

Influence of Expandable Graphite on Physical-Mechanical Properties and
Fire Behaviour of Flame Retarded PIR-PUR foams

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Influence of expandable graphite on the physical-mechanical properties and fire behaviour of flame retarded PIR-PUR foams

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ABSTRACT

Rigid Polyisocyanurate-Polyurethane foams (PIR-PUR) have been synthesized with expandable graphite (EG) as the flame retardant halogen free additive. In order to study possible synergistic effects, mixtures of EG and triethylphosphate (TEP) were used to make fire retardant, pentane-blown PIR/PUR foams with a constant NCO index equal to 250. To this point, there has been no commercial production of such rigid PIR/PUR foams using expandable graphite as the fire retardant additive.

This study investigated the influence of the flame retardant additives on the foam physical and mechanical properties, such as compression strength and thermal conductivity. In order to evaluate fire performance, the foams were studied using cone calorimeter analysis and the oxygen index test.

EXPERIMENTAL

The raw materials employed were the following:

- Polymeric MDI (methane diphenyl diisocyanate): Tedimon 385 (Enichem): NCO% = 30.5; average functionality = 2.8;
- Polyester polyols: Glendion 9801 (Enichem): n°OH = 351 mgKOH/g, viscosity to 25°C = 5600 mPa·s; Kitane (Enichem) n° OH = 435 mgKOH/g viscosity to 25°C= 1100 mPa·s;
- Catalyst: pentamethyldiethylentriamine (Abbot), potassium octoate (Air Products);
- Surface-active agent: polysiloxane-polyether copolymer Tegostab B8469 (Goldschmidt-Italy);
- Blowing agent: n-pentane (Carlo Erba);
- Flame retardant: expandable graphite: Grafguard 160-80N (Graftech Inc.); triethylphosphate (Eingenmann & Veronelli)

The formulations of the foams are reported in Table 1. We prepared foams characterized by a constant isocyanate index (250) using hand mixing techniques. The foam density was normalized to about 38 kg/m³ by varying the dosage of n-pentane. After that, the foams were placed in an oven at 70°C for 24 hrs before carrying out physical-mechanical and fire behavior characterization.

Table 1. Foams formulations

Formulation	Ref	EG1	EG2	EG3	EG4	TEG1	TEG2	TEG3	TEG4	TEG5
Glendion 9801	70	70	70	70	70	70	70	70	70	70
Kitane	30	30	30	30	30	30	30	30	30	30
PMDETA	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.17
K-15	1.8	2.5	2.5	2.2	2.2	2.5	2.5	2.5	2.2	2.0
B 6489	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
H ₂ O	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
n-pentane	10	12	14.5	20	24	24.2	25.7	27.2	24	26.3
Tedimon 385	290	290	290	290	290	290	290	290	290	290
GRAF Guard 160-80N	0	45.4	72.5	104.1	140	22.9	48.5	77.5	76	75.5
Triethylphosphate	0	0	0	0	0	13.7	14.5	15.5	10.1	5

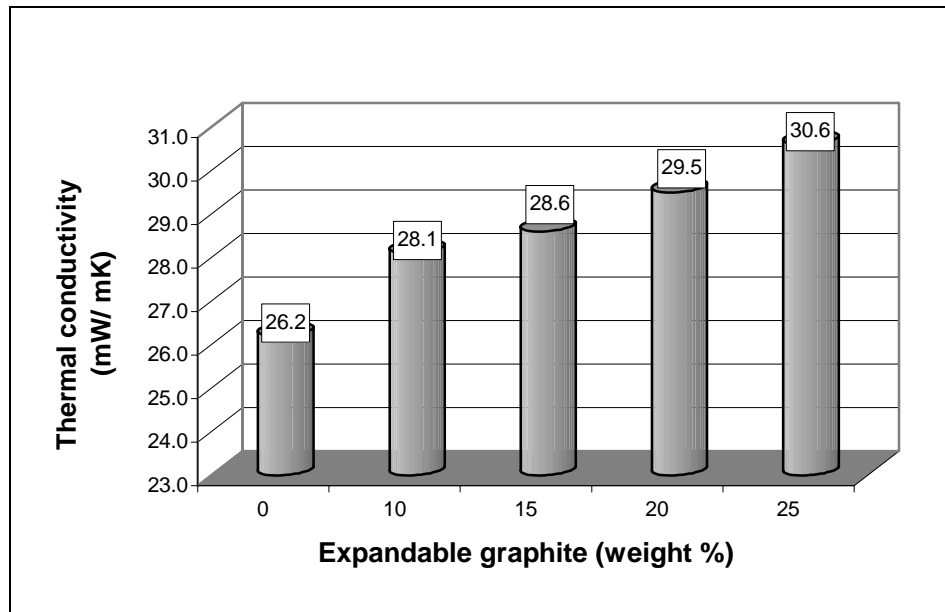


Figure 1. Thermal conductivity of EG filled foams.

