

IMD international medical devices

magazine

www.imdmagazine.com

Volume V | Issue I | Winter/Spring 2010



UHMWPE via Macromolecular Design

Robert L. Jones Jr., Mahmoud Z. Armoush, Tjhunina Harjati - DSM PTG

Reprint

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International Medical Devices is published quarterly.

*Offices are located at
5305 Plymouth Rd.
Ann Arbor, Michigan 48105
Phone: (734) 418-2365
Fax: (734) 418-2356
www.imdmagazine.com*

ISSN 1931-3217

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UHMWPE via Macromolecular Design

Robert L. Jones Jr., Mahmoud Z. Armoush and Tjhunina Harjati

Introduction

To date, commercially successful arthroplastic joint couples consist of metal or ceramic on plastic. More than metal on metal, ceramic on ceramic or combinations thereof, the plastics advantage have been repeatedly proven in clinical trials [1]. More specifically, ultra high molecular weight polyethylene (UHMW-PE) has been the material of choice in hip, knee, and shoulders posing a balance between biological compatibility and durability [2]. UHMW-PE is one of the toughest plastics known having very high abrasion resistance and low coefficient of friction. Gear parts are machined from UHMW-PE, gel spun fibers are woven into bullet proof vests, bearings are machined from molded stock as gears, machine parts, and components of artificial joints.

UHMW-PE is a simple long chain molecule consisting of repetitive $-(CH_2)-$ units. The length of the (polymer) chains (= molecular weight, Mw) and the uniformity of distribution of chain lengths (= molecular weight distribution, MWD) play a significant role in the mechanical properties. As a semi-crystalline thermoplastic, polyethylene can form regular crystalline blocks (called lamella) where the chains fold back and forth making a rigid hard segment; chain(s) can also find their way between the lamella and become part of the space between and connecting lamella in a plastic (amorphous) region. Especially long chains entangle, wind and twist between the crystalline and amorphous regions and provide a unique material having the ability to absorb and distribute energy throughout its structure. Incorporation of vinyl terminated end groups or addition of co-monomers creates branches which increase the amorphous region at the expense of crystallinity.

Commercially available UHMW-PE polymer raw material is a powder having a specific bulk density range, average particle size, and particle size distribution. There are well established standards for this commercially mature material, especially pertaining

to biomedical applications [3]. The processing and the way in which it is handled and formed have a direct impact on

the durability of the finished product. Many studies have been done on post-modification of existing materials towards better performance, and overall improvements in the properties have been made. It is our goal to understand the conditions required for optimizing UHMW-PE for arthroplastic applications in general (i.e., not for fibers, gears, or coal chute liners) and most specifically for hip vs. knee vs. shoulder, etc.; something that the polyolefin industry has yet to address.

The most important component in the synthesis of such a designer polyolefin is the catalyst. It is an organometallic reaction center which plays a crucial role in tailoring the macromolecular chain sequence. Following product specifications and operability, catalyst selection criterion is based on commercial availability or synthetic accessibility. Polyolefin catalysts come in a wide variety having been developed over many years for unique performance characteristics being tailored for specific applications.

Depending on the organometallic complexes selected (especially for single site catalysts such as metallocenes), a support system for heterogenizing the catalyst and activator is required. Many different catalyst supports are also available to choose from [4]. Along with classic methods [5], in situ methods of single site catalyst supportation have developed which are simple and effective [6, 7]. As with the classic Ziegler-Natta catalysts, control of particle morphology is a crucial aspect for preparing molded parts from highly viscous polymers such as UHMW-PE (vide infra). The controlled morphology of a support can play a significant role in expression of the catalyst productivity and polymer processing properties [8].

Classic Z/N catalysts with their many different active sites producing broad MWD polymers and (in the case of co-polymer) having co-monomer distributed in the low molecular weight fractions may not be suitable for all UHMW-PE arthroplastic implant applications. Moreover, single site catalysts and combinations of single site catalysts that give varying polymer architectures and property mixtures may ultimately provide a more optimized product. In any case, the operability of a catalyst system and the ability to incorporate co-monomer and produce UHMW-PE is a challenge.

Co-polymers of UHMW-PE have not received a lot of attention possibly due to commercially challenging production quotas and market position of such material. UHMW-PE copolymers have been studied in such applications as creep resistance in fibers, reactor fouling and morphology control. In the first in a series of studies targeting UHMWPE copolymers and copolymer scale up using a variety of polyolefin catalysts, we reported our initial foray into making these polymers. Here we provide analysis into the synthetic chemistry of these polymers.

Materials and Methods

Polymerizations were carried out in a jacketed 4L stainless steel stirred tank reactor, 2.5 L of heptane or hexane was used as the solvent; 0.7 mmol triethyl aluminum (TEAL) was used as a scavenger. Depending on the system, catalysts were activated with diethylaluminum chloride (DEAC), triisobutyl aluminum (TiBAI), or methylalumoxane (MAO) at the levels indicated in the tables. Temperature was thermostatically controlled as indicated; pressure remained constant during the campaign with continuous monomer feeding.

