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Multipolymers with Fischer-Tropsch Olefins

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SUMMARY: Multipolymers consisting of ethylene, 1-heptene, 3-methylpentene and 4-methylpentene were prepared with a heterogeneous Ziegler-Natta catalyst. The polymers were prepared in such a way that the molar fraction of the comonomers remained the same. Copolymers of ethylene/1-heptene and ethylene/4-methylpentene were prepared in order to study the changes in polymer characteristics as one moves from an ethylene/linear alpha olefin copolymer through ethylene multipolymers to an ethylene/4-methylpentene copolymer. The mechanical, rheological and application properties showed expected trends.

Introduction

Traditionally, even carbon number α-olefins were responsible for the unprecedented growth of the polyethylene industry. While ethylene oligomerization remains a stable source for even carbon number α-olefins, a more complex pool is now available from the Fischer Tropsch process. This process offers the polyolefin industry, in addition to the currently known even carbon number α-olefins, some less explored possibilities[1]:

i. Odd carbon number α-olefins in ethylene copolymerization

ii. Branched α-olefins in ethylene copolymerization

iii. Even and odd carbon number branched α-olefins in terpolymerization

iv. Multiple polymerization with Fischer Tropsch α-olefins.

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It was previously shown[2] that the properties of ethylene polymers are strongly dependent on the type of comonomer used. The use of primarily linear, even carbon number α-olefins limited the application range of the ethylene polymers produced. By introducing uneven carbon number α-olefins, the change in density between different α-olefin-based polyethylenes increases the processing margins.

As previously shown[2] for copolymers of ethylene having similar molar comonomer contents, densities decrease with increased branch length. WAXD measurements on ethylene / α-olefin copolymers show an increase in the *a* and *b* dimensions with increasing comonomer content, which could be interpreted as incorporation of co-units into the crystalline lattice. However, with increased comonomer content, the crystallizable ethylene sequence lengths decrease, leading to decreased lamellar thickness. The heterogeneous distribution of comonomer units which results in very long and very short crystallizable sequences is therefore responsible for a range of lamellar thicknesses and the thick ones have higher melting temperatures than the thinner ones.[3] The same trend as that observed for density can be seen for tensile strength and a very close correlation was observed between branch length and observed tensile strength. However, the modulus shows a significant deviation from this trend, resulting in modulus values being higher than expected from calculations based on branch length. The slopes of the impact strength curves increase with increasing carbon number of the comonomer. By calculating the average ethylene sequence lengths it was found that, in general, the ethylene sequences in the copolymers containing the higher α-olefins were longer than those of e.g. the 1-butene copolymers. A simple model considering active sites having different accessibilities that reject co-units based on size was constructed and ethylene sequence lengths of different suggested microstructures were calculated. It was found that by introducing clustered co-units into the model, the average ethylene sequence lengths can be adjusted to correspond with the experimental finding.

It was expected that the densities of the terpolymers should be between those of the corresponding copolymers, but this was not observed with all the comonomers. At very low (high) 1-butene : 1-pentene ratios, the terpolymer densities were similar to those of the ethylene / 1-pentene (ethylene / 1-butene) copolymer densities, but at intermediate

1-butene 1-pentene ratios, densities were even lower than those of the ethylene / 1-pentene copolymers. For the ethylene / 1-pentene / 1-hexene copolymers the effect was smaller, although densities of terpolymers having intermediate 1-pentene : 1-hexene ratios were very similar to those of the ethylene / 1-hexene copolymers.

