

Research Article

Synthesis and Characterization of Polyurethane-Nanoclay Composites

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Received 17 December 2012; Revised 5 May 2013; Accepted 13 May 2013

Academic Editor: Hao Wang

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In this study polyurethane (PUR)-nanoclay composites were synthesized using methylene diphenyl diisocyanate, polyol, and hectorite clay. The weight percentage of hectorite clay was varied at three different levels to study its effect on the properties of the thermoplastic polyurethane nanocomposite. The nanocomposite polyurethane foam was synthesized in a 2-step reaction process. The first step involved the addition and dispersion of nanoclay into the isocyanate. The mixture was then mixed with the polyol, and the foam was cast in a preheated closed mold. The PUR-nanocomposite foams were analyzed for cell structure, physical, mechanical, and thermal properties. The composite foam showed significant increase in tensile and flexural strengths, abrasion resistance, and thermal properties.

1. Introduction

Polyurethanes are a unique class of polymer materials with a wide range of physical and chemical properties. Polyurethanes are characterized by the presence of urethane linkages, although other groups such as ether, ester, and amide may be present in the polymer molecule [1]. The ease of processing with relatively low tooling and manpower costs, as well as flexibility for long and short production runs, makes polyurethanes desirable for various applications [2]. This has increased the use of polyurethanes in the automotive, furniture, construction, insulation, coating, adhesives, fibers, footwear components, and biomaterials industries. The outstanding abrasion resistance of polyester polyol-based polyurethanes has led to their extensive use in surface coating and footwear applications; the superior thermal and oxidative stability of the aromatic polyesters is exploited in the manufacture of rigid isocyanurate foams for thermal insulation.

The properties of pristine polymers can be improved by nanocomposites, which cannot be matched by microcomposites with microfiller particles, such as carbon black, talc, glass fibers, and glass beads. These materials can exhibit many superior properties to conventional composites, such

as tensile properties, stiffness, heat distortion temperature, barrier properties, and resistance to flammability [3]. Clays especially can increase the barrier properties by creating a tortuous path that retards the progress of the gas molecules through the polymer matrix [4]. The nanoscale clay particles can be dispersed to a scale of few nanometers in the polymer matrix, and such dispersions are produced by shear or chemical reactions or a combination of both [5].

Polyurethane/clay nanocomposites are relatively a new class of composite materials. These nanocomposites are expected to show high mechanical and thermal properties compared with conventional composites. Polymer-layered silicate nanocomposites have gained a great deal of attention due to their superior properties like high dimensional stability, high heat deflection temperature, reduced gas permeability, improved flame retardancy, and enhanced mechanical properties compared to pure polymers [6, 7].

The development of polyurethane nanocomposites was first reported by Wang and Pinnavaia in 1988 [8]. They found that compatibility of clays with various poly diols improved by organic treatment, resulting in an intercalated structure. They intercalated clay layers with various polyols before reacting with diisocyanates and observed that the montmorillonite clay exchanged with long chain onium

ions and was compatible with those polyols. This led to the expansion of the clay galleries to some extent. The cross-linked polyurethane nanocomposites formed by in situ polymerization showed clay particles in intercalated state with a d-spacing of 5 nm and significant improvement in properties such as tensile strength, tensile modulus, and strain at break. A high optical transparency was also observed in these polyurethane/clay nanocomposites. Jisheng et al. [9] prepared PUR-nanocomposites by varying the clay content and also followed the different synthesis routes of clay compounding. They found a maximum d-spacing of 4.5 nm in the case of PUR-nanoclay route. In another study, X-ray analysis of polyurethane nanocomposites prepared by solution method has confirmed that with the increase of the number of hydroxyl groups in quaternary ammonium ions, the dispersion of layered silicates in polyurethanes transformed from an intercalated to an exfoliated state [10].

Tien and Wei [10] reported that the increase in the tensile strength depends on the interaction between clay and polyurethane. Clay modified by ammonium ion with trihydroxyl groups provides more tethering points with polyurethane molecules than clay treated by ammonium ion with monohydroxyl and dihydroxyl groups. Thus its enhancement in tensile strength was the most significant.

This paper discusses the synthesis and characterization of hectorite clay based PUR-nanoclay composites.

