Implications of LDPE Branching and Mw on Thermal and Mechanical Properties of PP/LDPE Blends

*Mohammed A. Suleiman, Ibnelwaleed A. Hussein**

Summary: The influences of short chain branching (SCB) and molecular (M_w) weight of low density polyethylene (LDPE) on the solid state properties of polypropylene (PP)-LDPE blends were investigated by mechanical and thermal techniques. DSC analysis of all blends exhibit a double melting peak at all compositions studied thus suggesting that both PP and LDPE crystals exist separately in the solid state. It was found that the SCB and Mw of LDPE influenced the modulus and ultimate tensile strength of the blends. However, elongation at break seems to be independent of the molecular characteristics of the pure homopolymer especially at PP blend composition greater than 50%. LDPE with high SCB showed broader melting peaks. Addition of a small amount of a low Mw LDPE (10%) resulted in a higher elongation at break than a high Mw LDPE. There is likely a correlation between the presence of a new peak in the thermograms of PP-rich blends and the observed poor elongation at break.

Keywords: blends; low density polyethylene; molecular weight; polypropylene; short chain branching

Introduction

Polymer blending is an interesting economic alternative to synthesizing new products tailored towards a specific processing and performance requirements. Improved material properties in plastics are often achieved by blending two or more polymers with different molecular characteristics.[1–3] Even though blends of polypropylene (PP) and polyethylene (PE) are common especially in waste recycling due to large volume consumption of polyolefins,[4,5] PE has also been used to modify the physical and mechanical properties of PP as a result of the poor impact behavior of PP.[6]

PE is commercially available in different grades, such as high density polyethylene (HDPE), LDPE, linear low density polyethylene (LLDPE), ultra high molecular weight polyethylene (UHMWPE), and very low density polyethylene (VLDPE). These PE's are widely used to form blends with PP and the melt and solid state properties of the resulting blends analyzed. Films prepared from blends of isotactic-PP (i-PP) and LDPE has been reported to be more convenient for various applications than those prepared from the parent homopolymer.[7] However, it is important to note that improvements in the properties of a polymer blend in the melt or solid state is determined by the compatibility of the blend.

Various authors have reported that blends of PP with LDPE are not compatible (immiscible) due to the low interfacial adhesion between the phases which leads to phase separation. This phase separation is usually dictated by molecular parameters such as the molecular weight distribution (MWD), average molecular weight (Mw), branch content (BC) and composition of the blend.[8–14]

Livanova et al.[15] investigated the properties and phase structures of PP/LDPE blends in isotropic and oriented states by

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
E-mail: ihussein@kfupm.edu.sa

WILEY InterScience®

the methods of differential scanning calori-metry (DSC) and polarization infra red spectroscopy. It was found that the pre-sence of LDPE in the blend increases the degree of PP orientation and the mechan-ical strength of the blend samples. Also, Albano et al.[16] investigated the morphol-ogy and microstructure of pure PP, pure LDPE and PP-LDPE blends by electron microscopy techniques. It was observed that addition of small amounts of LDPE inhi-bited the growth of PP spherulites. As the concentration of LDPE increased, defor-mation of PP spherulites occurred along with a decrease in size. It was concluded that there was poor miscibility and adhe-sion of component microstructures in the blends.

Dhoble et al.[17] recently investigated the mechanical properties of PP-LDPE blends with novel morphologies produced with a continuous chaotic advection blen-der. Chaotic advection involves the recur-sive stretching and folding of melt domains in response to shear flows occurring in conventional compound equipment. It was observed that the droplet morphology that is typically obtained with conventional blend-ing equipment provided tensile strength, tensile modulus, and impact toughness that were mostly smaller than those produced by chaotic advection. The tensile and impact behavior of PP/LDPE blends pro-duced via injection molding carried out under various injection temperatures was recently studied by Strapasson et al.[4]. It was found that the blends yielded stress-strain curves very dependent on their composition, especially for the elongation at break and necking was reported. An irregular behavior for the 50/50 w/w blend was reported. Nevertheless, a linear varia-tion of the yield strength and elastic modulus with the blend ratio was observed. They concluded that the mechanical beha-vior of the blend was very dependent on processing temperature.