For the α-olefins larger than 1-hexene, this effect was not observed and the densities and mechanical properties of the ethylene / 1-pentene / higher α-olefin terpolymers were found to lie between those of the ethylene / 1-pentene and the corresponding ethylene / higher α-olefin copolymers. Calculations of the average ethylene sequence lengths from ^{13}C NMR confirmed that $\tilde{n}_E$ for ethylene / 1-butene copolymers was longer than those of the ethylene / 1-pentene / 1-butene terpolymers.[4]

The slope of the copolymers containing the branched α-olefins was steeper than that of the corresponding copolymers containing linear α-olefins, and was very similar to the slope observed for ethylene / 1-octene and ethylene / 1-nonene copolymers. High impact strength can thus be obtained using branched α-olefins at relatively low content.[5]

Experimental

Ethylene was copolymerized with 1-heptene in a heptane slurry at 80°C using a magnesium dichloride-supported Ziegler-Natta catalyst and tri-ethyl aluminum in the presence of hydrogen as transfer agent to control molecular weight. Ethylene and 1-heptene were introduced into the reactor at the desired feed ratio. After addition of amounts of the monomers the reaction was continued for a total of 60 minutes. The reactor was then depressurized and the catalyst deactivated by the addition of 100 ml *iso*-propanol. The slurry was filtered and the polymer washed with acetone and dried under vacuum at 80°C.

Preparation of the multipolymers of ethylene containing 1-heptene, 3-methyl-1-pentene and 4-methyl-1-pentene as main components was conducted in a similar fashion, but the comonomers were introduced as a mixture, having the desired composition.

The comonomers used were obtained from the Fischer-Tropsch process but were not extensively purified prior to use.

As an example, the analysis of the 1-heptene used is presented below.

1-Heptene was analyzed on a GC-MS (GC HP 5890 Series II and MSD HP 5972) using a *non-polar* 50m DB-Petro column (PONA equivalent). A GC-FID equipped with a DB-Petro column was used for quantification of the components in this sample, using *iso*-pentane as an internal standard.

Mechanical properties were determined on injection-moulded samples according to the appropriate ASTM methods. Density was measured on a density gradient column, using a water / *iso*-propanol mixture. Samples dissolved in a *o*-dichlorobenzene were analysed by ^{13}C NMR spectroscopy at 120°C on a Varian 400 MHz machine, using a 90° pulse angle, a pulse width of 10, 25 000 scans with a 30 sec. delay. Mechanical properties on injection-moulded test pieces including tensile strength at yield, Young's modulus and Izod impact strength were determined using the appropriate ASTM methods. Molecular weight and polydispersity were determined on a Waters 150CV GPC with a HT6, HT5, HT4 and HT3 set of styragel columns, using tri-chloro benzene as solvent and a refractive index detector. Rheological measurements were performed on an MCR-500 rheometer from Paar-Physica. The cylindrical (25 mm diameter) parallel plate measurement system, fitted with a temperature control unit, was used in oscillation mode (1% strain amplitude) to determine the rheological properties of the polymers in this study.

Multipolymerization with Fischer-Tropsch Olefins

For the preparation of the multipolymers the molar content of the total branched and linear olefin fed to the reactor was kept constant while the linear vs. branched ratio was changed. A sizeable difference between the densities of the ethylene / branched C6 terpolymers and the ethylene / linear C6 copolymers was previously observed.[2,5] By changing the molar comonomer feed composition from purely linear C6 to purely branched C6, the density was seen to progress directly to that of the ethylene / branched C6 multipolymer, with the resulting densities very close to the mathematical average expected for the feed composition. At the same ethylene / comonomer feed composition the linear C6 content in the copolymer is higher and the copolymer density is lower than that of the corresponding reaction in which branched C6, was used but at the same comonomer content, the branched α-olefin is more effective at reducing density.

In the series of experiments presented here, 1-heptene was considered. Analytical results are tabulated in Table 1.

Table 1. Identification and quantification of the individual components in Fischer-Tropsch derived 1-heptene obtained on a DB-Petro column.

