

Properties of Polypropylene Structural Foam Crosslinked by Vinyltrimethoxy Silane

YU-DER LEE and LI-FANG WANG, *Institute of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China*

Synopsis

Polypropylene containing the blowing agent azodicarbonate was first grafted with vinyl trimethoxy silane, then crosslinked using the hot water treatment. Two heating stages initiated the blowing agent and formed polypropylene structural foam. The effects of such reaction variables as initiator, cross-linking agent, cross-linking accelerator, and blowing agent on the gel fraction, density, and expansion ratio of polypropylene foam were studied. Furthermore, cell dimension, compression strength, and volume resistivity were also measured and analyzed.

INTRODUCTION

Thermoplastic structural foams comprise a low-density cellular core bounded by solid skins, and can be produced by both injection molding and extrusion procedures. Typically, gas is introduced into the polymer, either by adding a chemical blowing agent or by direct metering of gas into the molten polymer. The interrelationship between the structural parameters and the mechanical properties is complex. It relies on the expansion rate, density of the foam, the skin-to-core thickness ratio, the surface texture of the molding, and the crystalline morphology present in the cell walls.^{1,2} Also, among these factors expansion rate plays an important role because it relates directly to the volume ratio of polymer and foaming gas. The most effective methods to control the expansion rate are through adjustment of the blowing agent amount and of the degree of crosslinking.³ For polypropylene, crosslinking can be done either by irradiation or by a chemical method.^{4,5} Traditionally, the chemical cross-linking method uses free radical generating agents such as polysulfoazide⁶ or azide.⁷ However, the high-cost performance ratio, low decomposition temperature of azide, and degradation of polypropylene during crosslinking do not favor that method.⁸ Instead, a combination of organic peroxide and multifunctional monomer has become the choice for the new cross-linking agent system for polypropylene.⁹

In this paper, polypropylene foam was prepared by using azodicarbonate (ADCA) as the blowing agent, benzyl peroxide (BPO), as the initiator, di-*n*-butyltin dilaurate (CAT) as the cross-linking accelerator, and vinyl trimethoxy silane (VTMOS) as the cross-linking agent. The effects of those reagents on the properties of the polypropylene foam were also investigated.

TABLE I
Extruder Operating Conditions

VTMOS (phr)	Temperature of heating zone 1 (°C)	Temperature of heating zone 2 (°C)	Temperature of die (°C)
0	180	195	220
1	180	195	210
2	180	185	220
3	170	180	190

EXPERIMENTAL

Material

Polypropylene containing steric-hindered-type antioxidant (PP 6331, MI = 10) was supplied by Taiwan Polypropylene Co. Ltd. Benzyl peroxide (BPO), azodicarboxamide (ADCA), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were products of Merck, West Germany. Vinyl trimethoxy silane and di-*n*-butyltin dilaurate (CAT) were obtained from Tokyo Kasei Co., Japan.

Sample Preparation

PP 6331 grains with a diameter of 1 mm were dried in a vacuum oven at 80°C for 4 hours before being mixed with preselected amounts of BPO and VTMOS. Then cross-linking agent VTMOS, initiated by BPO, was grafted on the PP chain through an extruder. The operating conditions of the extruder, dependent upon the amount of VTMOS, are listed in Table I.

The VTMOS-grafted PP pellets were powdered using a high-speed grinder; then blowing agent ADCA and cross-linking accelerator CAT were added and mixed in an extruder equipped with a static mixer. Finally testing samples were prepared by injection molding.

Cross-linking and Foaming of Testing Sample

The injection-molded samples were crosslinked by immersing them in water at 90°C for 5 hours; the cross-linking mechanism has been studied by Bloor.¹⁰ They were then preheated at 180° for 30 min, after which they were foamed in a mold housed in a nitrogen-circulating oven at 200°C for a preselected time.

Testing

Density, compressive strength, and volume resistivity were measured according to methods described in ASTM D-792, D-1621, and D-257, respectively. Gel fraction of cross-linked PP was determined by extraction in toluene at 135°C until a constant weight was obtained. The expansion ratio was arrived at by comparing the thickness of the sample before and after the foaming.