2. Experimental Work

2.1. Materials. The materials used for the PUR foam were the following. (1) Diisocyanate: methylene diphenyl diisocyanate [containing 4,4'-diphenylmethane-diisocyanate, CAS 101-68-8; modified MDI; and diisooctyl phthalate, CAS 27554-26-3] with a flash point above 230°F, average molecular weight of 250 g/mol, supplied by Huntsman. (2) Polyol: polyester polyol and 1,4-butanediol, CAS 110-63-4 with a flash point above 446°F, average molecular weight of 250 g/mol supplied by Huntsman. (3) The nanoparticle chosen was flake-type nanoclay with the trade name EA-3300-hectorite, supplied by Elementi. The nanoclay is a smectite-group mineral with a chemical formula $\text{NaO}_3(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. It has a monoclinic prismatic crystal system and hardness of 1-2, which is in between talc and gypsum and a cell size of 100 nm×20 nm.

2.2. Synthesis of PUR-Nanoclay Composites. Polyurethanes based on MDI often form crystalline hard segments which lead to phase separation. The reactivity of the isocyanate group influences how rapidly a polymer cures, which determines the length of time between mixing and gelation. The mixing time was hence varied for the samples.

The polyol was preheated at 120–140°F for 24 hrs. The nanoclay was preheated in the furnace at 200°C for 24 hrs. Plain polyurethane foams were prepared by mixing 60 g of methylene diphenyl diisocyanate with 48 g of polyol using a shear mechanical stirrer at 1200 rpm for about 10 seconds, and the mixture was cast into a preheated closed mold. The samples were cured for one week at room temperature.

TABLE 1: Sample composition.

Sample	Composition (iso : polyol : nanoclay) g
0% nanoclay	48 : 65 : 0.000
1% nanoclay	48 : 65 : 1.032
2% nanoclay	48 : 65 : 2.070
3% nanoclay	48 : 65 : 3.105

PUR-nanoclay composites were synthesized in a 2-step process as follows.

In step-1, preweighed amount of nanoparticles was mixed with the isocyanate to a desired specific weight ratio. The mixture was mixed slowly from the bottom until the clay was well dispersed, and then it was mixed at a high speed of 1200 rpm thoroughly for 15 minutes. The isocyanate was selected for infusion as it was less reactive. This mixture was kept in an oven at 120–140°F for 24 hours.

In step-2, nanoparticulated isocyanate was mixed thoroughly at 1200 rpm for 15 minutes, and the polyol was added to it at a ratio of 48 : 65 g. The entire mixture was then mixed using a mechanical stirrer at 1200 rpm for about 10 s until it became homogeneous. The mixture was then poured into a preheated closed mold (6 in × 2 in × 0.5 in).

Once cured, the nanophased foam was removed from the mold and cured for an additional week at room temperature. The process was repeated for various nanoclay compositions as shown in Table 1.

3. Results and Discussion

3.1. Cell Morphology and Foam Diameter. The microstructures of plain and nanophased foams were viewed under an Olympus BH2-UMA Optical Microscope. The cell size (d) was measured from the total area of the image and by counting the total number of cells including half cells at the edges. Dividing the total area by the number of cells gives the area of each cell as a square with side d . Then the square root was taken to determine the average diameter of a cell. Optical micrographs of plain and nanophased PUR foams are shown in Figures 1(a)–1(d). Agglomeration of nanoparticles due to their high surface energy [11] can be observed in the figures. It is seen that the average cell size decreases due to nucleation as the clay content increases.

3.2. Thermogravimetric Analysis. Thermogravimetric Analysis (TGA) was performed to measure the thermal stability of the nanophased PUR foam using SDT 2960 simultaneous DSC-TGA. TGA output of the form (percentage weight loss as a function of temperature) is shown in Figure 2. It can be observed that decomposition behavior of all the foam samples is in the form of a two-step degradation process, and hence the decomposition temperature represents the temperature corresponding to 80% decomposition of the material. It can also be observed that the decomposition temperature