Peak	**Compound/Isomer**	**Area %(m/m)**	**Normalized Area %**
1	Isopentane (Internal Standard)	0.86	
2	1-Hexene	0.04	0.04
3	n-Hexane	0.01	0.01
4	3-Methylenecyclopentene or Methyl-1,3-cyclopentadiene	0.05	0.06
5	3-Methylenecyclopentene or 1,3-Cyclohexadiene	0.04	0.04
6	Methyl-1-hexene	0.03	0.03
7	5-Methyl-1-hexene	0.04	0.04
8	4-Methyl-1-hexene	0.05	0.05
9	2-Methylhexane	0.03	0.03
10	3-Methylhexane	0.25	0.25
11	2-Methyl-1-hexene	1.67	1.69
12	1-Heptene	94.46	95.27
13	1,5-Heptadiene	0.07	0.07
14	Methylhexene	0.14	0.14
15	3-Heptene	0.22	0.23
16	3,5-Dimethylcyclopentene	0.43	0.44
17	2-Methyl-2,4-hexadiene + Methylhexene (17a &17b)	0.49	0.49
18	4,4-Dimethylcyclopentene	0.89	0.89
19	1,5-Dimethylcyclopentene	0.15	0.15
20	1-Methyl-2-methylenecyclopentane	0.01	0.01
21	Diels Alder Product	0.06	0.06
Total		100.00	100.00

In Figure 1 below, the composition of the additional components in the 1-heptene is summarized.

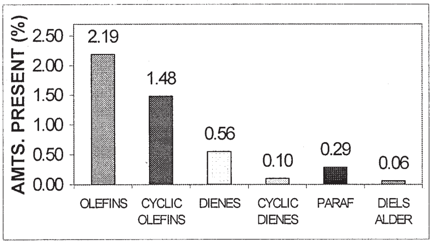


Figure 1. Composition of components remaining in 1-heptene after purification.

In five experiments, multiple polymerization of ethylene with 3-methyl-1-pentene, 4-methyl-1-pentene and 1-heptene was conducted where 1-heptene was replaced with a 1:1 mixture of 3-methyl-1-pentene and 4-methyl-1-pentene. The amount of hydrogen was adjusted to maintain a melt flow index of between 1 and 3 g/10 minutes. In Table 2 the comonomer composition and hydrogen content is shown:

Table 2. Comonomer feed composition for the preparation of ethylene / 1-heptene / 3-methyl-1-pentene / 4-methyl-1-pentene multipolymers.

Hydrogen (mg)	**Ethylene (mol)**	**1-Heptene (mol)**	**3/4 MP1 (mol)**
0	14	6	0
25	14	4.5	1.5
50	14	3	3
80	14	1.5	4.5
125	14	0	6
30	14	0	6*

* Pure 4-methyl-1-pentene

Reactivity of 3-methyl-1-pentene is much lower than that of 1-heptene. Using a 1:1 ratio of 3/4-methyl-1-pentene results in an ethylene terpolymer containing these comonomers in a 1:9 ratio. By direct replacement of 1-heptene with the 3/4-methyl-1-pentene, clearly more 1-heptene will be incorporated. Consequently, as can be seen from Figure 2, lower densities are achieved when only 1-heptene is used.

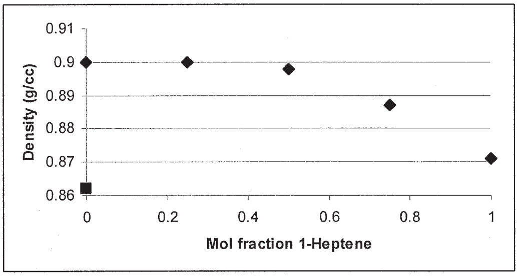


Figure 2. Density as a function of the mol fraction of 1-heptene in the feed.

The data point at a density of 0.862g/cc represents the ethylene / 4-methyl-1-pentene copolymer and it can be seen that the density is lower than that of the ethylene / 1-heptene copolymer.