Petronyuk et al.[18] investigated the local elastic properties and microstructural fea-tures of LDPE/i-PP blends using acoustic microscopy, DSC and IR spectroscopy. The focused ultrasonic beam of an acoustic microscope was used to measure elastic wave velocities, bulk and shear elastic moduli and Poisson ratio. The mechanical proper-ties of immiscible LDPE/PP blends were found to be non-additive and maximum moduli values were achieved with a small addition of LDPE to PP. DSC curves show no significant deviations in melting tem-perature and crystallinity degree for differ-ent components of PP and LDPE phases.

In general, no study to our knowledge, has investigated how the individual poly-mer characteristics affect the mechanical and thermal properties of these blends. Thus, the aim of this study is to investigate the influence of short chain branching (SCB) and molecular weight (Mw) of LDPE on the solid state properties of PP/LDPE blends.

Experimental Part

Materials and Blend Preparation

Three commercial samples of LDPE and one PP were used in this study. The LDPE were designated as LDPE1, LDPE2 and LDPE3. LDPE1 and LDPE2 were obtained from ExxonMobil while LDPE3 and PP were from Nova chemicals and SABIC, respectively. The characterization data for the resins are presented in Table 1. The density and melt flow index (MFI) for all resins were provided by the manufacturers. The number average and weight average molecular weights of the resins were determined by gel permeation chromato-graphy (GPC) in a WATERS GPC2000 instrument. Details of GPC and NMR

Table 1.
Characterization of resins.

Resin	Density (g/cm^3)	M_w*	MWD	BC**
PP	0.9000	211	5.86	–
LDPE1	0.9230	100	4.14	8.3
LDPE2	0.9230	84	4.16	9
LDPE3	0.9190	107	6.50	22

*kg/mol;
**CH$_3$/1000 C.

characterization are given elsewhere.[11] ^{13}C NMR was used for the determination of SCB. LDPE1 and LDPE3 blends were chosen for the investigation of effect of SCB. The effect of Mw of LDPE on the mechanical and thermal properties of PP/LDPE blends was investigated by comparing PP/LDPE1 and PP/LDPE2 blends.

The blends were prepared in a Haake PolyDrive melt blender at appropriate compositions to cover the entire composition range (10, 20, 30, 50, 70, 90 wt% LDPE). The melt blender is designed for use as a computer-controlled torque rheometer. The pure resins and blends were conditioned in the melt blender at 50 rpm and 200 °C in the presence of 3000 ppm of anti-oxidant (AO) for 10 minutes. The AO is a 50/50 blend of Irganox 1010 (the primary AO) and the phosphorous-containing compound Irgafos 168 (the secondary AO). It is added in order to prevent thermomechanical degradation of the samples during blending.[19]

In all cases, samples obtained from the blender were subjected to a controlled thermomechanical history in a Carver press in order to prepare flat circular discs (25 mm diameter, 2 mm thick) for insertion between the rheometer platens. Flat sheets (2 mm thick) for blends and pure resins were prepared in the Carver Press.[20] ATS FAAR Pneumatic Puncher was used to cut samples based on ASTM D638 (type V) for mechanical testing.

Thermal Analysis

The thermal behavior of the pure resins and blends was determined using a TA Q1000 DSC. Samples of 6–8 mg were weighed and sealed in aluminum non-hermetic pans. Since the samples were already subjected to a defined thermal history in the Carver press, only a heat–cool regime was adopted. Melting and crystallization temperature measurements were performed by heating samples from room temperature to 200 °C, isothermal at 200 °C for 3 minutes then cool to 35 °C. A heating and cooling rate of 10 °C/min was applied and nitrogen was used as the purge gas at a flow rate of 50 ml/min.

Mechanical Testing

The tensile tests were performed on an Instron 5567 tensile testing machine at room temperature. The gauge length was kept at 25 mm with a crosshead speed of 10 mm/min. All samples ruptured within 0.5–5 minutes of testing time and mechanical parameters were reported based on an average of five samples.

