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Microstructural Polymer Design through Coordinative Polymerization of Semi-Crystalline Poly-1-Olefins

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Summary: The polymer micro structure of poly(butene-1) can be designed by the introduction of comonomers like ethylene (poly(ethylene-co-butene-1)) as well as the dedicated use of special polymerization catalysts. With the use of ethylene as comonomer the change of polymer micro structure also leads to changes in the macroscopic material parameters leading to polymers with a new application profile which are of special interest as hot melt adhesive raw materials. The use of dedicated polymerization catalysts allows the production of new poly(butene-1) hot melt adhesive raw materials without the use of additional comonomers.

Keywords: adhesives; hot melt; poly(butene-1); polymerization catalysts

Introduction

Semi-crystalline poly(1-olefin)s have seen a tremendous career. Starting from an unbeloved byproduct of the isotactic propylene polymerization (so-called. ‘‘atactic’’ or ‘‘amorphous’’ polypropylene/aPP) with hardly any commercial use, these polymers were often used for landfill or directly passed to thermal utilization. The good compatibility of aPP with bitumen and their extremely high capacity for inorganic fillers lead to first commercial applications in road constructions, roofing membranes and carpet backing. Because of the low commercial value of these applications there were only very small budgets for industrial research for a long time and hardly any product development. The industrial break-through started with the implementation of dedicated semi-crystalline poly(1-olefin)s as raw materials for hot melt adhesives. Today a broad variety of semi-crystalline poly(1-olefin)s are used in diverse applications. During the industrial product (re)development big progress in influencing the material properties were made through a specific design of polymer micro structure, leading to unique material property combinations and paving the way to more and more applications like low temperature packaging films, oil additives or directly melt sprayable adhesive systems. Therefore the dedicated design of polymer micro structure is the key success factor to achieve these new material property combinations. The two most effective ways towards a specific polymer micro structure are therefore the dedicated use of comonomers and the use of different polymerization catalysts. Both methods are useful tools to yield polymers with block like structures of different comonomers and/or blocks of different monomer tacticity within one comonomer block (so called ‘‘stereo-block (co)polymers’’)

The Role of Comonomers

It is important to know, that some 1-olefin monomers are particularly suitable to interfere the tacticity of comonomer blocks of other 1-olefins like for example ethylene in propylene segments (blocks)[1] as well as in butene-1 segments.[2] At the same time the high differences in comonomer reactivity can be used to create comomer blocks for example in the copolymerization of ethylene and 1-butene[3,4] whereas espe-

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cially the crystallinity and crystallization ability can be influenced due to the fact that there is no co-crystallization between ethylene and 1-butene comonomer segments.[2] Additionally a crystalline ethylene-phase in poly(ethylene-co-1-butene) requires an ethylene content of >90 mol%,[5] and/or a minimum (ethylene) block length of 20 carbon atoms in the polymer backbone.[1,6]

While the polymerizing of semi crystalline poly(butene-1) at low temperatures is known for a long time[7,8] these polymers are rarely described for the use in hot melt adhesives. The solution polymerization of butene-1 with $TiCl_3{}^*AlCl_3$/Triisobutylaluminia in an autoclave reactor at 115 °C using hydrogen as chain transfer agent yields a low molecular weight semi crystalline poly(butene-1) with quite good material properties in terms of an adhesive raw material (Table 1).

From the ''point of view'' of the material properties the semi crystalline character of the poly(butene-1) polymer is indicated by its relatively low softening point of 121 °C, the relatively high needle penetration of 0,3 mm and of course also the low melting temperature and the low heat of fusion. Compared with data from literature for 100% crystalline poly(butene-1) of phase I crystalline polymer[9] our poly(butene-1) has a crystallinity of only 17% which corresponds well with the isotacticity of the butene-1 triads of only 79%. The low lab shear strength on untreated isotactic poly (propylene) surfaces together with an adhesive failure mechanism shows that there might be a lack of surface wetting which can be changed through a change in polymer micro structure. The introduction of ethylene as a comonomer leads to a dramatically change in material properties of the polymers. While the number of melting peaks remain 3 within an ethylene concentration of 0 to 10 ma%, there is a clear decrease of the melting temperatures which shows the deterioration of the polymer poly(butene-1) microstructure through the ethylene comonomer units. In comparison with the data from Koivumäki[10] for poly(ethylene) using butene-1 as comonomer (obtained on a $TiCl_4{}^*MgCl_2$-System at 60 °C) we see a shift towards lower melting temperatures of about 30 K as expected while the shape of the graph is nearly the same (Figure 1).