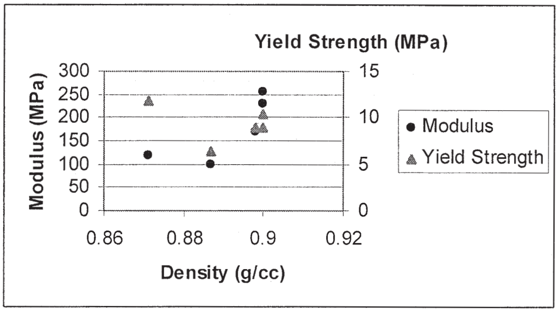


Figure 3. Modulus and tensile strength at yield as a function of density.

As the density increases from 0.887g/cm^3 the modulus and tensile strength increase. This is due to the lower incorporation of the increasing branch:linear ratio, which is explained in Figure 2. However, both the modulus and tensile strength values are higher at the lower density (0.871g/cm^3) than at the higher density (0.887g/cm^3). This could be explained by the fact that there are more linear polyethylene chains in the former copolymer (0.871g/cm^3) than in the latter (0.887g/cm^3) because the physical diameter of the branched C_6 is smaller than the linear C_7, which means that more catalyst sites are accessable to the branched olefins than to the C_7 olefin. Therefore it was argued that a decrease in the number of linear ethylene chains results in a decrease in the modulus and tensile strength.

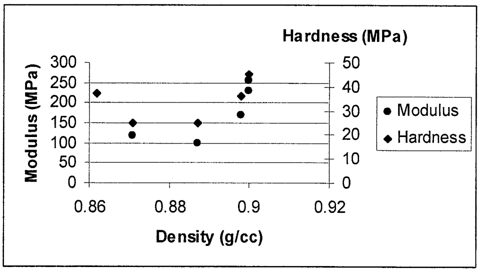


Figure 4. Modulus and hardness as a function of density.

Figure 4 illustrates the point made in the previous argument, where the hardness of the multipolymer first decreases to a minimum and then increases as the number of linear chains increases

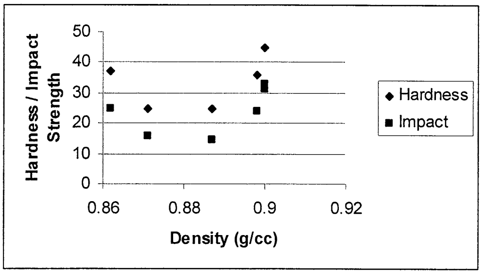


Figure 5. Impact strength and hardness as a function of density.

The impact strength of the multipolymers (Figure 5), follows the same trend as the modulus and hardness do. The impact strength first decreases, from a copolymer prepared with only C_7 in the feed to the first multipolymer where the comonomer feed consists of C_7 (75%) and branched C_6 (25%) to higher concentrations of the branched olefin at higher densities.

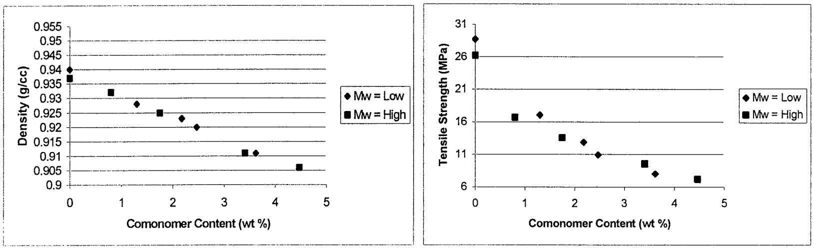
Multipolymerization of Ethylene and 1-Heptene Containing Small Amounts of Other Olefins

Two sets of ethylene / 1-heptene copolymers were prepared having different molecular weights. The fundamental properties of the ethylene / 1-heptene copolymers are presented in Table 3.

Table 3. Fundamental properties of C_2/C_7 copolymers.