RESULTS AND DISCUSSION

Effect of Reagent on Gel Fraction

Figure 1 shows a linear relationship between the amount of cross-linking agent (VTMOS) and the gel fraction of PP foam. As expected, the gel fraction of PP foam increased with increasing amounts of VTMOS. A lower dosage of cross-linking accelerator (CAT) was demonstrated to reduce the gel fraction of PP foam. A more detailed observation of the CAT effect on the gel fraction of PP foam is presented in Figure 2. It indicates that the gel fraction of PP foam levels off as CAT reaches a minimum value, a value very close to 0.15 phr when the amount of BPO is 0.5 phr. The effect of the initiator (BPO) is shown in Figure 3. It appears that the gel fraction of PP foam reaches a limitation of 34% at approximately 0.8 phr BPO. This phenomenon is contradictory to the idea that BPO is a high-efficiency free radical generator.¹¹ However, the formation of a cross-linking bond does not depend on the number of free radicals alone; it is also influenced by the diffusion rate of the free radical and the possibility of polymer fragmentation.⁹ Chodák and Lazár⁵ have studied the effect of initiator amounts on the degree of crosslinking of PP as well. Their results showed that the gel fraction of PP could reach 40% only, while as many as 10 phr BPO were added.

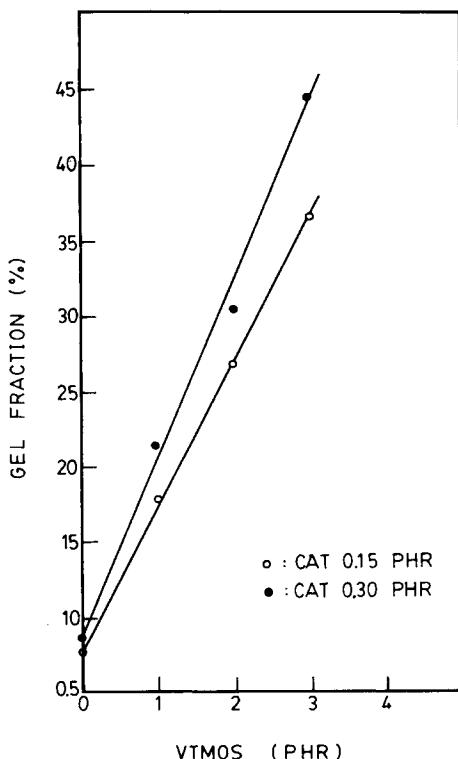


Fig. 1. Effect of cross-linking agent (VTMOS) on the gel fraction of PP foam. (BPO: 0.5 phr.)

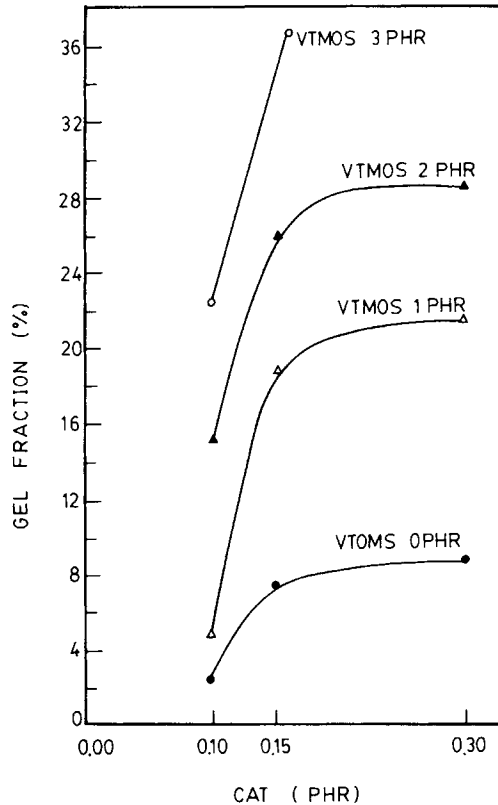


Fig. 2. Effect of cross-linking accelerator (CAT) on the gel fraction of PP foam. (BPO: 0.5 phr.)

Effect of Reagent on Density

The important factor in controlling the density of PP foam is the quantity of blowing agent used.¹⁰ As shown in Figures 4 and 5, a higher blowing agent (ADCA) dosage resulted in lower density, especially when the foaming time was long. Density also changed with the amount of cross-linking agent (VTMOS) (Figs. 4 and 5). Minimum density was observed as the amount of VTMOS increased. This observation was most apparent when the foaming time was short. The higher density exhibited at lower VTMOS content was the result of increasing open cell numbers. When the gel fraction was low, the pressure produced by the decomposition of the blowing agent was much higher than the cell wall could bear; consequently more open cells were formed. On the other hand, when the gel fraction was high, the gas pressure could not expand the cell wall and the dimension of the cell was reduced, thus increasing the density of PP foam. The expansion ratio is also of interest: Figure 6 shows the effects of both blowing agent and cross-linking agent on the expansion ratio which decreased with lower ADCA and higher VTMOS amounts.