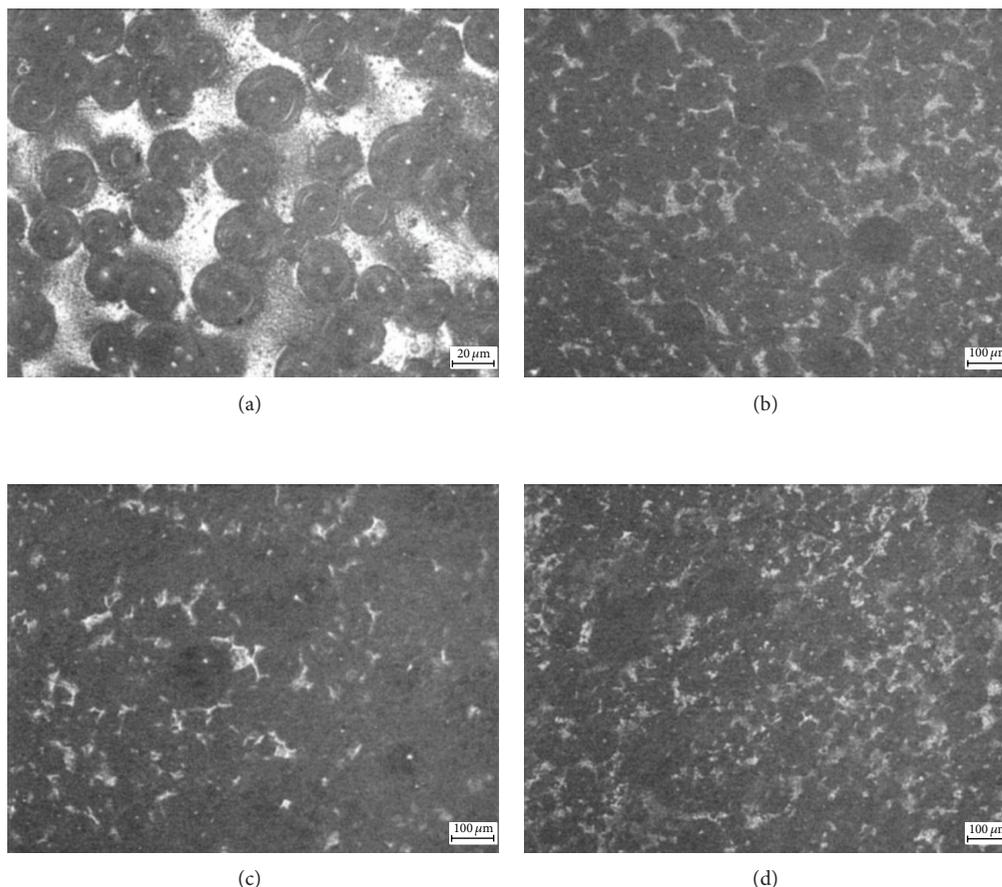


FIGURE 1: (a) Plain PUR (b) PUR + 1Wt.% NC (c) PUR + 2Wt.% NC (d) PUR + 3Wt.% NC.

increases as the composition of the nanoclay increases. This means that the incorporation of nanoparticles into PUR foam stabilizes it against decomposition by keeping the PUR chains and the original molecular structure intact [12].

It was also observed that the addition of nanoclay (NC) increased the char content from 8% (plain PUR) to 12% (PUR + NC). This can be attributed to the presence of minerals like silica, which is a major content of nanoclay, and since they do not degrade at lower temperatures, a higher weight percent at the end of the experiment can be expected. However a deviation was observed with the 2 wt.% nanoclay sample. The initial weight loss temperature of this sample shifted to a higher temperature in comparison to 1 wt.% and 3 wt.%. This discrepancy may be due to incomplete dispersion and exfoliation of the clay particles in 2 wt.% nanoclay.

3.3. Abrasion Resistance. Abrasion resistance was determined for plain and nanophased PUR foams using a Buehler polishing machine. The samples were tested at 2400 rpm on a 120 grit sand paper with a load of 4.5 kg. The results are shown as a function of weight loss in Figure 3. It can be observed that the abrasion resistance increased (decrease in weight loss) as the composition of nanoclay increased in the foam. This can be attributed to the higher hardness of nanoclay relative to PUR.