Results and Discussion

Influence of Branch Content

The DSC melting endotherms for the blends of PP/LDPE1 and PP/LDPE3 (and their pure resins) are shown in Figures 1 and 2, respectively. Both blend systems show similar trends, with two melting peaks corresponding to the constituents of the blends. Li et al.[1] reported similar observations. The pure resins and LDPE in the respective blend system show a single (sharp) melting peak at all compositions. However, the 50%, 70%, 80% and 90% PP/LDPE3 displayed a sharp peak with a shoulder. Even though similar results were observed in the PP/LDPE1 at the same compositions, the peaks were relatively broader in the latter. This shoulder suggests the formation of co-crystals of PP/LDPE. With the exception of the 50% PP/LDPE1 blend, the melting temperature (T_m) of LDPE was observed to decrease slightly in both blend
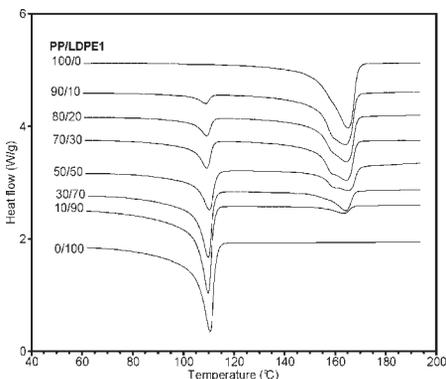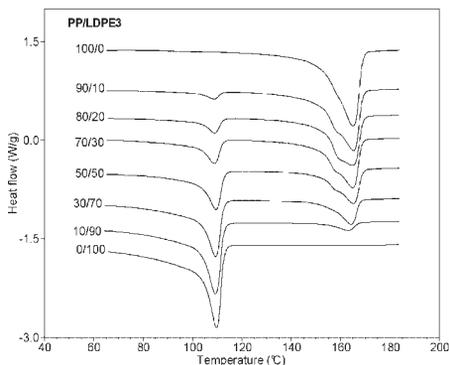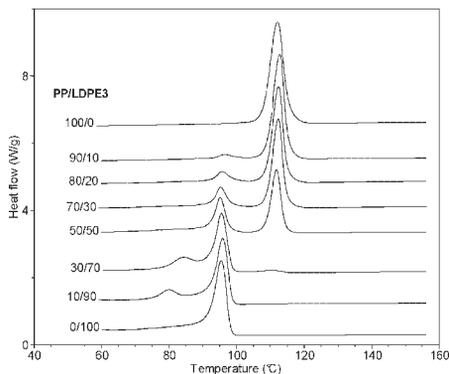

Figure 1.
DSC heating scans for PP/LDPE1 blends.

Figure 2.
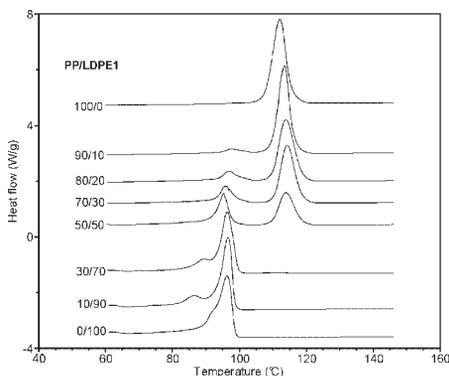DSC heating scans for PP/LDPE3 blends.

Figure 4.
DSC cooling scans for PP/LDPE3 blends.

systems as the amount of PP increases. Similarly, a slight decrease in the T_m of PP was observed in both blend systems as the LDPE content increased. In order to obtain further information on the thermal properties of the blends, a cooling scan was conducted.