This leads to the conclusion that the mechanism of a more statistical disruption of the polymer micro structure during the first 3 to 4 ma% and a more block-like disruption at higher comonomer concentrations is the same even if the different reactivity of the two monomers[11] implies that the introduction of ethylene in a poly(butene-1) polymer chain should be more ''blocky'' while the introduction of butene-1 comonomer units in a poly(ethylene) chain should be more statistical. While the melting temperature is only of secondary practical relevance for a semi

Table 1.
Material properties of a semi crystalline poly(butene-1) homo polymer polymerized.

	Poly(butene-1)
M_w [g/mol]	95 000
Shear viscosity@ 190 °C [mPa*s]	6 300
Softening point (Ring&Ball) [°C]	121
Needle Penetration [*0,1 mm]	3
Glass transition temperature* [°C]	−35
Melt temperature (maximum peak)* [°C]	110
Melt enthalpy* [J/g]	23
Isotactic butene-1 triads [ma%]	79
Open time [s]	45
Lab shear strength [N/mm^2] wood/wood (beech, untreated)	1.70 (adhesive failure)
Lab shear strength [N/mm^2] polypropylene/polypropylene (untreated)	0.55 (adhesive failure)

*DSC, second heating.

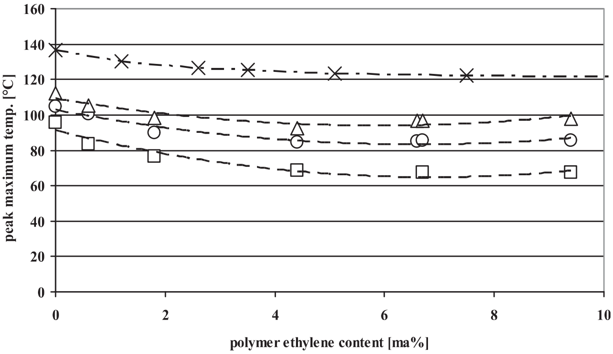

Figure 1.

DSC melting peaks (second heating) of poly(butene-1) (ethylene content = 0 ma%) and poly(ethylene-co-butene-1) solution polymers. Reaction conditions: T = 115 °C; solvent: n-butane; catalyst: 0,09 g $TiCl_3{}^*AlCl_3$ per 1.000 g monomer(s), cocatalyst: 5.50 g triisobutylaluminia per 1 g catalyst. □ = peak 1 ($T_{M,\ low}$), ○ = peak 2 (main peak/maximum peak), △ = peak 3 ($T_{M,\ high}$), × = reference data for poly(ethylene-co-butene-1) polymers with low butene-1 content from Koivumäki.[10]

crystalline adhesive raw material, it is perfectly reproduced through more macroscopic material parameters like e.g. the softening point and also the needle penetration (Figure 2).

The dramatically increase in needle penetration is also an excellent expression of the changing material parameters. While the poly(butene-1) homo polymer is a hard and inflexible material with a relatively low needle penetration of 0,3 mm, the Poly (ethylene-co-butene-1) polymer with about 9,4 ma% of ethylene comonomer units shows a needle penetration of about 2,2 mm which is app. seven times higher, indicating that the poly(ethylene-co-butene-1) is a soft and flexible polymer. The same effect (even if inverse) can be stated with the softening temperature (the temperature at which the polymer starts flowing under load). This material parameter which is of special interest for semi crystalline polymers gives on the one hand a good idea about the maximum temperature of use and on the other hand a good idea about the minimum processing temperature. The

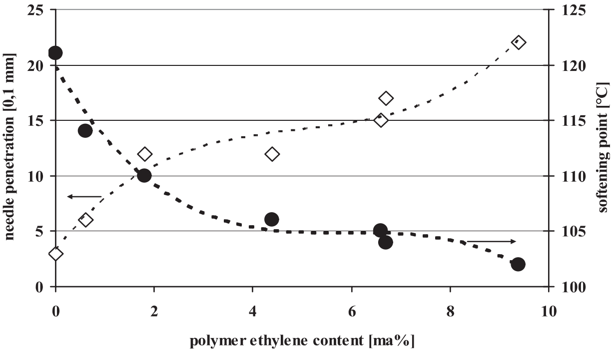

Figure 2.

