Nr 4 (193—256) KWIECIEŃ 1996 Tom XLI

POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

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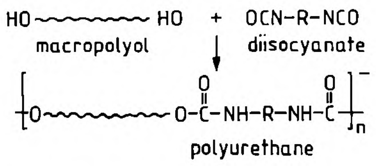
An Overview of Recent Technical Developments in Polyurethanes

PART I. GENERAL INTRODUCTION AND SUBSTITUTES FOR CHLOROFLUOROCARBONS (CFCs) AND THEIR APPLICATIONS

Summary — An overview of recent technological developments in polyurethanes is presented. Substitutes for CFCs in foams are reviewed in light of environmental considerations (ODP — ozone depletion potential and GWP — global warming potential). New developments in raw materials for the polyurethane industry are cited.

INTRODUCTION

Polyurethanes (PURs) are undoubtedly the most versatile class of polymers due to the great variety of types, molecular weights, and functionalities of the principal components. Although PURs can be produced by a variety of procedures, the classical polyaddition process, developed by Otto Bayer, still remains the principal process for their production as shown in the equation:



$$\mathrm{HO{\sim\sim\sim}HO} + \mathrm{OCN{-}R{-}NCO} \longrightarrow \left[\mathrm{O{\sim\sim\sim}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}} \right]_n \qquad (I)$$

The most common macropolyols are still hydroxyl-terminated polyethers or polyesters, but other hydroxyl-containing oligomers, such as polybutadienes, acrylics, and epoxies are widely used. In addition, combinations of hydroxyl-terminated polyols are also commercially available, such as polyester—polyether polyols or polyester-carbonates and polyether carbonate polyols.

The functionality of the polyols can be varied as can be the nature of the terminal hydroxyl groups which consist of either primary or secondary hydroxyl groups.

In addition, there are many other types of polyols used in the industry, notably graft copolymers such as acrylonitrile or acrylonitrile/styrene graft copolymers of polyether polyols, also termed „polymer polyols". These are widely used in molded flexible foams in combination with other primary hydroxyl-terminated polyether polyols.

Another class of polyether polyol derivatives are PHD or PUD, which are polyurea dispersions in polyether polyols and which perform similarly to the polymer polyols.

In the past, the preparation of high molecular weight polyols based on propylene oxide employing an alkali metal catalyst such as KOH was difficult due to the formation of terminal unsaturated groups. A newer approach for producing high molecular weight polyether polyols with exceptionally low levels of unsaturation and exhibiting narrow molecular weight distribution, was first developed by „General Tire" and was later licensed by „Arco Chemical Co". The preferred complex catalyst is a zinc hexacyanocobaltoate of the following formula:$\{Zn[Co(CN)_6]_2\}x\ (ZnCl_2)\ y$ glyme . $2H_2O$*).

Due to the absence of significant side reactions in the propoxylation step, the molecular weights of the resultant polyols are very close to the theoretical values. These polyols have exhibited better physical properties in elastomers and sealants than conventional polyols of the same molecular weight due to the lower monool content.

While toluene diisocyanate (TDI) has been for a long time the most widely used isocyanate for flexible slabstock in the USA and to a certain extent also in Europe and the Pacific Rim, MDI-(MDI — diphenylmethane diisocyanate isomers) based foams have been making great inroads into both slabstock and molded flexible foams. A key to the successful production of MDI slabstock is the flexibility of modifying the isocyanate side by optimization of the isomer ratio, the polymeric MDI content, and the free isocyanate percentage of the MDI component to meet the desired range of physical properties. Of particular importance is the effect of 2,4'-MDI isomer. A high level of 2,4'-MDI results in a relatively low density, low hardness slabstock with improved overall fatigue resistance. In contrast, a low level of 2,4'-MDI results in improved tensile and tear properties. These trends also hold true for all MDI molded foams. 1,5-Naphthalene diisocyanate (NDI) still enjoys a special role in selected elastomers areas, particularly where high dynamic mechanical properties are required. More recently, 1,4-phenylene diisocyanate (PPDI) has attracted attention for its superior dynamic mechanical properties but its use at present is restricted due to its high cost.