Figures 3 and 4 show the crystallization thermograms of PP/LDPE1 and PP/LDPE3, respectively. Again, both blend systems displayed similar profiles. The pure resins show a single sharp peak with LDPE1 exhibiting a very weak shoulder. Also, all blends showed double peaks. This suggests the presence of two crystal populations in the solid state. Blends of PP/LDPE1 and PP/LDPE3 containing 50%,

70%, 80% and 90% PP showed crystallization peaks at 113 °C and 112 °C, respectively. For 30% PP composition, this crystallization peak was very weak in the PP/LDPE3 system and it disappeared in the 10% PP blend composition of both blend systems. At 10% and 30% PP composition, another peak is observed in both blend system at crystallization temperature below that of the pure LDPE.

However, these peaks are clearly distinct in the high BC pair (PP/LDPE3) compared to the low BC pair (PP/LDPE1) and shifted by about 3 °C. Thus this peak can be attributed to the presence of branching since it is absent in the PP-rich region where LDPE is the minor component. Although, Dong et al.[20] had attributed this observation to the presence of a different crystallization process in the PP since this peak was absent in the pure LDPE. Nevertheless, further work is needed to investigate this peak. Hence, thermal analysis suggests the presence of multiple crystal populations in both blend systems and the appearance of such new peaks suggest a careful investigation of the crystal type and crystallization kinetics of PP/LDPE blends especially for LDPE with high BC (low density).

The modulus, ultimate tensile strength, and elongation at break for the pure resins and blends of both systems were extracted from their respective stress-strain curves
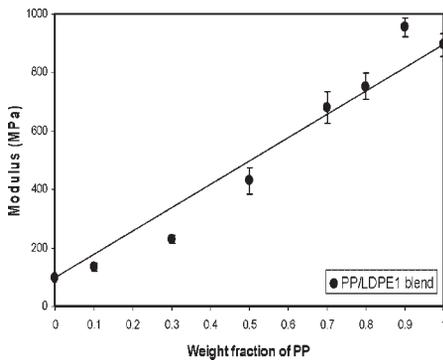

Figure 3.
DSC cooling scans for PP/LDPE1 blends.

Figure 5.
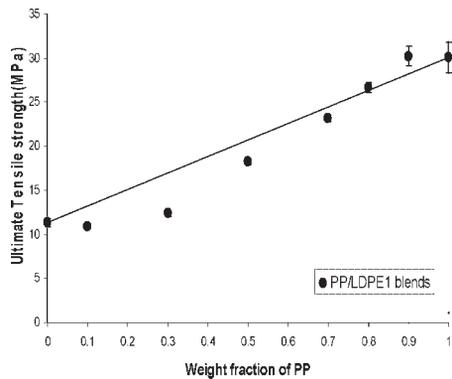Tensile modulus as a function of PP composition for PP/LDPE1 blends.

Figure 7.
Ultimate tensile strength as a function of composition for PP/LDPE1 blends.

and plotted as a function of PP composition as shown in Figures 5–9.

The modulus of PP is 894.13 MPa whereas that of LDPE1 and LDPE3 is 96.70 MPa and 80.35 MPa, respectively. The low value for LDPE3 as compared to LDPE1 is expected because the thermal analysis shows that it has a lower crystallinity which can be attributed to the high BC of LDPE3. Both blend systems generally have moduli close to the linear rule of mixture but the PP-rich blends in both systems with the exception of 90% PP/LDPE1; show a modulus very close to that predicted by additivity. However, the LDPE-rich blends of

both systems exhibited a NDB from the additivity rule. This shows that there is some interaction between the constituents of the blends as depicted in the cooling thermograms where LDPE1 & LDPE3 cooling peak is distinctly visible. This could suggest some co- crystallization. At 10% and 90% PP composition, it was observed that blends of PP/LDPE1 (low BC) exhibited a much higher modulus than blends of PP/LDPE3 (high BC) of the same PP composition. This implies that the addition of a less elastic component (LDPE1) to a more elastic component (PP) results in an increase in the elasticity of the blend. This
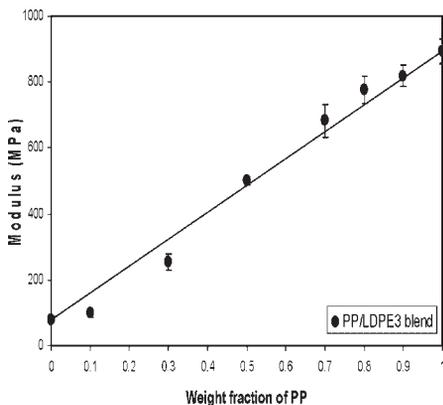

