

**INFLUENCE OF POLYMER STRUCTURE ON THE
CONFORMATIONS OF POLYOLEFIN MELTS AND
THEIR BLENDS: MOLECULAR DYNAMICS
SIMULATION STUDY**

BY

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THESIS ABSTRACT(ENGLISH)

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The effect of long chain branching (LCB) on the structure of m-LLDPE melts is investigated by using molecular dynamics simulation. The parameters like radius of gyration, pair correlation function; dihedral distribution and oriental correlation function were studied. In the MD simulation study, m-LLDPE with different short chain branches (SCB) like 0, 20, 60 branches/1000 carbons and with LCB of length ranging from 10 to 40 carbons are simulated in the NVT ensemble at 425°K with melt density of 0.779 g/cm³. The results of MD simulation study suggests that m-LLDPE with 3 LCB's of different lengths and with different SCB's has the highest value of radius of gyration as compared to m-LLDPE with 1 LCB and 5 LCB's. In addition the effect of tacticity on the miscibility of the blends of low density polyethylene (LDPE) and polypropylene (PP) with different tacticities are investigated by molecular dynamics simulation. The branch content of LDPE varied from 10 branches per 1000 carbons to 20 branches per 1000 carbons. Different compositions of the two polymers are simulated in the NVT ensemble at 500 °K at average experimental densities of the two polymers. Tacticity was found to influence the miscibility with LDPE, as the tacticity was decreased from isotactic to atactic there was increase in the value of radius of gyration making the blend more miscible. In addition it was found that as the branch content of LDPE is increased from 10 branches to 20 branches per 1000 carbons the blends became miscible in all composition ranges of PP. The parameters like radius of gyration, pair correlation function; dihedral distribution and oriental correlation functions were analyzed to study the effect of molecular structure on miscibility in blends.

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THESIS ABSTRACT (ARABIC)

ملخص الرسالة

الإسم : محمد عبد الكريم

العنوان : تأثير بنية البوليمير على تشاكيل مصهور البولي أوليفين و خلانطه : دراسة محاكاة باستخدام

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نوقش تأثير التفرع طويل السلسلة على بنية مصهور LLDPE - m دراسة محاكاة باستخدام ميكانيك الكم , حيث تم دراسة عدة متغيرات : قطر الحلقة , معامل الارتباط المزدوج , توزع ثنائي السطوح و معامل لإرنباط التشكيلي. تمت محاكاة أنواع مختلفة من LLDPE - m ذات فروع قصيرة السلسلة تتراوح بين 0-20 - 60 فرع \ 1000 ذرة كربون و فروع طويلة السلسلة تتراوح بين 10 - 40 ذرة كربون باستخدام ميكانيك الكم في مجموعة NVT و عند درجة حرارة 425K و لزوجة مصهور 0.779 غ/سم³ . أظهرت نتائج دراسة المحاكاة باستخدام ميكانيك الكم أن LLDPE - m ذو ثلاثة فروع طويلة السلسلة مختلفة الأطوال و فروع قصيرة السلسلة مختلفة الأطوال يملك أعلى قيمة من قطر الحلقة مقارنة بمثيلاتها ذات فرع واحد طويل السلسلة أو خمسة فروع طويلة السلسلة. أيضاً تم استخدام ميكانيك الكم لدراسة تأثير التوضع الفراغي لهذه الفروع على قابلية المزج لخلانط من البولي إيتيلين (LDPE) منخفض الكثافة و البولي بروبيلين (PP) و التي تتميز بتوضعات فراغية مختلفة, حيث استخدمت عينات من LDPE تحتوي فروعاً تتراوح بين 10 - 20 فرع \ 1000 ذرة كربون, ودرست مزائج مختلفة التركيب من المادتان البوليميريتان دراسة محاكاة في مجموعة NVT عند درجة الحرارة 500K و عند متوسط الكثافات التجريبية لكلا البوليميرين. وُجد أن التوضع الفراغي النسبي للفروع يؤثر على قابلية المزج ب LDPE , فكلما إتجهنا من الإنتظام إلى العشوائية كلما زادت قيمة قطر الحلقة جاعلاً الخلانط أكثر قابلية للمزج . كما وجد أنه عندما زاد محتوى LDPE من الفروع من 10 إلى 20 فرع لكل 1000 ذرة كربون أصبحت الخلانط قابلة للإمتزاج في كل مجال النسب الممكنة من (PP). تم تحليل متغيرات مختلفة : قطر الحلقة , معامل الارتباط المزدوج, توزع ثنائي السطوح و معامل الارتباط التشكيلي, لدراسة تأثير البنية الجزيئية على قابلية المزج للخلانط