A significant development in isocyanates is the significant increase in aliphatic and cycloaliphatic diisocyanates and their derivatives (adducts, trimers, etc.) due to their expanding use in primarily coatings but also adhesives and other specialty uses (*e.g.* medical applications). In particular, 4,4'-methylene bis(cyclohexyl isocyanate) (H_{12}MDI), isophorone diisocyanate (IPDI) and *m*-tetramethylxylylene diisocyanate (TMXDI) have greatly increased their use. There are many other developmental aliphatic diisocyanates which are currently being evaluated. These include among others 1,4-cyclohexane diisocyanate (CHDI), hydrogenated xylylene diisocyanate (H_6XDI), 1,12-dodecane diisocyanate (C_{12}DDI), *etc.*

While the growth of foams has been slowed, the noncellular PURs, especially the CASE areas (coatings, adhesives, sealants and elastomers) have made continued progress and are growing at a faster rate than foams.

Today, the polyurethane industry faces a number of formidable challenges. These are:

1. The substitution of CFCs by suitable blowing agents which are safe and economical.
2. The challenge to PURs by competitive materials, especially by thermoplastic resins in certain application areas, *e.g.* automotive uses, due to presumably easier recycling of these materials.
3. The recycling and safe disposal of PUR waste (derived from manufacturing processes and post-consumer items).

SUBSTITUTES FOR CFCs AND THEIR APPLICATIONS*)

The ozone depletion problem which has led to the establishment of the United Nations Environmental Program Protocol, also referred to as the Montreal Protocol, originally required the complete phase-out of CFCs by the year 2000. However, this deadline has been brought forward, and the 1992 Copenhagen Conference has brought tight restrictions and earlier phase-outs. In the search of CFC substitutes, many factors must be taken into consideration. Ideally, some of the goals are as follows:

Zero ozone depletion potential (ODP), zero global warming potential (GWP), low or no toxicity, low thermal conductivity (*k*-factor), performance in processing and acceptable physical properties of the resulting foams, and last but not least, affordable costs of the viable candidates.

In the case of flexible foams where CFCs are only used as auxiliary blowing agents, it was obvious to use all water-blown CO_2 systems. However, in order to achieve low density foams with good properties, some reformulations had to be carried out along with the use of modified polyether polyols, and special surfactants and catalysts.

The elimination of CFCs in flexible foams has been very successful in the USA, as it has been in most West European countries and in Japan.

Carbon dioxide-blown, rigid PUR foams were being viewed as the ultimate environmental solution. However, a number of well-known disadvantages of the CO_2-blown foams using water include poor adhesion due to surface friability, relatively high thermal conductivity, a narrow processing window, and the difficulty of maintaining acceptable dimensional stability because of high CO_2 diffusion.

Hydrochlorofluorocarbons, also referred to as „soft" CFCs, foremost HCFC-141b ($CCl_2F\,CH_3$) and HCFC-22 ($CHClF_2$) and combinations with HCFC-142b ($CClF_2CH_3$) are intermediate substitute blowing agents after the phase-out of CFCs for insulation applications. However, their lifetime is limited due to their ODP (ozone depletion potential) and they are supposed to be phased out within the next decade, if not earlier.

Hydrofluorocarbons (HFCs) represent the next generation of fluorine-containing blowing agents, in particular HFC-134a (CF_3CH_2F) and HFC-143a (CHF_2CH_2F). The latter has the advantage of a higher boiling point

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*) Glyme stands for dimethyl ether of ethylene glycol.

*) A similar review on substitutes for CFCs has been published by Z.Wirpsza in Polish, in *Polimery* 1995, **40**, 208.

(5C as compared to -26.3C for HFC-134a), a higher solubility in polyols and lower gas phase thermal conductivity, but it is flammable. HFCs have zero ODP.