Figure 6.
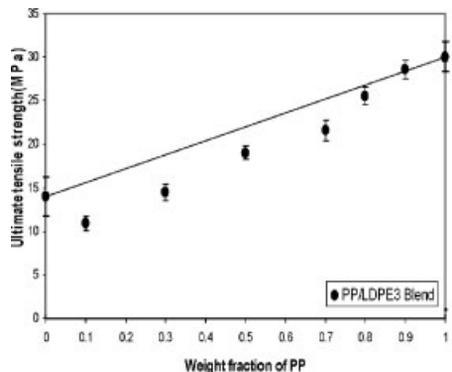Tensile modulus as a function of PP composition for PP/LDPE3 blends.

Figure 8.
Ultimate tensile strength as a function of composition for PP/LDPE3 blends.

increase in elasticity was reported by many researchers[11,22–26] for the melt state as well as the solid state.[16,18]

The ultimate tensile strength for the different blends is given in Figures 7 and 8. Again, the blends follow the same pattern as the modulus data, exhibiting a NDB for the PP/LDPE1 and PP/LDPE3 blends at PP composition of 10% to 70% and 10% to 80%, respectively. It is therefore indicative from the modulus and ultimate tensile strength of both blend systems that improved material property is obtained where LDPE is the minor phase, particularly a 10% LDPE composition. However, a low BC LDPE gives a better modulus at this LDPE composition.

Figure 9 shows the elongation at break for the two blend systems. It was observed that both blend systems follow similar trend. The increase in the content of the stiff PP in the blends decreased the elongation at break. For $\phi_{PP} \geq 0.5$, the elongation at break remained constant at ~9% which is the same as the elongation at break for pure PP. This suggests that for $\phi_{PP} \geq 0.5$ PP is the major phase and LDPE is likely to be sandwiched between PP layers. Similar observations were reported by Strapasson et al.[4]. It is interesting to note that the poor elongation at break for PP-rich blends is observed in the same composition range where the DSC data showed the presence
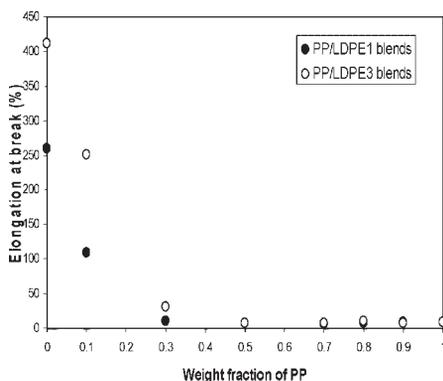
of a shoulder in PP melting peaks suggested to be due to co-crystals of PP/LDPE. Thus, the important question is whether these new peaks are responsible for the brittle behavior of PP-rich blends?

These co-crystals may be responsible for the poor adhesion between PP and LDPE phases as suggested earlier.[16] These co-crystals may act as buffer zone between PP and LDPE rich crystals. If that is the case, then it could be suggested that further research that can increase this buffer zone (may be through annealing) can lead to a better results in elongation at break.

Influence of Mw

The tensile modulus as a function of composition for the PP/LDPE2 blends is shown in Figure 10. The modulus of LDPE2 is 89.11 MPa, which is lower than that of LDPE1. This was expected, due to the difference in Mw. It can be seen from the Figure that blends with 70% and 90% PP composition show linear variation with composition. Similar observation was seen in the PP/LDPE2 blends but at PP composition of 70% and 80%.