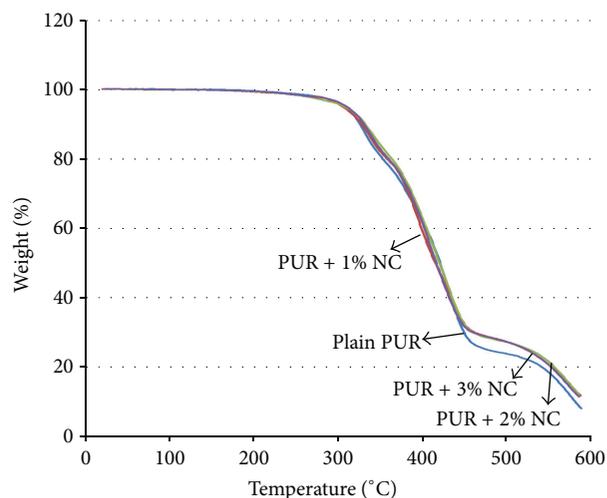


FIGURE 2: TGA analysis of PUR-Nanoclay composite foams.

3.4. Tensile Properties. Tensile tests were carried out using a SATEC-Universal Testing Machine. Tensile stress-strain curves of plain and nanophased PUR foams are shown in Figure 4. It can be observed that the stress-strain curves are closely linear, up to about 0.2 in/in strain, indicating

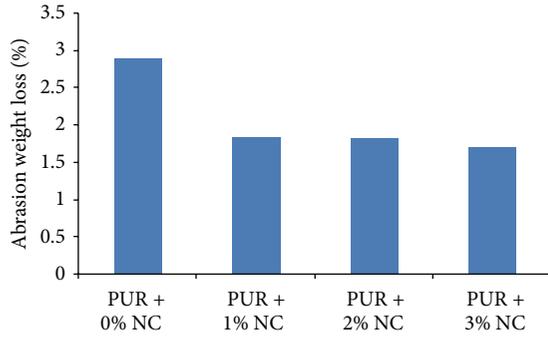


FIGURE 3: Abrasion resistance.

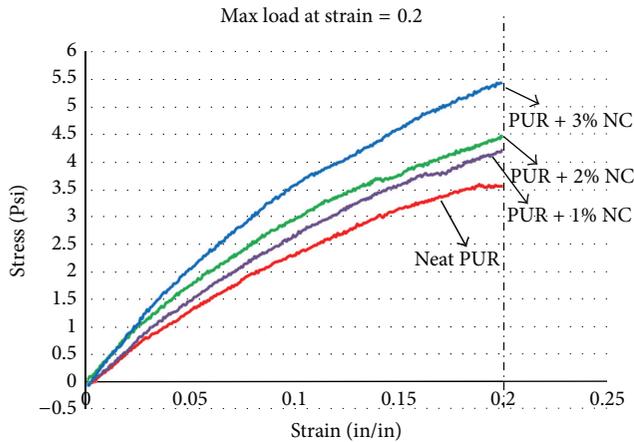


FIGURE 4: Stress-strain curves of PUR-nanoclay composites.

that the material behaves fairly elastic in that range. The nanophased foams showed higher tensile strength, yield strength, and toughness compared to the pristine foam. The tensile properties are summarized in Table 2. The presence of nanoclay lowers the crack propagation and leads to higher strength of nanophased foams. Enhanced toughness in nanocomposites has also been predicted to result from a critical interparticle spacing. A hypothesis by Wu [13] states that if the stress fields of adjoining particles overlap, a critical ligament thickness will exist which will lead to toughening of the matrix due to stress field interaction. Toughness is thus achieved when a large volume of bulk composite has its stress altered by the filler, favoring more an energy absorbing-yielding mechanism.

3.5. Flexural Strength. Flexure test was performed on SATEC Universal Testing Machine at a speed of 0.5 in/min. Specimens of dimensions $6'' \times 0.7'' \times 0.5''$ were cut from foam in the in-plane direction using a high speed diamond cutter and loaded under three-point bending. Figure 5 shows the load versus position curves of plain and nanophased PUR foams. It can be observed that the curves are fairly non-linear. The slopes of the flexure curves are higher for all nanophased foams compared to the plain foam. It can also be observed that the flexure strength increases as the nanoclay