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CHAPTER 1

INTRODUCTION

Polyolefins polymerized using metallocene-based technologies offer important performance attributes that meet a wide range of applications. The ability to design new polyolefin variants with enhanced properties and processing attributes has undergone much advancement over what was available a decade ago. The control of Long chain branching distribution and molecular weight distribution within the context of "designer" polymers directed towards specific applications is very remarkable. The ability to introduce LCB into what would otherwise be linear polyethylene has opened up a broader range of processing possibilities.

Metallocene catalysts make it possible to introduce low and well-controlled levels of long chain branching in which molecular weight distribution (MWD) is relatively narrow and quite reproducible. Systematic study of the relationships between molecular structure and rheological behavior of polyolefins has been seriously limited in the past by the lack of samples with controlled and well characterized distributions of molecular weight and long chain branching (LCB). The crystallizability is affected by molecular weight, concentration of branches, and their distribution along the copolymer backbone. To well understand the crystallization behavior of the branched molecules, more homogeneous fractions of the copolymer are needed.

Polyethylene is the most widely used polymer nowadays. Nevertheless, it is distinguished by some peculiarities making it a unique polymer. It has an extremely high crystallization rate, arising from its high chain flexibility, mostly from its perfect chain structure. For this reason, PE is not commonly available in amorphous state, and

therefore many characteristics of amorphous PE are derived via extrapolation of semi crystalline samples. PE is produced in different forms, each of which has different properties resulting from variations in structure. Low-density polyethylene (LDPE) contains short-chain branches as well as long chain branches with density in the range of 0.910 to 0.925 g/cm (Cho et al., 1998). The second type is linear low density polyethylene (LLDPE), which is produced by copolymerizing ethylene with alpha-olefins such as 1-butene, 1-hexene or 1-octene and has a wide range of branch contents depending on catalyst and concentration of added comonomer. The density of conventional LLDPE is in the range 0.900 to 0.930 g/cm. The third type high density polyethylene (HDPE) molecule is mainly linear and it may contain very little branching with density in the range 0.940 to 0.965. It has long been recognized that one of the major differences between LLDPE prepared by metallocenes catalysts is the distribution of the comonomers along the backbone of the molecule (Karbashewski et.al. 1992).

In particular, LLDPE prepared by Ziegler-Natta catalysts has more uneven comonomer distribution. However, LLDPE synthesized by metallocene catalyst is claimed to possess relatively uniform distribution. It is generally believed that such differences in comonomer distribution is mainly attributed to the difference in the number of active sites available in the two catalysts and manifests itself in the rheology and mechanical properties of the polymers as well as their melt miscibility.

Metallocene linear low density polyethylene (m-LLDPE) is available in different grades and finds use in different applications either as pure resins or blended with other polymers. The main distinguishing feature of all these commercial grades is the comonomer type, branch content and composition distribution. The details of branching strongly influence the processing and the properties of final product. Also the details of

branching affect molecular conformations and dimensions, which again affect solution and melt properties of LLDPE. In addition, molecular structure influences the miscibility of PEs as acknowledged in both theoretical (Fredrickson et al., 1994; Fredrickson and Lui, 1995) and experimental research (Hussein and Williams, 2001; Tanem and Stori, 2001; Lee and Denn 2000; Hill and Barham, 1997).

Researchers have demonstrated unanimously that the average number of branches per thousand backbone carbons of LLDPE is the major factor that controls miscibility (Hill et al., 1993; Alamo et al 1997; Choi., 2000). It was also predicted by the small angle neutron scattering (SANS) and molecular dynamics simulations that the cut off value for this blend is around 40 branches/1000C carbons (Alamo et al.1997). But the authors (Alamo et al., 1997) made no comments on the miscibility of such blends with branch contents of LLDPE intermediate between 40 and 80. On the other hand, using transmission electron microscopy (TEM) different researchers (Hill et al., 1993; Hill and Barham, 1994) have shown that the threshold value for the same blends is about 60. Thus the question is not simply whether linear and branched molecules are miscible, because it is evident that there will be miscibility when the branch level is very low and immiscibility when it is high (Hill et al., 1993; Hill and Barham, 1994 and Alamo et al., 1997). Rather the question is about the level of branches that is required to phase separate the system. Recently, Fan et al., (2000) and Choi (2000) used MD simulation to calculate Flory-Huggins interaction parameter, and infer miscibility of LLDPE blends.