An interesting observation in the LDPE-rich region of both blend systems was that addition of 30% or 50% PP to LDPE2 (low Mw: 84 kg/mol) resulted in a higher modulus in comparison with LDPE1 (high Mw: 100 kg/mol). This could be useful in improving the mechanical property of
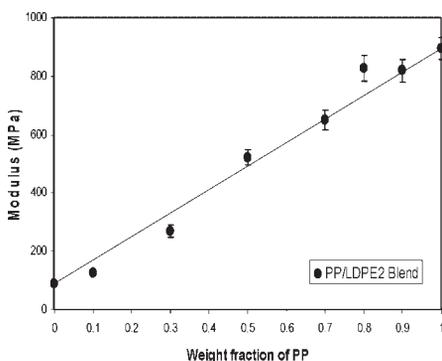
Figure 9.
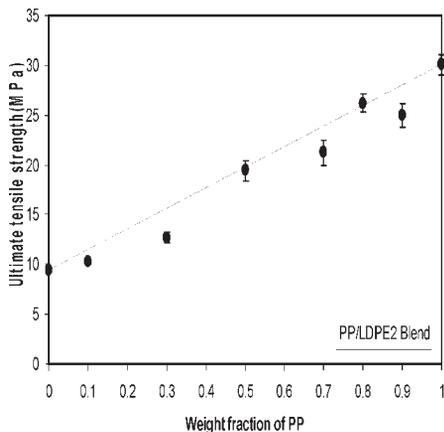Elongation at break as a function of composition for PP/LDPE blends.

Figure 10.
Tensile modulus as a function of PP composition for PP/LDPE2 blends.

Figure 11.
Ultimate tensile strength as a function of composition for PP/LDPE2 blends.

Figure 13.
DSC heating scans for PP/LDPE2 blends.

LDPE in film applications. A small amount of a low Mw LDPE is better than the same amount of a high Mw LDPE.

The ultimate tensile strength for the PP/LDPE2 is shown in Figure 11. With the exception of 50/50 and 80/20 blend compositions, all other blends displayed a NDB from the linear rule of mixtures. However, the extent of NDB was greater in the PP1/LDPE1 blends with only the 90/10 blend following the linear rule of mixtures. Generally, the ultimate tensile strength for both blends system (excluding 10/90 PP/LDPE1 blend) increases linearly with the addition of PP.

The elongation at break for PP/LDPE2 blends is shown in Figure 12. It follows the
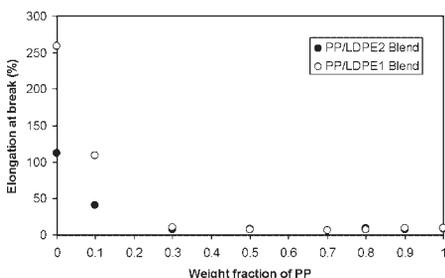

Figure 12.
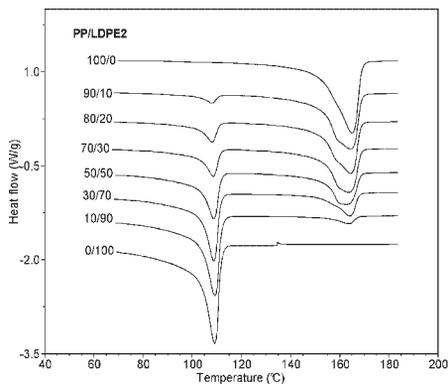Elongation at break as a function of composition for PP/LDPE blends.

same pattern as those of PP/LDPE1 blends. The effect of LDPE Mw was apparent in the LDPE-rich region where PP composition is 10% and 30%. However, at PP composition greater than 50%, no significant influence of the Mw of LDPE on ultimate tensile strength was noticed.

DSC melting endotherms for the PP/LDPE2 blends are shown in Figure 13. The blends show similar peaks to those observed in the high Mw blends. In order to obtain information on the crystallization mechanism of the PP/LDPE2 blends, cooling-run measurements (not shown) were performed. Again they show similar pattern to the other blend systems.