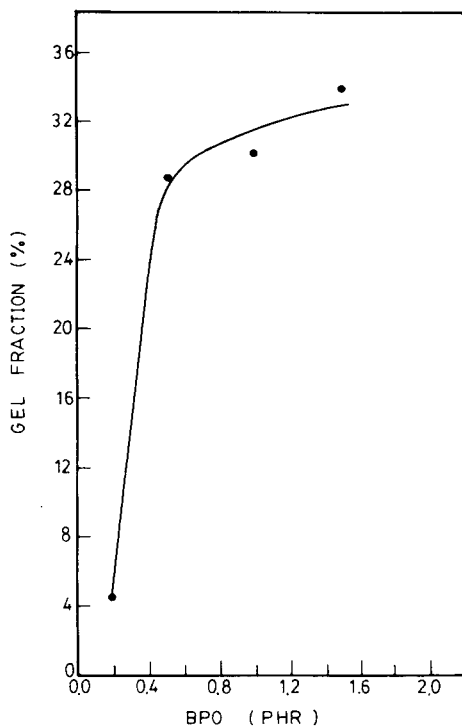


Fig. 3. Effect of cross-linking initiator (BPO) on the gel fraction of PP foam. (VTMOS: 2 phr; CAT: 0.3 phr.)

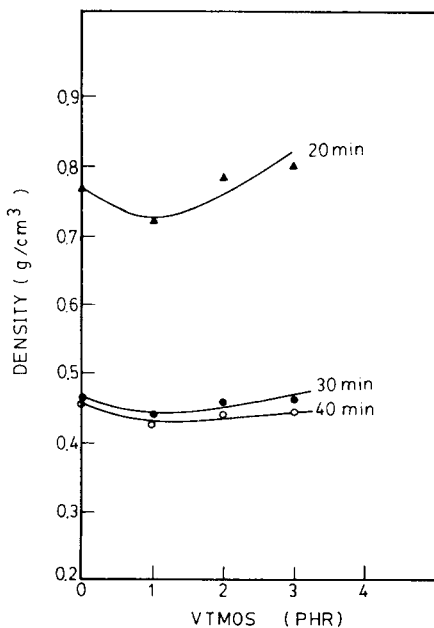


Fig. 4. Effects of blowing time and cross-linking agent (VTMOS) on the density of PP foam at 0.5 phr ADCA. (BPO: 0.5 phr; CAT: 0.15 phr.)

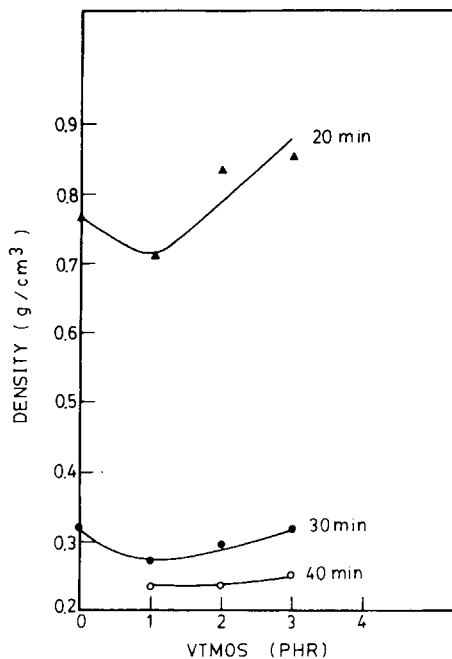


Fig. 5. Effects of blowing time and cross-linking agent (VTMOS) on the density of PP foam at 1.0 phr ADCA. (BPO: 0.5 phr; CAT 0.15 phr.)