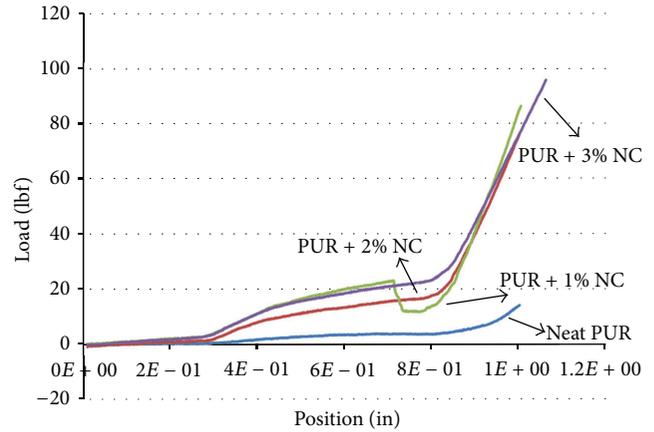


FIGURE 5: Flexural strength of PUR-nanoclay composites.

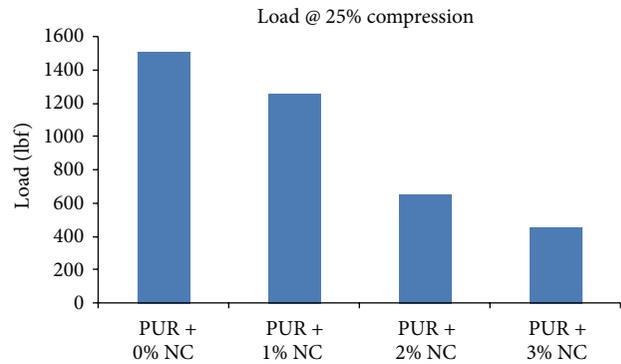


FIGURE 6: Compression strength.

composition increases in the foam. This can be attributed to the hectorite clay in the PU matrix. It has been found that rigid fillers like hectorite clay when added to the soft polymer matrix carry the major portion of applied load to the polymer matrix under stress conditions, if the interfacial interactions between filler and matrix are adequate [14, 15]. From the mechanical properties observed, it is evident that adequate interfacial interactions have led to better properties in the composite foam. Surface inspection of the flexure-failed samples suggests that failure/crack was initiated on the tensile side of the specimen.

3.6. Compression Strength. Compression test was performed on SATEC-Universal Testing Machine. The applied load was measured at 25% compression. Results show that the compression strength of the composite generally decreases with increasing the clay content, as shown in Figure 6. This may be due to the lower density of the foam. The compression strength is closely related to the dimensional stability of closed-celled foams. As the temperature goes up, gas pressure inside the cell increases and the pressure difference relative to the atmosphere increases. If the foam is to be dimensionally stable under these conditions, the compression strength must be greater than the pressure rise [16].

TABLE 2: Tensile properties.

Sample	Tensile strength (Mpa)	Max load at strain = 0.2 (lbf)	Elongation (%)	Yield strength (Mpa)	Toughness (Pa·m ³)
0%	0.0253	22	22	0.0144	5300
1%	0.0399	34.7	40.42	0.0199	16750
2%	0.0537	46.75	51.27	0.022	32200
3%	0.055	47	77.49	0.0234	49500

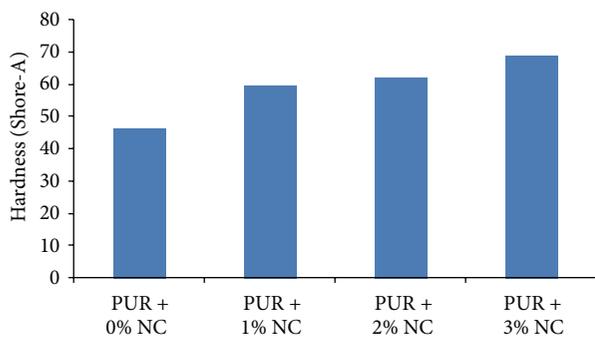


FIGURE 7: Hardness of PUR-nanoclay composites.

3.7. Hardness. Hardness was measured using a Shore-A Durometer according to ASTM D-2240 standards. It was observed that the foam hardness increased with the addition of nanoclay, Figure 7. Introduction of the active monomers will increase the cross-linking efficiency of nanoclay induced PUR, and thus nanoparticles can more efficiently improve the hardness.