The presence of even a fairly small number of LCBs (1 to 4 per 10,000 carbon atoms) considerably increases shear thinning, processability, and strain hardening, while keeping the molecular weight distribution (MWD) narrow, with polydispersity indices typically between 2.0 to 2.5. Consequently, polyolefins made with this family of catalysts

combine the excellent mechanical properties of narrow-MWD polymers with the good processability of broad-MWD resins. The mechanism of LCB formation with these catalysts is essentially terminal branching, i.e. macromonomers formed during polymerization are incorporated into the growing polymer chains. Because of the mechanism of LCB formation, the polymers made with these catalysts have a complex LCB architecture composed of linear and comb-branched and tree-branched chains.

Metallocenes are unquestionably the most important development in the area of olefin polymerization since the discovery of Ziegler-Natta catalysts in the early fifties because they permit the synthesis of polyolefins with uniform molecular properties. Metallocene catalysts can produce polyolefins with narrow molecular weight distributions (MWD) with greater dimensional stability, higher impact resistance, greater toughness at low temperatures, and higher resistance to environmental stress cracking. Unfortunately, these polyolefins are also difficult to process. This has been considered to be one of the limiting factors to a wider application of metallocene-made polyolefins. Polyolefins with broader MWD and better processability can be produced with either two or more metallocenes in the same reactor or in a series of reactors but this approach may lead to polymers with inferior mechanical properties.

As mentioned before various PE's exhibit different characteristics and properties. Therefore different types of polyethylenes are often blended together with different polypropylenes to meet various kinds of requirements of processing, mechanical properties and final product properties. The polyethylene/polypropylene melt processing industry is concerned about the miscibility of the components because miscibility affects the melt rheology. This in turn is expected to affect the solid-state morphology and final product properties.

Polyethylene and polypropylene blends are the focus of increasing attention because such polymers are the thermoplastics of highest consumption, given their special and varied physical and mechanical properties. Furthermore, polyolefin blends attract additional interest because of the possibility of recycling the plastic wastes, thus avoiding the expensive and difficult process of component separation. Galeski, A.; Pracella, M.; Martuscelli et al. [30] studied the thermal and mechanical properties of i-PP and PE blends and concluded that i-PP crystallization is not influenced by the presence of PE

Blends of PP and metallocene VLDPE and ULDPE have attracted broad attention because of their performance importance and economical value. Several researchers have investigated the impact properties of PP blended with ULDPEs. Wu et al.[4] found that ULDPEs were superb impact modifiers for PP at a subambient temperature ULDPE and found that the lower the density of ULDPE, the better was the performance of the blends. Because of their low crystallinity, metallocene ULDPE and VLDPE offer good low-temperature properties such as toughness. They serve primarily as modifiers for brittle materials, particularly as impact modifiers for polypropylene (PP). The addition of ULDPE to PP improves impact strength, flexibility, tear strength, and low-temperature heat-sealing characteristics.

Polypropylene is synthesized in three different tacticities, atactic (a-PP), isotactic (i-PP), and syndiotactic (s-PP). The microstructure of PP is a critical determinant of the polymer physical properties. a-PP is totally amorphous with a glass transition temperature (T_g) of approximately 255K, and iPP and s-PP are semicrystalline at room temperatures. The melting points of iPP and sPP are strongly affected by the crystallizability of the chains, which depends in turn on defects in their stereochemical structure.

The blends of polyethylene and polypropylene are commercially very important because of their high impact strength and low temperature toughness, furthermore, these polyolefins are the major constituents of plastic wastes and scraps and their recycling as blends is of considerable value. Addition of polyethylene into polypropylene increases the impact strength of polypropylene and addition of polypropylene into polyethylene improves the environmental stress crack resistance of polyethylene. Hence these blends are technologically very important. The combination of polyethylene and polypropylene is particularly important because it is very difficult to separate these polymers from each other in waste recovery operations. The difficulty arises due to the structural similarity of these polymers.