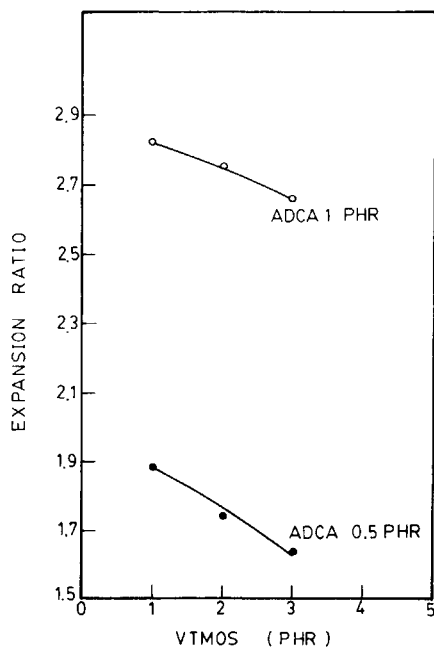


Fig. 6. Effect of cross-linking agent (VTMOS) on the expansion ratio of PP foam. (BPO: 0.5 phr; CAT: 0.3 phr; blowing time: 30 min.)

TABLE II
 Properties of PP Foams with Various Formulation
 (BPO: 0.5 phr, Foaming Time: 30 min)

Sample	VTMOS (phr)	ADCA (phr)	CAT (phr)	Average Cell Diameter (mm)	Compressive modulus (N/m ²)	Volume resistivity (Ω · cm)
1	0.0	0.5	0.15	0.84	3.72 × 10 ⁷	1.97 × 10 ¹³
2	1.0	0.5	0.15	0.83	4.59 × 10 ⁷	2.17 × 10 ¹³
3	2.0	0.5	0.15	0.75	4.78 × 10 ⁷	2.50 × 10 ¹³
4	3.0	0.5	0.15	0.70	4.85 × 10 ⁷	2.75 × 10 ¹³
5	0.0	1.0	0.15	1.00	3.69 × 10 ⁷	2.35 × 10 ¹³
6	1.0	1.0	0.15	0.82	2.98 × 10 ⁷	2.20 × 10 ¹³
7	2.0	1.0	0.15	0.80	3.29 × 10 ⁷	2.78 × 10 ¹³
8	3.0	1.0	0.15	0.77	3.77 × 10 ⁷	2.90 × 10 ¹³
9	1.0	0.5	0.30	0.95	3.70 × 10 ⁷	2.54 × 10 ¹³
10	2.0	0.5	0.30	0.60	4.80 × 10 ⁷	2.68 × 10 ¹³
11	3.0	0.5	0.30	0.53	4.95 × 10 ⁷	2.73 × 10 ¹³
12	1.0	1.0	0.30	0.87	3.00 × 10 ⁷	2.70 × 10 ¹³
13	2.0	1.0	0.30	0.62	4.21 × 10 ⁷	2.76 × 10 ¹³
14	3.0	1.0	0.30	0.52	4.30 × 10 ⁷	2.80 × 10 ¹³

Mechanical Properties of PP Foam

One of the important mechanical properties of polymer structural foam is the compressive strength. The compressive load of a structural foam is borne by the polymer cell wall and the gas within the cell. It is expected that the three-dimensional network structure via crosslinking will increase the compressive properties of polymer foam. In addition, the dimensions and numbers of the cell will also affect the compressive resistance significantly. Table II

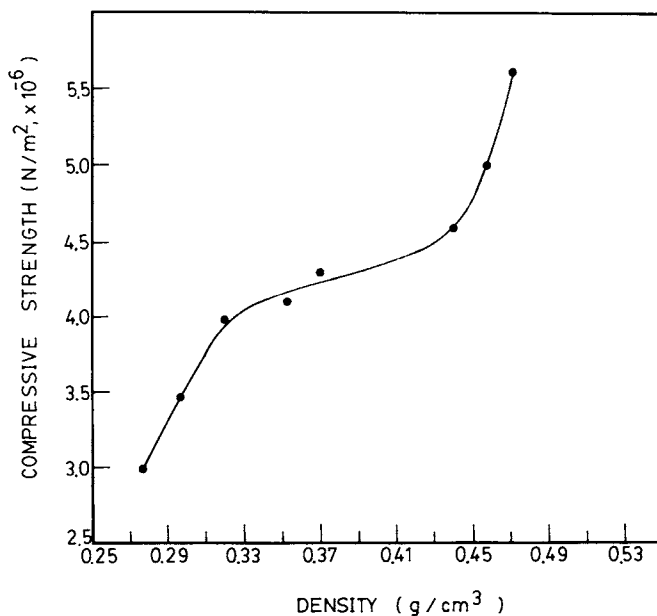


Fig. 7. Relationship between compressive strength and density of PP foam.