4. Conclusions

Nanoparticles have a higher specific surface area in comparison to microparticles; this facilitates better adhesion between particles and PUR foam. It was observed that the effect of the mechanical bonding on the surface of nanoparticles and the stress field around them was a result of shear mixing, which led to improved properties in comparison to the plain foam. The average cell size of the composite foam decreased as the clay content increased. Decrease in cell size was attributed to the nucleating effect of clay. The thermal properties, tensile properties, flexural strength, and abrasion resistance were significantly enhanced in the composite foam compared to the plain foam. Compression strength of the composite foam was found to decrease with increasing clay content; this may be due to decreased density of the foam. The improvement in mechanical properties can also be attributed to the load bearing property of the nanoclay used as filler.

References

- [1] P. F. Bruins, *Polyurethane Technology*, John Wiley & Sons, New York, NY, USA, 1969.
- [2] G. L. Wilkes and R. Wildnauer, "Kinetic behavior of the thermal and mechanical properties of segmented urethanes," *Journal of Applied Physics*, vol. 46, no. 10, pp. 4148–4152, 1975.
- [3] G. L. Wilkes and J. A. Emerson, "Time dependence of small-angle x-ray measurements on segmented polyurethanes following thermal treatment," *Journal of Applied Physics*, vol. 47, no. 10, pp. 4261–4264, 1976.
- [4] G. L. Wilkes, S. Bagrodia, W. Humphries, and R. Wildnauer, "The time dependence of the thermal and mechanical properties of segmented urethanes following thermal treatment," *Journal of Polymer Science*, vol. 13, no. 6, pp. 321–327, 1975.
- [5] J. H. Park and S. C. Jana, "Mechanism of exfoliation of nanoclay particles in epoxy-clay nanocomposites," *Macromolecules*, vol. 36, no. 8, pp. 2758–2768, 2003.
- [6] M. J. Gintert, S. C. Jana, and S. G. Miller, "A novel strategy for nanoclay exfoliation in thermoset polyimide nanocomposite systems," *Polymer*, vol. 48, no. 14, pp. 4166–4173, 2007.
- [7] K. Yano, A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito, "Synthesis and properties of polyimide-clay hybrid," *Journal of Polymer Science A*, vol. 31, no. 10, pp. 2493–2498, 1993.
- [8] Z. Wang and T. J. Pinnavaia, "Nanolayer reinforcement of elastomeric polyurethane," *Chemistry of Materials*, vol. 10, no. 12, pp. 3769–3771, 1998.
- [9] M. Jisheng, S. F. Zhang, and Z. N. Qi, "Synthesis and characterization of elastomeric polyurethane/clay nanocomposites," *Journal of Applied Polymer Science*, vol. 82, no. 6, pp. 1444–1448, 2001.
- [10] Y. I. Tien and K. H. Wei, "High-tensile-property layered silicates/polyurethane nanocomposites by using reactive silicates as pseudo chain extenders," *Macromolecules*, vol. 34, no. 26, pp. 9045–9052, 2001.
- [11] S. H. Kim, M. C. Lee, H. D. Kim et al., "Nanoclay reinforced rigid polyurethane foams," *Journal of Applied Polymer Science*, vol. 117, no. 4, pp. 1992–1997, 2010.
- [12] M. C. Saha, M. E. Kabir, and S. Jeelani, "Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles," *Materials Science and Engineering A*, vol. 479, no. 1-2, pp. 213–222, 2008.
- [13] S. Wu, "A generalized criterion for rubber toughening: the critical matrix ligament thickness," *Journal of Applied Polymer Science*, vol. 35, pp. 544–553, 1998.
- [14] M. Tortora, V. Vittoria, G. Galli, S. Ritrovati, and E. Chiellini, "Transport properties of modified montmorillonite/poly(caprolactone) nanocomposites," *Macromolecular Materials and Engineering*, vol. 287, no. 4, pp. 243–249, 2002.
- [15] G. Gorrasi, M. Tortora, V. Vittoria et al., "Vapor barrier properties of polycaprolactone montmorillonite nanocomposites: effect of clay dispersion," *Polymer*, vol. 44, no. 8, pp. 2271–2279, 2003.
- [16] G. Oertel, *Polyurethane Hand Book*, Hanser, Berlin, Germany, 1985.



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