In a typical campaign, the reactor was heated to above 90°C and purged with nitrogen for a minimum of 30 minutes prior to cooling under positive nitrogen pressure. Solvent (heptane) was added followed by co-monomer (hexene) and scavenger. The temperature was set at the desired set-point then polymerization grade ethylene gas was added to run pressure. Catalyst and activator solution (prepared in a nitrogen dri-box prior) were injected using a pressurized stainless steel syringe pump (for the 4 L reactor), or from a cylinder using nitrogen pressure. Molecular weight of the polymers was calculated from the intrinsic viscosity (ASTM D4020); comonomer composition was measured using FTIR (see ASTM D5576, D6248 and references therein). 13C-MAS-NMR was carried out by Acorn NMR Inc. (Livermore, CA).

Results

The amount of incorporated co-monomer (hexene) was directly related to catalyst type, temperature of the polymerization, pressure and co-monomer concentration. For the classic Ziegler-Natta catalysts used (see table 1), increasing the molarity of the co-monomer initially added to the reactor resulted in increasing amounts of co-monomer incorporated into the polymer (as measured by 13CMAS-NMR). Either propylene or hexene added to the reactor resulted in a decrease in the polymer molecular weight and in general a decrease in catalyst productivity.

Table 1. Copolymer results at 60°C, 2.5L hexane with TiCl3

ID #	Cat amt [mg]	Co-monomer	[M]	Time [h]	Press. [psi]	Yield [g]	M-E mole		M _w ^a [g mol] x 10 ⁻³	Bulk Density [g ml]
							[%]	13C-MAS NMR		
12	67.0	None	-	4.0	100	435	-	2.5	5,058	-
31	67.0	Propylene	0.18	4.5	100	350	5.8	2.3	4,521	0.923
34	67.0	Propylene	0.88	4.0	200	400	9.0	1.8	3,387	0.923
36	67.0	Propylene	1.23	5.0	110	290	13.0	1.4	2,388	0.913
23	67.0	1-Hexene	0.30	5.0	100	345	6.0	1.4	3,624	0.921
35	67.0	1-Hexene	0.48	6.0	120	315	7.0	1.8	1,680	0.920
19	67.0	1-Hexene 5-MHD	0.30 0.19	3.5	100	427	3.5	1.2	1,954	0.924

a) calc. from viscosity

Co-polymerizations using a commercial Si/MgCl₂ supported TiCl_n (n = 3 and/ or 4) are shown in Table 2. Hexene and decadiene were co-polymerized with ethylene under different conditions of pressure and temperature: higher amounts of co-monomer incorporation decreased catalyst productivity and also resulted in a polymer having lowered molecular weight.

An additional ethylene co-polymerization was performed using allyl-amine which had been masked with an aluminum alkyl prior to addition to the reactor. Polymerization yield was decreased even at low level of addition.

Table 2. Copolymer results with Mg/Si supported TiCl3

ID #	Amt [mg]	Comonomer ID	Amt [M]	Amt [ml]	Temp [°C]	Press [psi]	Time [min]	Yield [g]	IV [dl g]	M _w [g mol] x 10 ⁻³	Bulk Density [g ml]
059a	30	1-Hexene	0.32	100.0	60	40	240	154	28	7,317	-
424	35	1-Hexene	0.08	25.0	60	200	180	518	27	7,301	0.92
425	35	1-Hexene	0.16	50.0	60	200	180	420	23	5,783	0.96
688 ^b	50	Decadiene	0.11	55.0	25	200	60	10	NS	NS	0.91
067 ^c	32	Decadiene	0.09	46.0	80	80	90	98	NS	NS	0.95
438	60	Allyl amine	0.02	5.0	65	30	300	40.0	30	6,615	-

a) scavenger: DEAC, 12 mmol; b) Scavenger DEAC, 0.8 mmol; c) scavenger: TiBAI, 6.25 mmol; NS = not soluble

Single Site Catalyst Co-polymerizations

A variety of metallocenes were used in co-polymerizations with selected comonomers. In table 3 results from ethylene-bis(fluorene) zirconium(VI)chloride (Et(Flu)2ZrCl2 unsupported) co-polymerization with ethylene with hexene showed a dramatic decrease in polymer molecular weight with increasing hexene content in the reaction mixture. This decrease could be compensated to some extent by lowering the polymerization temperature or increasing the ethylene pressure. At decreasing temperatures however, less comonomer is incorporated into the final polymer.

Table 3. Ethylene Copolymerizations with Et(Flu)2ZrCl2 (unsupported)

ID #	Amt [mg]	Al Zr	Hexene Amt [M]	Temp [°C]	Press [psi]	Time [min]	Yield [g]	IV [dl/g]	Mw [g/mol] x 10 ⁻³
17005	2	447	0.0	45	100	30	85	7.1	995
17007	2	594	0.0	50	100	30	76	8.0	1,201
17019	3	992	0.08	30	100	60	5	7.1	997
17018	3	992	0.16	30	100	60	14	5.2	632
17017	3	992	0.16	60	100	45	101	3.3	315

Co-polymerization results using bis-ethylcyclopentadienyl hafnium dichloride (EtCp)2HfCl2 are included in table 4 for the homogeneous (unsupported) co-polymerizations and table 5 for co-polymerization using the catalyst supported on silica.

