs. alumina, and 10 wt % of filler in the foam-forming

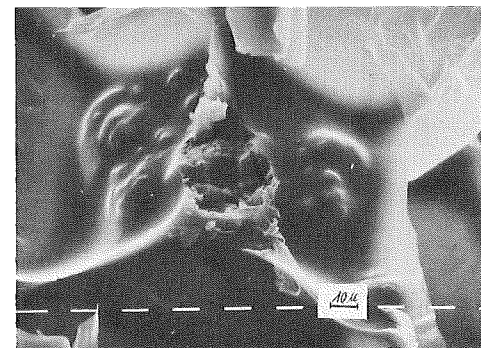


Fig. 4. PUR foam containing 10 wt % of untreated alumina (Merck).

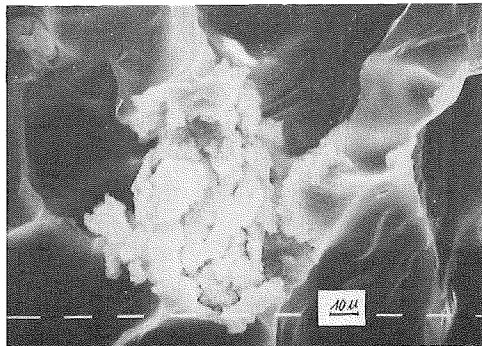


Fig. 5. PUR foam containing 10 wt % of alumina (Merck) coated with diethylene glycol.

mixture are the most convenient ratios to avoid severe splitting or collapse of the polyurethane foam prepared from the usual formulations. In order to limit the viscosity increase at the addition of the polyol, a low molecular weight diol, i.e., diethylene glycol (DEG), may be used. In that case, as much as 40% of alumina are easily loaded in PUR foams. The morphology of PUR foams containing 10% alumina has been investigated again by SEM to analyze the effect of alumina coating. Figure 4 is another look at aggregates of untreated alumina which are roughly imbedded within the polymer at the corners of the foam cells. When treated with TIBA (1% vs. alumina) and subsequently with DEG (25 wt % of alumina), the filler aggregates appear to be loose and formed of finely divided particles, whereas the adhesion of the filler to the polyurethane wall seems to be improved (Fig. 5). The best result is obtained by modifying the alumina surface with the polyol of the foam-forming formulation (TIBA: 1 wt % vs. alumina). Figure 6 illustrates that now the alumina aggregates are formed by strongly interacting fine particles, and the adhesion of the aggregate to the polyurethane is greatly improved.

These results provide an illustrative example of what can be achieved by a judicious choice of the bridging molecule between filler and polymer. From Figures 5 and 6, DEG appears to be a less efficient adhesion promoter than is the polyether polyol. Compared to DEG, a dimer of ethylene oxide type, the

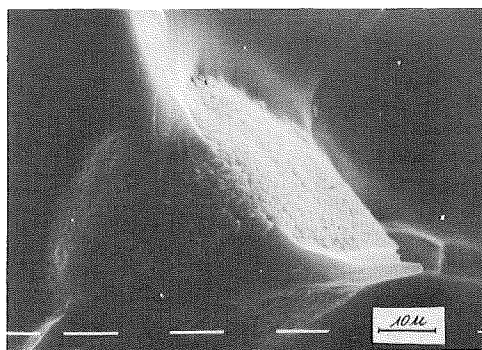


Fig. 6. PUR foam containing 10 wt % of alumina (Merck) coated with the polyol used in the foam-forming formulation.

used polyol is a polymer mainly formed of propylene oxide. In other words, modification of the molecular weight and chemical nature of the bridging molecules could control the morphology exhibited by filled PUR foams.

Last but not least, a 40 wt % content of DEG-coated alumina imparts a remarkably improved fire resistance to PUR foams. In laboratory-scale flammability tests, the loaded foam behaves as a self-extinguishing material.

Conclusion

This research on adhesion properties between filler and polymer in foamed materials is quite encouraging. Organofunctional silanes and titanates are commonly used as "coupling agents" for surface modification of fillers and reinforcement in plastics, as well as suitable crosslinking agents.¹¹ The results reported herein show that a polymer miscible and reactive with the foam-forming ingredients is also an adhesion promoter when chemically grafted onto the filler surface. In fact, it seems that polyethers may do for PUR foams what the silanes did for glass fiber reinforced plastics in the past.

In order to take advantage of these preliminary results, the viscosity of the reactive medium is to be carefully controlled and the foam-forming formulation adjusted to succeed in the suitable foaming of materials with a high filler content. Nevertheless, the formulation and processing of rigid polyurethane foam is not only a science but also an art, since only minimal changes can result in foams with completely different appearance and physical properties.¹² Further research is accordingly needed to achieve a careful adjustment of the foaming parameters of alumina-loaded formulations.

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