RESULTS

The results obtained show that an increase in the amount of expandable graphite or triethylphosphate does not significantly degrade mechanical properties. Increasing the amount of expandable graphite does cause an increase in thermal conductivity (Fig.1), probably due to an increase in the dimensions of the foam cells. Increasing the triethylphosphate content had the opposite effect. A decrease in thermal conductivity of about 1 mW/m K was observed. This could be due to the plasticizing effect of TEP, that causes a decrease in the size of the cells in the foam, leading therefore to a decrease in thermal conductivity.

Evaluating the fire behaviour, we found a considerable increase in the O.I. values, particularly for EG-TEP foams (Fig.2). It can be seen that the O.I. increases in a linear way with an increased E.G. content, while in combination with a constant amount of TEP (3%) the O.I. increases in an exponential manner. Even if the E.G. filled foams provide a satisfactory improvement in O.I. values, for TEP-E.G. filled foams the results are surprising: in the case of 15% E.G. and 3% TEP the O.I. is 75% greater than for unfilled foams.

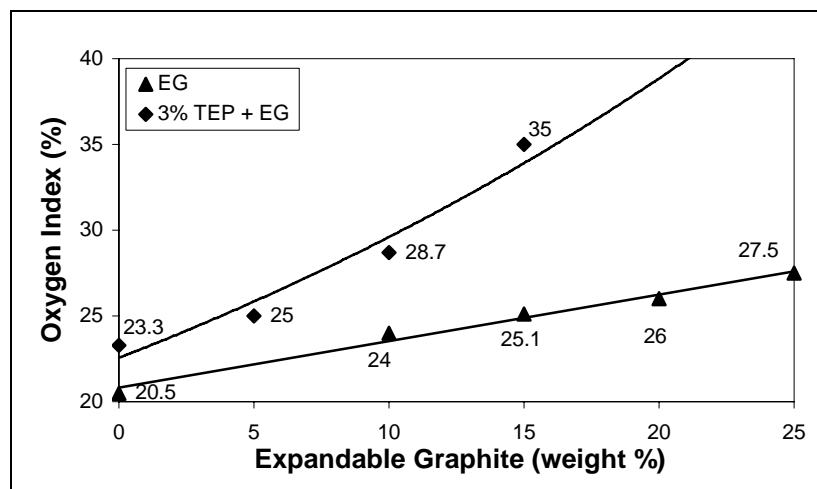


Figure 2. Oxygen index of EG and EG-TEP filled foams.

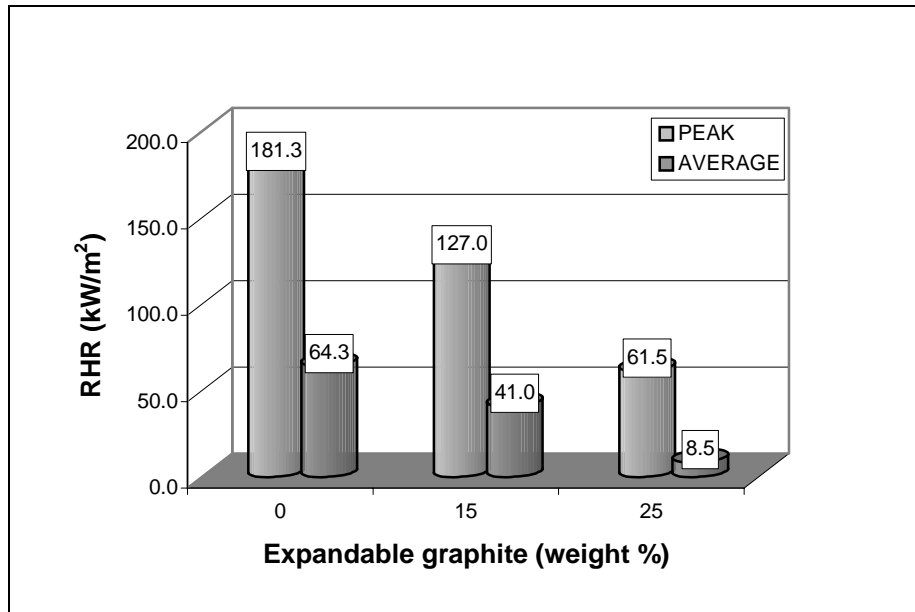


Figure 3. RHR peak and average values in function of the expandable graphite amount.