Table 4. Ethylene Copolymerizations with hexene using (EtCp)2HfCl2 (unsupported)

ID #	Amt [mg]	Al Hf	Hexene Amt [m]	Temp [°C]	Press [psi]	Time [min]	Yield [g]	IV [dl/g]	Mw [g/mol] x 10 ⁻³	FTIR (%)
17168	12	1031	-	45	100	60	108	12.0	2,191	-
17147	12	1028	-	45	100	120	158	10.5	1,790	-
17151	12	1031	0.16	44	100	60	120	6.5	881	1.50
17152	12	1031	0.32	44	100	90	58	5.4	670	2.25
17154	12	1031	0.64	42	100	120	219	3.2	297	4.75

For either co-polymerization the data indicate that the molecular weight effects of adding co-monomer are similar for supported or unsupported polymerization. The lowering of molecular weight by co-monomer content of the reaction solution can be offset to some extent by increasing the reaction pressure and decreasing reaction temperature however, both create lower co-monomer content in the resulting polymer.

Figure 1. Graphical display of results from ethylene-hexene co-polymerization using (EtCp)2HfCl2 supported on silica (see text for explanation of results).

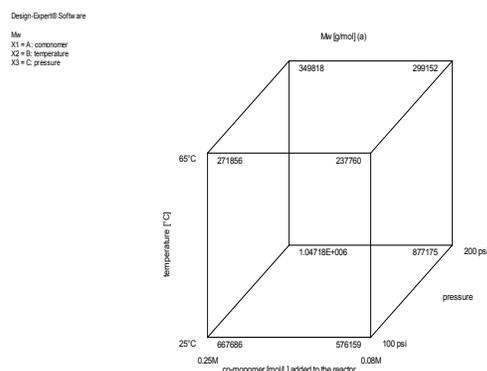


Table 5. Ethylene co-polymerizations using Silica supported (nBuCp)2HfCl2..

ID #	Amt [mg]	Al Hf	Co-monomer	Co-monomer Amt [M]	Temp [°C]	Press [psi]	Time [min]	Yield [g]	IV [dl/g]	Mw [g/mol] x 10 ⁻³
180407	20	161	1-Hexene	0.08	25	150	180	310.0	5.4	667,686
180412	20	178	1-Hexene	0.08	27	200	180	299.0	7.3	1,047,182
180411	20	178	1-Hexene	0.08	62	100	110	248.0	3.0	271,856
180414	11	178	1-Hexene	0.08	62	200	45	193.5	4.0	427,780
180444	16	175	1-Hexene	0.12	65	100	60	225.0	2.8	245,454
180580	8	176	1-Hexene	0.12	45	150	60	90.0	3.8	394,713
180581	8	176	1-Hexene	0.12	45	150	60	147.0	3.8	391,591
180623	19	173	1-Hexene	0.24	18	250	60	65.0	7.5	1,085,209
180448	16	175	1-Hexene	0.24	25	100	60	97.0	4.9	576,159
180449	16	175	1-Hexene	0.24	25	200	60	135.0	6.5	877,175
180453	6	175	1-Hexene	0.24	62	200	60	285.0	3.2	299,152
180445	16	175	1-Hexene	0.24	65	100	60	210.0	2.7	237,760
170606	7	238	Allyl amine	0.07	65	80	60	134.0	2.5	214,346
190069	20	157	1,9-Decadiene	0.05	25	200	120	50.0	NS	-
190072	20	155	1,9-Decadiene	0.10	25	200	390	280.0	NS	-

The data was generated for a multi factorial DOE using Design-Expert® ver 7.1.1 [9]: a graphical display of the results is included in figure 1. The ranges of effects of temperature and pressure which are indicated are useful in further developing conditions to produce UHMWPE copolymers and for scaling up to larger production levels.

Conclusion

Here we have presented results for preparing copolymers using UHMWPE catalysts. Classic Ziegler-Natta catalyst, commercially available Ziegler-Natta catalysts, and unsupported and silica supported metallocene single site catalysts having three independent structural types were used. These results show the effects of varying comonomer content in the reactions

mixture on the molecular weight of the final polymers. In general increasing the co-monomer amount in a polymerization reaction mixture resulted in an overall decrease in polymer molecular weight: this could be compensated by increasing pressure and temperature of the reaction conditions. In many cases however, the molecular weight was lowered below what could be considered to be the UHMWPE range.

These results are the first in a series of studies initiated to examine the application of macromolecular design to UHMWPE. The polyethylene macromolecule is known to be different for classic and commercially relevant catalysts of the (heterogeneous) TiCl₄ type, than for single site catalysts where all reaction centers are the same. Additional studies qualifying these differences and the further characterization of these polymers are in progress.

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[9] Stat-Ease, Inc.; 2021 E. Hennepin Avenue, Suite 480, Minneapolis, MN 55413-2726
e-mail: info@statease.comp; phone 612.378.9449, f: 612.746.2069