Partly fluorinated hydrocarbons such as HFC-134a, HFC-143a, and possibly HFC-356 (hexafluorobutane) are some of the frontrunners, as far as fluorinated blowing agents are concerned, although their costs are relatively high and some of the toxicological testing is not quite completed. Very recently Shankland *et al* [1] reported on the favorable properties of HFC-245 fa ($CF_3CH_2CHF_2$) which in nonflammable and miscible with most polyols. Foams blown with HFC-245 fa exihibit generally *k*-factor values which are similar to or better than those of HCFC-141b blown foams.Previous work by Volkert of „BASF" [2] and Focquet of „3M" [3] has shown that erfluoroalkanes (FCs) are suitable as blowing agents if they are first dispersed in a polyol using a fluorinated surfactant to form emulsions. This is necessary since perfluoroalkanes such as perfluoropentane (C_5F_{12}) and perfluorohexane (C_6F_{14}) are insoluble in both polyols and isocyanates. During the blowing process, the evaporation of fluorocarbon droplets provides nucleating sites for cell generation and thus promotes the formation of a microcellular structure.

Researchers from the „Center of Applied Engineering Inc." (formerly „Jim Walters Research Corp.") [4] have found that the addition of a perfluorinated hydrocarbon produced by „3M" to either PUR or PIR formulations led to a 6—8% improvement in the initial *k*-factor which was maintained on aging. This improvement was shown to be due to the ability of the perfluoroalkanes to reduce the cell size of the foams, thereby reducing the *k*-factor due to the reduction in the radiation factor. However, despite the fact that perfluoroalkanes have a zero ODP, their global warming potential (GWP) is very high.

In Europe, and particularly in Germany, hydrocarbon blowing agents such as the pentanes (normal, iso- and especially cyclopentane) have become the most important blowing agents for rigid urethane foams despite their flammability characteristics. In Germany, the insulation must be halogen-free for freezers to qualify for the blue „angel seal". This seal, originally established by UNEP, has a considerable impact on buying decisions, at least in Europe. These pentane blowing agents have a zero ODP and a zero GWP. There have to be obviously precautionary measurements taken to insure complete safety in the production of these foams. Volkert of „BASF" [5] reported on the use cyclopentane as a blowing agent for rigid foams for refrigerators. Other pentanes such as *n*-pentane and isopentane have also been employed but cyclopentane was judged to be the best choice. The physical properties of the three pentanes are shown in Table 1.

Over the last two years the use of hydrocarbons as blowing agents has spread from Europe to Australia, New Zealand and Japan with strong interest being shown in other Pacific Rim countries. It should be pointed out that these foams are finding applications not only in appliances but also in the construction industry. Evans and coworkers [6] have recently reported on foam systems for the construction industry in Asia Pacific in which they showed an interesting comparison of foams blown with HCFC-141b with foams blown with various pentane isomers. They found that cyclopentane gave a lower compressive strength than either *n*- or isopentane and poorer dimensional stability. Cyclopentane has a lower thermal conductivity than *n*- and *i*-pentane isomers but has a higher boiling point (50C) and hence, a high condensation temperature. Cyclopentane has better solubility in polyol blends but tends to soften the PUR matrix. Therefore, in combination with the low cell gas pressure due to condensation, it makes it necessary to use higher densities in order to obtain the required dimensional stability. Optimum performance is obtained with high levels of hydrocarbons which requires in-line mixing of the hydrocarbon with the polyol blend using suitable machinery such as „Cannon"or „Kraus Maffei". The fire performance clearly indicated the adverse effect of pentanes relative to HCFC-141b.

Table 1. PHYSICAL PROPERTIES OF PENTANE ISOMERS

	bp, °C	P (25°C), mbar	*k*-factor, W/mK
n-Pentane	36	687	0.0148
i-Pentane	28	913	0.0148
Cyclopentane	49	421	0.0121

Recently, Nicola and Weber [7] reported on normal and cyclopentane-blown urethane and isocyanurate foams for U.S. constructions applications. Rigid polyisocyanurate (PIR) foams are used in over half of the new insulated commercial roofs installed in the U.S.A. In addition, several billion board feet of PIR foam sheathing products are used annually in residential construction. PIR foams are generally preferred due to their strength, durability and Factory Mutual Class 1 (FM1) approval which allows installation on steel roof decks without reinforcement of the foam core or the use of thermal barriers. This work concentrated primarily on foams with isocyanate index ranging from 175 to 300 and using preferentially aromatic polyester polyols. Flame retardants were used in all formulations. The pentane-blown foams were processed on a „Hennecke" high pressure foam laminator which was modified for use with flammable blowing agents.