Softening point (Ring&Ball method, DIN EN 1427) and needle penetration (DIN EN 1426) of poly(butene-1) (ethylene content = 0 ma%) and poly(ethylene-co-butene-1) solution polymers. Reaction conditions: T = 115 °C; solvent: n-butane; catalyst: 0,09 g $TiCl_3{}^*AlCl_3$ per 1.000 g monomer(s), cocatalyst: 5.50 g triisobutylaluminia per 1 g catalyst. ● = Softening point; ◇ = needle penetration.

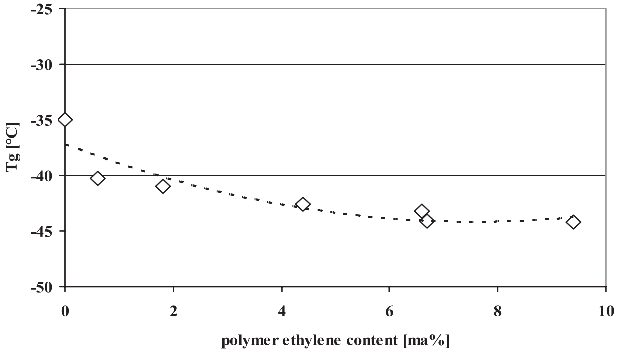

Figure 3.
◇ DSC glass transition temperatures (second heating) of poly(butene-1) (ethylene content = 0 ma%) and poly(ethylene-co-butene-1) solution polymers. Reaction conditions: T = 115°C; solvent: n-butane; catalyst: 0,1 g $TiCl_3{}^*AlCl_3$ per 1.000 g monomer(s), cocatalyst: 5.50 g triisobutylaluminia per 1 g catalyst.

decrease of the softening temperature from pure poly(butene-1) to poly(ethylene-co-butene-1) with an ethylene content of about 9,4 ma% of about 15% indicates a significant loose of crystallinity. A very similar behavior can be stated for the glass transition temperature (DSC, second heating) which decreases with increasing ethylene content within the copolymer (Figure 3).

Through the introduction of a relatively low amount of ethylene comonomer a significant shift of the glass transition temperature from −35 °C to nearly −45 °C is possible which enables this polymer system for low temperature adhesive applications like freezer packaging. This means that the lower temperature stability of the polymers is compensated by the lower working temperature possible. An analysis of the polymer micro structure via ^{13}C-NMR[6,12,13] shows that the shift in the glass transition temperature goes well ahead with a decrease of absolute content of butene-1 triads and an increase of the atactic triads (Figure 4)

As can be clearly seen there is a strong decrease in butene-1 triads of about 35% within the range of 0 to 9,4 ma% of ethylene comonomer content. At the same time

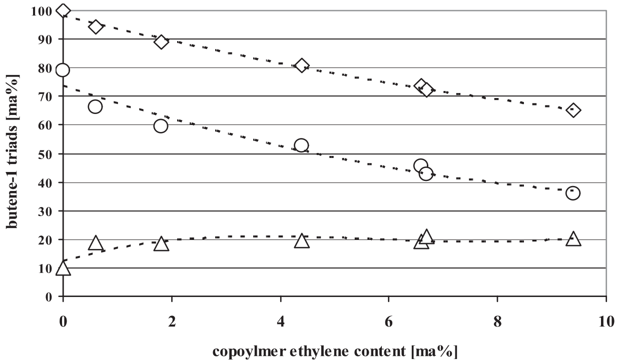

Figure 4.
Absolute content of butene-1 triads (◇), isotactic butene-1 triads (○) and atactic butene-1 triads (△) of poly(butene-1) (ethylene content = 0 ma%) and poly(ethylene-co-butene-1) solution polymers. Reaction conditions: T = 115 °C; solvent: n-butane; catalyst: 0,1 g $TiCl_3{}^*AlCl_3$ per 1.000 g monomer(s), cocatalyst: 5.50 g triisobutylaluminia per 1 g catalyst.