Sample	**Comonomer**	**Comp. (%)**	**Mw (g/mol)**	**Density (g/cc)**
PE00/160	-	0	225000	0.937
PE00/165	-	0	114200	0.94
PE00/169	C7	1.3	90000	0.928
PE00/180	C7	3.62	106000	0.911
PE00/177	C7	2.47	113000	0.92
PE00/178	C7	2.18	138000	0.923
PE00/173	C7	1.51	153000	0.934
PE00/174	C7	1.75	184000	0.925
PE00/182	C7	3.41	196000	0.911
PE00/172	C7	0.8	197000	0.932

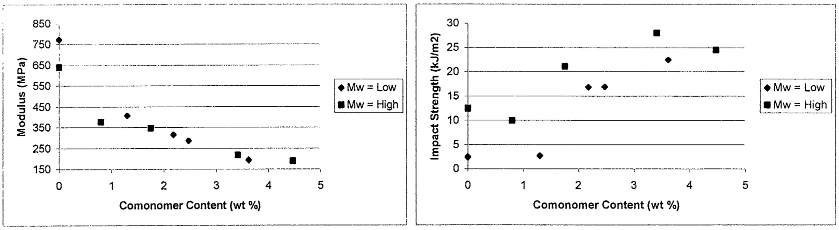
Because of entanglements between the high molecular weight chains, mobility of these chains decreases and even crystallizable sequences may be prevented from crystallization, resulting in a decrease in density. The entanglements of the high molecular weight chains are responsible for increased tensile strength. However, from Figure 6 (a) and (b) and 7 (a) it is clear that the differences in the molecular weights of the polymers under investigation are not sufficient to show differences in density, tensile strength and modulus. On the other hand, a substantial difference in impact strength was observed between the copolymers with different molecular weights (Figure 7b), as was expected.



(a) **(b)**

Figure 6. Density (a) and tensile strength (b) versus comonomer content for different molecular weights.

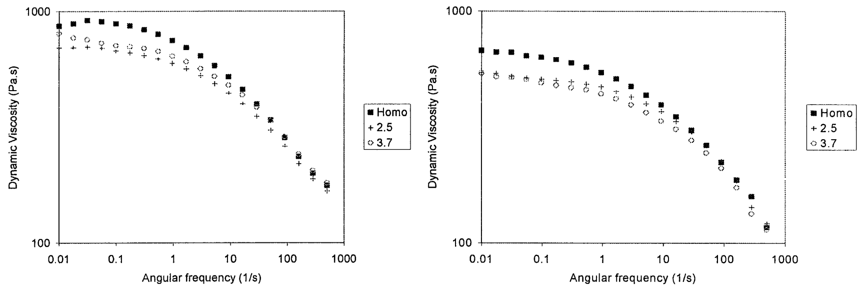
Figure 6 (a and b) illustrates that the density of the copolymers decreases as the C_7 content increases. This is the case for both the high and lower molecular weight copolymers. The tensile strength also decreases with increasing comonomer content. This is due to the fact that the copolymer becomes less crystalline (shorter crystallisable ethylene sequences) with an increase in the C_7 olefin content. The same arguments can be used for the modulus of the C_2/C_7 copolymers.



(a) **(b)**

Figure 7. Modulus (a) and impact strength (b) as function of comonomer content for different molecular weights.

Dynamic viscosity curves of the C_2 homo and C_2/C_7 copolymers The rheological properties of the ethylene/1-heptene copolymers were determined and compared with the properties of the ethylene homopolymers. The dynamic viscosity versus frequency curves for the homopolymer and different 1-heptene content copolymers of similar molecular weights at 170 °C and 190 °C are depicted in Figure 8 (a) and (b).



(a) **(b)**

Figure 8. Dynamic viscosity for homopolymers and 1-heptene copolymers with the same molecular weight (≈110 000 g/mol) at (a) 170 °C and (b) 190°C.

The dynamic shear viscosities of the 1-heptene copolymers are slightly lower than that of the ethylene homopolymer. The decrease in viscosity with the addition of comonomer is as expected and results mainly from an increase in the free volume of polymer chains due to the presence of the comonomer side chain.[6] An increase in free volume allows for more free movement of the polymer chains and hence a reduction in viscosity.