The results of this investigation showed that good quality pentane-blown PIR foams could be made safely. Increasing the isocyanate index, more pentane and less water can be used in the formulations which should improve *k*-factors. The higher isocyanate index should obviously also improve the foam flammability performance.

If the pentane-blown foams do not have to pass the FM1 approval, lower index PUR foams can be used and lower *k*-factors may be obtained by reducing water levels which is possible when the isocyanate index is lowerd.

European pentane-blown PUR foams, some of which pass ASTM E-84/UL 723 tests, have been studied for about six years and have been produced commercially for about three years.

An interesting concept for the rigid foam insulation industry is the formation of so-called „vacuum insulation panels", which utilize microcellular, open cell, rigid urethane foams as core materials. The evacuated insulators have an insulation efficiency four times greater than those of conventional polyurethane or polyisocyanurate foams (the thermal conductivity is 0.005 W/mK). Vacuum insulation panels were produced by placing the core material and absorbents in a film-like laminated plastic container which is capable of maintaining a vacuum, followed by sealing in the industrial vacuum level (0.01—0.1 mm Hg or 1.3—1.3 Pa). The microcellular structure is indispensable since the thermal conductivity is dependent on the cell size. Obviously a suitable surfactant is an important factor in the production of these foams. Using special prepolymers modified with monool, microcellular rigid PUR foam was obtained which consisted of cells about 200 μm. Alkaline earth metal salts of stearic acid, *e.g.* calcium stearate, were found useful as cell opening agents [8].

A method of producing vacuum panels was first disclosed in a Japanese patent [9] which describes the use of plastic honeycomb as the core material and metal-plated plastic sheets as the substrate. When vacuum is applied, the plastic honeycomb resists the effect of atmospheric pressure. A number of other patents [10] for the production of vacuum panels having an open cell foam core have appeared. One of these methods consists of breaking of cell walls of closed rigid foams using a high vacuum and employing 100% humidity and a temperature of 100C. However, this method is time-consuming. Another method is based upon the use of cell opening agents such as calcium stearate, in combination with the use of CFC-11 which can no longer be used.

The development of microcellular open cell rigid PUR foams, useful as core materials for vacuum insulation panels with very low thermal conductivity has recently been reported by Kodama *et al* (11).

Ashida and Kashiwame [12] have described a novel type of rigid isocyanurate foam with open cells. This method employs a one-shot process using a blend of methylene chloride and *n*-pentane, and using an isocyanate index (NCO/OH) x 100 = 1500. A necessary condition is that the rise time must be greater than the tack-free time. It was suggested that the greater tack-free time was related to the faster formation of the isocyanurate rings due to the high polarity of the solvent (methylene chloride). The type of isocyanurate catalyst proved to be very important. In this investigation, DABCO[*] TMR-2 and DABCO TMR-3 were found to be best. Potential applications for open cell isocyanurate foams include core materials in vacuum panels such as refrigerators, freezers, and industrial cryogenic tanks for a variety of gases.

Burkhart and Schator [13] described a new technique for producing open cell rigid urethane foams which can be termed as a controlled defoaming process. The key of this technique is the use of a balanced antifoaming agent, Tegostab B 8919, in combination with a suitable silicone surfactant. Applications for open celled rigid foams included not only their use as supporting core material for vacuum insulation panels but also for thermoformable rigid foams for the production of automotive headliners. Other potential applications include foams for flower arrangements and packaging.

De Vos and Rosbotham [14] reported recently of PUR foams in vacuum panel technology, but did not identify the composition of the rigid open cell foam panels.

In addition to the huge amount of work in finding suitable substitutes for CFCs in rigid urethane foams, the long term aging of rigid urethane and isocyanurate foams presents a problem since it results in an increase in thermal conductivity with time unless the foam is provided with an air impermeable facing such as steel, aluminium, *etc.*Many studies have been undertaken to understand the basic phenomena and to develop methods for monitoring the egress of low boiling blowing agents and the ingress of air. Studies by Glicksman *et al* [15, 16] have shown that a substantial portion of the heat transfer (loss) is due to the thermal radiation within the foams, as measured by an FTIR technique. The model used by the these investigators predicted that the radiative heat transfer was inversely proportional to the square root of the foam density and directly proportional to the cell diameter, in close agreement with the experimental results.