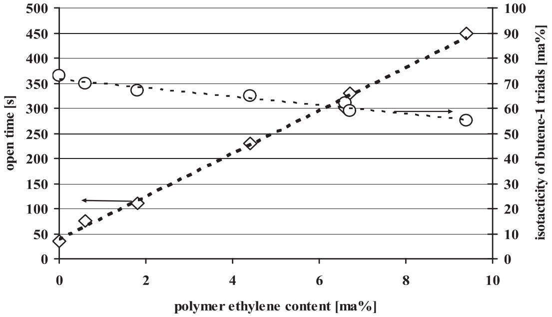

Figure 5.
Open time (◇) and rel. butene-1 triad isotacticity (○) of poly(butene-1) (ethylene content = 0 ma%) and poly(ethylene-co-butene-1) solution polymers. Reaction conditions: T = 115 °C; solvent: n-butane; catalyst: 0,1 g $TiCl_3{}^*AlCl_3$ per 1.000 g monomer(s), cocatalyst: 5.50 g triisobutylaluminia per 1 g catalyst.

there is a disproportionate decrease of isotactic triads of about minus 44% while the increase in atactic triads is about 100%. It is also clear that the increase in atactic butene-1 triads is more or less done within the addition of the first 2 ma% of ethylene comonomer which correlates quite well with the graph shape of the melting peaks (Figure 1), the needle penetration and the softening point (Figure 2), leading to the conclusion that the biggest deterioration of the buten-1 comonomer structure is done through a statistical integration of the ethylene comonomer units in the polymer chains which is than displaced by a more block like monomer integration with further rising ethylene content. Of special interest for non reactive hot melt adhesive raw materials is the correlation between the content of isotactic butene-1 triads and the "open time" (time within a contact of the surface of the molten polymer (starting temperature: 180 °C) and another material (e.g. paper) is reversible) which is shown in Figure 5.

The dramatically increase in open time from 45 s for poly(butene-1) homo polymer to 450 s again shows the deterioration of the crystalline structure of the copolymers which is closely correlated to the content of isotactic butene-1 triads within the copolymer (as well as to the overall content of triads (Figure 4)) which decreases app. 22%. After all there is of course also an influence on the cohesive and adhesive properties of the polymers (Figure 6).

The increase in lab shear strength indicates a change in wetability of the

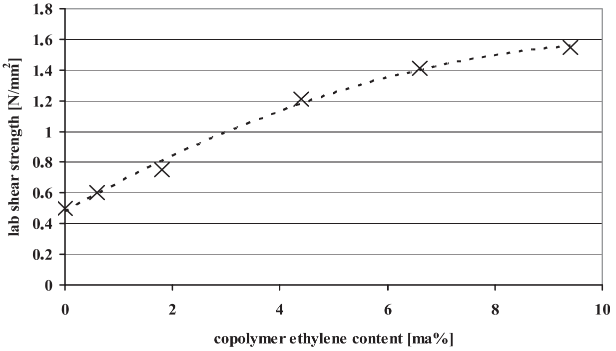

Figure 6.
Lab shear strength of poly(butene-1) (ethylene content = 0 ma%) and poly(ethylene-co-butene-1) solution polymers on untreated poly(propylene).

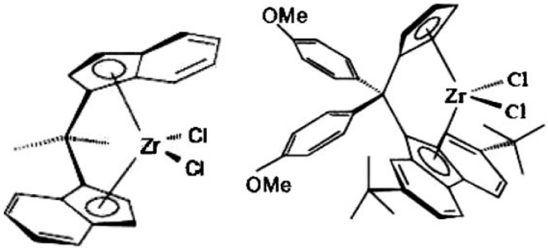

Figure 7.
Homogeneous metallocene single site catalysts used for the polymerization of butene-1.

poly(propylene) surface by the poly(ethylene-co-butene-1) polymers. The biggest rise of lab shear strength can be observed between 2 and 4 ma% of ethylene comonomer content. So a relatively small change within the (co)polymer composition leads to a significant change of polymer micro structure and to a dramatical change of the (adhesive) material properties, which makes it possible to adjust the macroscopic material properties to very different applications. A different approach to gain different poly(1-olefin) micro structures from the same polymer composition is the use of different catalyst systems.

The Role of Polymerization Catalysts

The use of dedicated polymerization catalysts is a very powerful tool to gain special polymer micro structures. Especially the use of homogeneous single site polymerization catalysts e.g. metallocene catalysts (Figure 7) allow a specific block and tacticity design through an appropriate adaptation of the ligand structure.[14] On the other hand within the classical Ziegler-Natta heterogeneous (multi site) titanium based catalysts foremost there is the question of support and/or the use of donor additives.