The sensitivity of the rheological properties to changes in the high molecular weight fraction of a polymer can be clearly seen when comparing two C_2/C_7-copolymers with similar comonomer content (refer Figure 9). Both have an almost similar C_7 comonomer content (3.6 mole %), M_w (106500 and 103700 g/mol respectively) and M_n (18600 and 18500 g/mol respectively) values, but the clear difference in their dynamic viscosities arises from a difference in M_z-values (414200 and 374200 g/mol respectively). The copolymer with the higher molecular mass fraction also exhibits a higher dynamic viscosity.

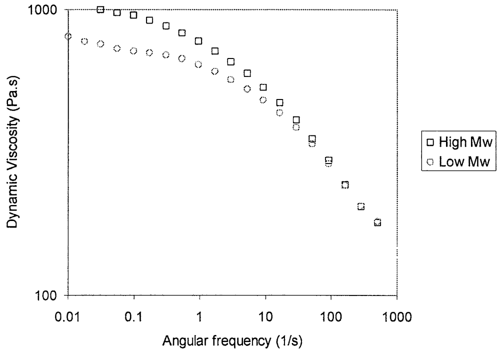


Figure 9. Viscosities of high and low M_w ethylene/heptene-1 copolymers with the same C_7 content (3.6 mole % 1-heptene).

Energy of flow activation The viscosity of the heptene-1 copolymers also shows, as expected, a higher temperature sensitivity than that of the homopolymer. The temperature dependence of the zero shear viscosity can be described by an Arrhenius-type equation

$$\eta_0 = Ae^{E_a/RT}$$

where E_a is the energy of flow activation. The activation energy of flow was calculated from the zero shear viscosities obtained from the loss-modulus.

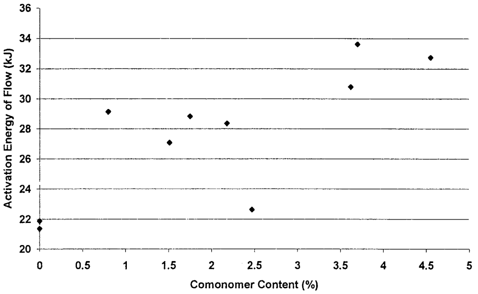


Figure 10. Energy of flow activation versus comonomer content of ethylene homopolymers and heptene-1 copolymers calculated from zero shear viscosity.

The flow activation energy of the homopolymers was between 21 and 24 kJ/mol and is comparable with the literature values of 25 kJ/mol for HDPE.[6] The flow activation energy of the C_2/C_7-copolymers was between 26 and 34 kJ/mol. Furthermore, the flow activation energy of the C_2/C_7-copolymers increased with comonomer content but reached a plateau level at a certain amount of comonomer. The higher flow activation energy of the PE/C_7 copolymers compared with the PE homopolymer is typical of what is expected from the balance that exists between free volume and friction, introduced by the short chain branches on the linear PE backbone.[7] A study reported by Shirayama and coworkers[7] shows that the activation energy of poly-α-olefins reaches a maximum for four carbon atoms in the side chain. Linear low-density polyethylene with six or more carbon atoms have lower activation energies. Beyond the maximum activation energy, the free volume is the predominant factor.

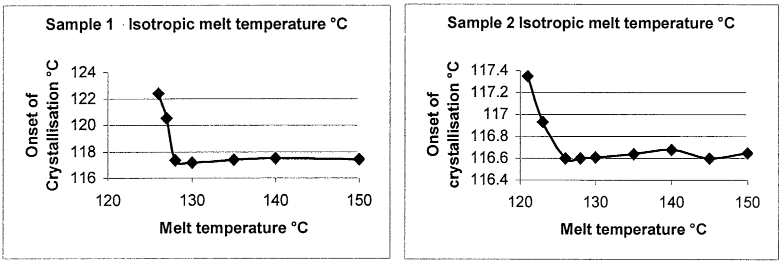
Processing Properties

Two large batches of the ethylene / 1-heptene copolymers were prepared for the determination of processing properties. The fundamental properties of these copolymers are shown in Table 4 below.