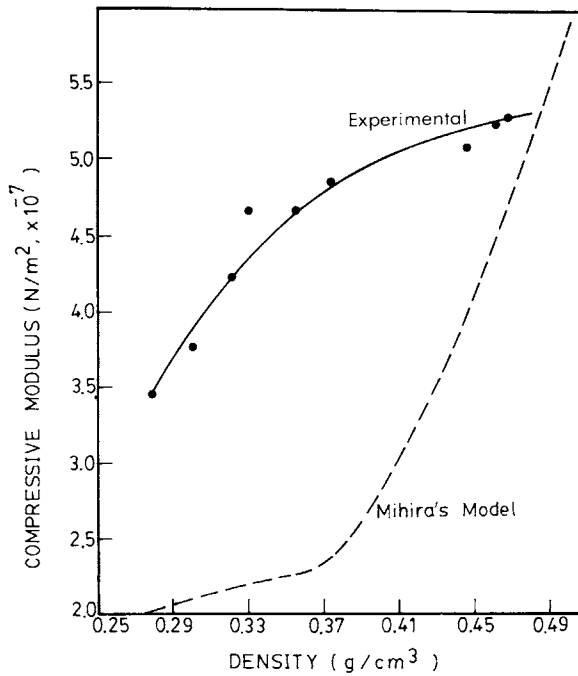


Fig. 8. Comparison of experimental compressive modulus and modulus predicted by Mihira's model.

lists the compressive modulus and the volume resistivity of PP foams with various average cell diameters. Generally, the compressive modulus and the compressive strength increased with smaller cell diameter or with higher density (Figs. 7 and 8). In Figure 8, experimental moduli were also compared with moduli calculated from Mihira's model.¹² The discrepancy between those values is caused by the assumptions made by Mihira. Mihira thought of each cell as an individual body and expected the distribution of cell dimension to follow a normal distribution; in fact, this is infrequently observed in actual polymer foams. The volume resistivities of PP foam were between $2-3 \times 10^{13} \Omega \cdot \text{cm}$, or 10 times higher than those of pure PP 6331 ($1.85 \times 10^{12} \Omega \cdot \text{cm}$).

CONCLUSIONS

In this research, PP foam was crosslinked with vinyl trimethoxy silane (VTMOS) under treatment by water. The apparent advantage of this method is that the gel fraction of PP increased in a water-containing environment. The reagent effects were found to be:

1. The gel fraction of PP foam would level off at approximately 34% so long as the amounts of BPO reached 0.8 phr, since free radicals initiated by BPO could not only form cross-linking bonds, but also degrade the PP chain.

2. The most important factor affecting the gel fraction was the amount of cross-linking agent VTMOS.

3. The optimum effective amount of cross-linking accelerator (CAT) was 0.15 phr.

In addition to the above findings, the physical properties of polypropylene foam were also investigated. Data showed that density, compressive strength, and compressive modulus increased with increasing gel fraction, while the expansion ratio showed a reverse trend. The volume resistivities of polypropylene foam were in the range of $2-3 \times 10^{13} \Omega \cdot \text{cm}$, or 10 times higher than that of pure PP 6331.

References

1. A. A. Ahmadi and P. R. Hornsby, *Plas. Rubber Proc. Appl.*, **5(1)**, 35 (1985).
2. A. A. Ahmadi and P. R. Hornsby, *Plas. Rubber Proc. Appl.*, **5(1)**, 51 (1985).
3. C. J. Benning, *J. Cell Plas.*, **2(5)**, 256 (1966).
4. N. Sawasaki, *Plastics*, **31(3)**, 51 (1980).
5. I. Chodák and M. Lazár, *Die Angewandte Makromolekulare Chemie*, **106**, 153 (1982).
6. G. B. Field, U.S. Patent 3,341,480 (1967).
7. D. A. Palmer, U.S. Patent 3,341,481 (1967).
8. C. J. Benning, *Plastic Foams*, **V.II**, 103 (1969).
9. I. Chodák, K. Fabianová, E. Borsig, and M. Lazár, *Die Angewandte Makromolekulare Chemie*, **69**, 107 (1978).
10. R. Bloor, *Plas. Technol.*, Jan. 83 (1981).
11. N. Akio, *Furukawa Rev.*, **2**, 34 (1982).
12. K. Mibira, *I & EC Prod. Res. Dev.*, **8(2)**, 128 (1969).

Received October 21, 1985

Accepted February 15, 1986