The radiative heat transfer was also shown to be due to the highly transparent cell walls, as reported by Glicksman *et al* (15, 16), Wiliams *et al* [17], and Cunningham [18]. Cunningham also found that the radiative heat loss increased with increasing cell size. Additional factors have also been recognized to reduce the heat loss such as the formation of more isotropic foams, greater mass (polymer matrix) in the cell walls, the emissivity of the polymer, the use of the various aromatic amine-based polyols, improved flowability of the foaming system and the influence of surfactants as regulators for cell geometry, in particular cell size, *etc.*

Other fundamental studies of great significance for the thermal conductivity aging of rigid foams have been carried out by Cunningham *et al* [19] which focussed on measurement of the effective diffusion coefficients of the gases in the cells. The method consisted of the determination of the concentration profiles of the gases across the foam sample width in the aging directions using gas chromatography with a specially developed sampling device.

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*) DABCO stands for 1,4-diazabicyclo-[2.2.2.]-octane.

Another method for the rapid measurement of gas diffusion and solubility in closed cell foam insulation was described by Brehm and Glicksman [20]. They used a constant volume sorption technique for the measurements of diffusion and solubility coefficient of gases in closed cell foams. The results of these measurements can be used for prediction of long term aging of foam insulating panels.

REFERENCES

1. Shankland I.R., Knopeck G.M., Williams D.T.: Proc. of UTECH Asia '95, May 1995, Suntec City, Singapore, Paper 20.
2. Volkert O.: Polyurethane World Congress, SPI/ISOPA, Nice, France, Sept. 1991, p.740.
3. Focquet K.: *Urethanes Technology*, Oct./Nov. 1992, 22.
4. Londrigan M.E., Snider S.C., Trout K.G.: Proc. of the SPI Annual Polyurethane Technical/Marketing Conference, New Orleans, LA., Oct. 1992, p. 12.
5. Volkert O.: Polyurethane World Congress, SPI/ISOPA, Vancouver, B.C. Canada, Oct. 1993, p.29.
6. Evans D.A.C., Stein R., Tweedale C.R.: Proc. of UTECH Asia '95, May 1995, Suntec City, Singapore, Paper 28.
7. Nicola W.J., Weber H.U.: 35th Annual Polyurethane Technical/ Marketing Conference, Oct. 1994, Boston, MA, p. 412.
8. *U.S. Patent.* 4,668,555, (1987).
9. *Jpn. Patent* Sho-43-20422 (1982).
10. *Jpn. Patent* Sho-57-133870 (1982).
11. Kodama V. *et al.*: *J. Cell. Plastics* 1995, **31**, 24.
12. Ashida K., Kashiwame J.: Proc. of the SPI Annual Polyurethane Technical/ Marketing Conference, New Orleans, LA., Oct. 1992, p. 158.
13. Burkhart G., Schator H.: Proc. of SPI 35th Annual Polyurethane Technical/Marketing Conference, Boston, MA., Oct. 1994, p. 31.
14. DeVos R., Rosbotham L.D.: Proc. of UTECH 94, The Hague, The Netherlands, Mar. 1994, Paper 29.
15. Glicksman L.R., Torpey M.R.: Proc. of the SPI-FSK-World Congress, Aachen, Germany, Sept./Oct. 1987, p. 80.
16. Reitz D.W., Schuetz M.A., Glicksman J.: *J. Cell. Plastics* 1984, **20** (2), 104.
17. Williams R.J.J., Alado G.M.: *Polym. Eng. Sci.*, 1983, **23** (6), 293.
18. Cunningham A.: Proc. Conference on Heat and Mass Transfer in Cryoengineering and Refrigeration, Sept. 1986.
19. Cunningham A., Sparrow D.J., Rosbotham L.D., DuCauze de Nazelle.: 32nd Annual Technical/Marketing Conference, San Francisco, CA, Oct. 1989, p. 56.
20. Brehm, T.R., Glicksman L.R.: **ibid**, p. 547.

Received 4 VII 1995.

Rapid Communications

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