Even without any comonomer the material properties of poly(butene-1) can be adapted within a very wide range. While the polymerization conditions have been as similar as possible ($T_R = 70\,°C$, 1000 g butene-1 in 1000 g n-butane, cocatalyst for heterogeneous Ziegler catalysts: 0,4 g of triisobutylaluminia, cocatalyst for homogeneous metallocene catalysts: 3,0 g of Al within a 7 ma% methylaluminoxane (MAO) solution in toluene, used amount of heterogeneous Ziegler catalysts: 0,1 g for the unsupported catalyst and 0,05 g for the supported one, used amount of homogeneous metallocene catalysts: 0,004 g, chain transfer agent: hydrogen) the resulting polymers show totally different polymer micro structure and therefore also totally different macroscopic material properties, especially adhesive properties (Table 2).

There is a clear difference in polymer micro structure of the four poly(butene-1) homo polymers. The isotactic fraction of the polymer EP 2 received from the $MgCl_2$-supported heterogeneous (multi site) catalyst is much lower than the isotactic fraction of the polymer EP 1 derived from the unsupported heterogeneous catalyst, probably due to the absence of stereo regulating additives (donors) in the system. At the same time the atactic fraction doubles its size.

By contrast the first homogeneous metallocene (single site) catalyst, a bisindenyl zirconocene leads to a polymer (EP 3) with much more isotactic structure which shows no glass transition temperature at all, indicating a highly crystalline polymer, while the second homogeneous zirconocene catalyst leads to a polymer (EP 4) with higher syndiotactic triad content due to its asymmetric ligand structure. The more syndiotactic poly(butene-1) shows no crystallinity at all and is a highly viscous liquid at room temperature. The influence of the

Table 2.
Material properties of 4 poly(butene-1) homo polymers from different polymerization catalysts. Cat 1: $TiCl_3{}^*AlCl_3$, Cat 2: $TiCl_4$ on $MgCl_2$, Cat 3: rac-$(CH_3)_2C(Ind)_2ZrCl_2$, Cat 4: p-$(MeOPh)_2C$(2,7-ditertbutylFlu)(Cp)$ZrCl_2$.

Sample		Unit	EP 1	EP 2	EP 3	EP 4
Polymerization catalyst		–	Cat 1	Cat 2	Cat 3	Cat 4
Triad tacticity		[ma%]				
Isotactic			79	63	94	36
Syndiotactic			11	16	1	40
Atactic			10	21	5	24
Shear viscosity η190 °C		[mPa*s]	6 500	5 500	5 200	6 800
$T_{Soft.\ (R\&B)}$		[°C]	121	108	113	< 20
PEN		[0,1 mm]	3	18	1	> 50
T_M	1st heating	[°C]	112	88, 103	111	none
	2^{nd} heating	[°C]	79, 96, 105, 112	88, 103	87	none
ΔH_M	1st heating	[J/g]	49.1	14.7	68.9	0 (not detectable)
	2^{nd} heating	[J/g]	22.5	13.3	26.4	0 (not detectable)
T_g		[°C]	−35	−36	not detectable	−26
Lab shear strength wood (beech, untreated)		[N/mm^2]	0.6	0.1	not measurable	0.1
Lab shear strength poly(propylene) (untreated)		[N/mm^2]	0.8	1.24	0.2	1.21

polymer micro structure on the macroscopic material properties are obvious: Softening point and needle penetration of the more isotactic poly(butene-1) polymers are differing within a broad range. Surprisingly the polymer with the highest isotactic fraction has not the highest softening point, even if the very low needle penetration indicates a high crystallinity. The reason for this can be found in the highly crystalline structure of the polymer which is indicated by the melt temperature (1^{st} heating) which is very similar to the softening point. The three isotactic poly(butene-1) polymers show big differences in their lab shear strength towards untreated isotactic poly (propylene) indicating that the polymer with the lowest isotacticity has the highest lab shear strength which is very similar to the lab shear strength of the more syndiotactic poly(butene-1) which also shows a very low isotactic content. The lab shear strength on untreated beech is poor for all four polymers. The influence of the catalyst leads to poly(butene-1) homo polymers which show adhesive properties in the same range than the poly(ethylene-co-butene-1) copolymers polymerized with only one heterogeneous Ziegler catalyst (Figure 6).

Conclusion

It has been shown that through the dedicated use of comonomers and polymerization catalysts it is possible to influence the polymer micro structure and therefore reach an advanced material property design which enables us to create hot melt adhesive raw materials which fit well to totally different applications.

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