The cone calorimeter results are in agreement with those of O.I: EG and EG-TEP filled foams showed a considerable decrease in the rate of heat release (Fig.3) with respect to unfilled foams. In particular, for EG-TEP foams, the higher the triethylphosphate content the greater the

decrease in the rate of heat release (RHR) (up to 50%). The CO/CO₂ weight ratio (Fig.4), used as an index of smoke toxicity, is quite constant even when varying the filler amount. Only in the presence of very high EG content (25%) does the ratio increase considerably.

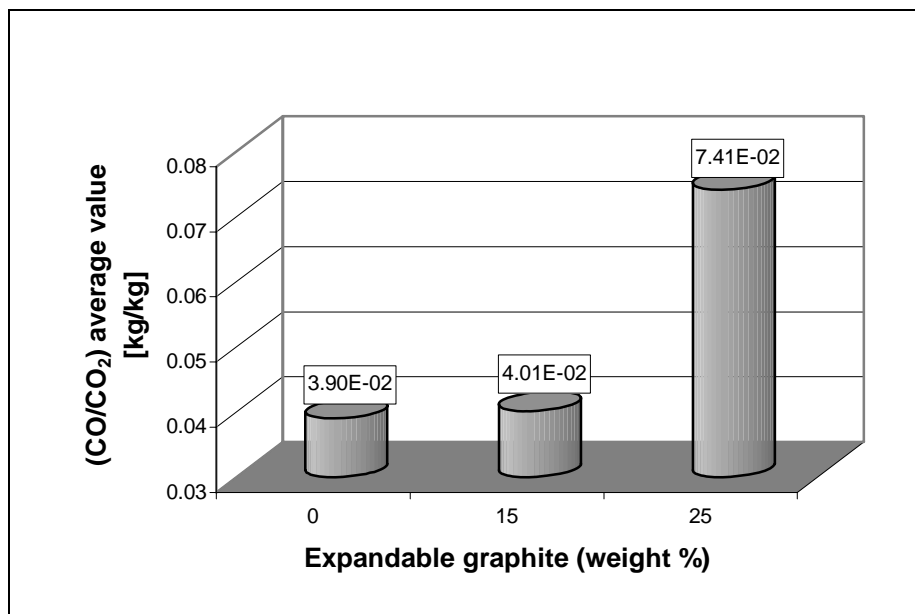


Figure 4. CO/CO₂ average values in function of the expandable graphite amount

CONCLUSIONS

In this work we analysed the influence of expandable graphite and triethylphosphate on physical-mechanical properties and fire performances of PIR-PUR foams.

The results of the physical-mechanical characterisation indicate that the presence of filler causes only slight degradation of the mechanical properties, while the presence of EG leads to a considerable increase in the thermal conductivity. On the other hand, the employment of low amounts of TEP, thank to its plasticizing effect, results in a decrease of about 1 mW/m K of the thermal conductivity of the foams.

Concerning the fire performance, we have observed that for filled foams there is an overall improvement of fire behaviour: the higher the filler content the higher the oxygen index and the lower the rate of heat release; in particular, the best fire performances are obtain in presence of both TEP and EG.

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BIOGRAPHIES

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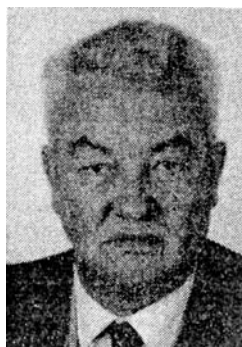


Michele Modesti graduated in Chemical Engineering from Padova University in 1984, and has developed his research in the field of polyurethanes. He attained the Ph.D. at the University of Padova in 1989, with a thesis on fire behaviour of polyurethane systems. He has been a researcher in Chem. Eng. Dept. of Padova since 1991 in the field of polyurethane recycling.



Alessandra Lorenzetti

Alessandra Lorenzetti received her degree in Chemical Engineering in 1999 from Padova University. Currently she is a Ph. D. student. Her research deals mainly with fire behaviour of polyurethane and interpenetrating polymer network (IPN), alternative blowing agents and ageing of polyurethane rigid foams.



Francesco Simioni

Francesco Simioni graduated in Chemical Engineering from Padova University in 1961. He was an organizer and teacher for the Engineering Faculty of Padova teaching a course in Technology of High Polymers until 1970. Since then he has become a Professor of Industrial Organic Chemistry and has also worked as a consultant for various industries

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Michael Gilbert

Michael Gilbert graduated in 1973 from Iowa State University with a B.S. in Ceramic Engineering. Since 1973, he has filled various positions including Project Engineer, Quality Assurance Manager, and Production Manager. His current responsibility is Customer Technical Service Manager for Graftech Inc.