Table 4. Fundamental properties of ethylene / 1-heptene copolymers.

Sample	**MFI (g/10min)**	**Stable Melt Region (°C)**	**OIT (min.)**	**Isotropic Melt Temp (°C)**
Low MFI	2.551±0.15	128 – 340	45	117.4°C
High MFI	9.872±0.661	128 – 340	20	116.6°C

The isotropic melt temperature is the temperature at which all the segments of the polymer chain are in motion, due to the energy supplied by heating, and is the lowest temperature at which the melt should be processed. The onset of crystallization as a function of the temperature to which the sample was repeatedly heated to a continuously decreasing temperature was plotted to obtain the isotropic melt temperatures shown in Figure 11 a and b:



(a) **(b)**

Figure 11. Isotropic melt temperatures of low MFI (a) and high MFI (b) ethylene/1-heptene samples.

Injection moulding trials were carried out on a Mannesmann-Demag D60 NCIII –K injection moulding machine fitted with a B screw. The mould that was used was a standard ISO tensile test piece mould. Due to the very small sample size required for use on this machine, only a limited number of tests could be carried out. A low backpressure was needed to enable rapid and thorough plasticisation. A feed zone temperature of 25°C proved to be ideal and ensured rapid feed of the material to the screw. For both samples a shot size / cushion relationship of 60/6mm was found to be adequate with an injection velocity of 18%. Due to the small sample size only the stroke dependent switch-over technique was used in both cases. The cycle time for both samples was 30 seconds. Due to the inherent stability of both materials and the short cycle time, no problem was experienced with the dwell time exceeding the OIT of both materials.

The in-mould as well as post-manufacturing shrinkage was determined by injection moulding samples at 25°C mould-temperature, using the abovementioned parameters. The in-mould shrinkage was determined after 24 hours at 23°C and the post-manufacturing shrinkage after 24 hours at 80°C. The results are shown in Table 5.

Table 5. Shrinkage of ethylene / 1-heptene copolymers.

	In-mould shrinkage %	**Post-manufacturing shrinkage %**	**Total Shrinkage %**
Sample 1	3.2	1.9	5.1
Sample 2	3.4	2.3	5.7

The low-temperature impact properties were determined between 20 and –25°C and the results are given in Table 6 (0br indicates no break. Values are given in kJ/m^2):

Table 6. Low temperature izod impact properties.

Temp (°C)	**20**	**15**	**10**	**5**	**0**	**-5**	**-10**	**-15**	**-20**	**-25**
Low MFI	0br	0br	0br	0br	0br	0br	65	69.5	75	69
High MFI	0br	0br	0br	0br	0br	0br	0br	0br	0br	0br

Conclusions

The multipolymers consisting of ethylene, 1-heptene, 3-methylpentene and 4-methylpentene showed a decrease in density with increasing 1-heptene in an equimolar feed. The modulus and tensile strength values were higher at 0.871g/cc (0% 3/4MP1 and 100% 1-heptene) than at 0.887g/cc (25% 3/4MP1 and 75% 1-heptene), although the density was lower. The higher tensile strength and modulus values can be explained by the fact that there are more linear polyethylene chains in this copolymer than in the multipolymer. This is due to the smaller kinetic diameter of the branched C_6, making it easier for these monomers to enter smaller catalyst sites.

It was shown that the density, tensile strength and modulus were not affected by changes in molecular weight, however, the impact strength of the higher molecular weight series was higher than that of the low molecular weight series.

The rheological behavior of the multipolymers was comparable to that of the corresponding copolymers, with similar comonomer content and molecular weight distribution.

The application properties of the high and low molecular weight copolymer series showed expected trends.

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