Conclusion

In conclusion, the influences of branch content and Mw of LDPE on the mechanical and thermal properties of PP/LDPE blends were investigated. DSC analysis of all blends exhibit a double melting peak at all the compositions studied thus suggesting that both PP and LDPE crystals exist separately in the solid state. Both the SCB and Mw of LDPE influenced the modulus and ultimate tensile strength of the blends. However, elongation at break seems to be independent of the molecular characteristics of the pure homopolymer especially at PP blend composition greater than 50%.

Addition of a small amount of a low Mw LDPE (10%) resulted in a higher elongation at break than a high Mw LDPE. There is likely a correlation between the presence of a new peak in the thermograms of PP-rich blends and the observed poor elongation at break.

[1] J. Li, R. A. Shanks, Y. Long, *J. Appl. Polym. Sci.* **1999**, *76*(7), 1151.

[2] Z. I. Ali, H. A. Youssef, H. M. Said, H. H. Saleh, *Thermochimica Acta* **2005**, *438*(1–2), 70.

[3] V. M. Marie de Fatima, P. Mariana, G. C. Erica, *Materials Research* **2001**, *4*(4), 251.

[4] R. Strapasson, S. C. Amico, M. F. R. Pereira, T. H. D. Sydenstricker, *Polymer Testing* **2005**, 25, 468.

[5] C. M. Tai, K. Y. L. Robert, C. N. Ng, *Polymer Testing* **2000**, *19*(2), 143.

[6] R. A. Shanks, J. Li, L. Yu, *Polymer* **1999**, *41*(6), 2133.

[7] L. Minkova, E. Lefterova, Ts. Koleva, *Polymer Degradation and Stability* **1992**, *37*, 247.

[8] M. Yamaguchi, S. Abe, *J Appl Polym Sci* **1999**, *74*, 3153.

[9] F. Chen, R. A. Shanks, G. Amarasinghe, *Polymer* **2001**, *42*, 4579.

[10] J. Xu, X. Xu, L. Chen, L. Feng, W. Chen, *Polymer* **2001**, *42*, 3867.

[11] T. Hameed, I. A. Hussein, *Polymer* **2002**, *43*, 6911.

[12] R. L. Morgan, M. J. Hill, P. J. Barham, C. J. Fyre, *Polymer* **1997**, *38*, **1903**.

[13] R. G. Alamo, W. W. Graessley, R. Krishnamoorti, D. J. Lohse, J. D. Londono, L. Mandelkern, F. C. Stehling, G. D. Wignall, *Macromolecules* **1997**, *30*, 561.

[14] B. S. Tanem, A. Stori, A, *Polymer* **2001**, *42*, 5389.

[15] M. Livanovan, E. S. Popova, O. A. Lednev, A. Popova, *Int. J. of polymeric materials* **2000**, *47*(2–3), 279.

[16] C. Albano, C. Urbina de Navarro, M. Ogura, N. Gonzalez, *Mem. - Simp. Latinoam. Polim.*, **1992**, *3*, 331.

[17] A. Dhoble, B. Kulshreshtha, S. Ramaswami, D. A. Zumbrunnen, *Polymer* **2005**, *46*(7), 2244.

[18] J. S. Petronyuk, O. V. Priadilova, V. M. Levin, O. A. Ledneva, A. A. Popov, *Materials Research Society Symposium Proceedings* **2002**, *740*, 261.

[19] I. A. Hussein, M. C. Williams, *Macromol. Rapid Commun* **1998**, *19*, 323.

[20] L. Dong, R. H. Olley, D. C. Bassett, *J. Mat. Sci.* **1998**, *33*(16), 4043.

[21] H. Grasmespacher, J. Meissner, *J. Rheol.* **1992**, *36*(6), 1127.

[22] C. Lacroix, M. Bousmina, P. J. Carreau, B. D. Favis, A. Michel, *Polymer* **1996**, *37*(14), 2939.

[23] D. Graebling, A. Benkira, Y. Gallot, R. Muller, *Eur Polym J* **1994**, *30*, 301.

[24] P. H. P. Macaubas, N. R. Demarquette, *Polymer* **2001**, *42*, 2543.

[25] W. Gleinser, H. Braun, C. Friedrich, J. Cantow, *J. Polymer* **1994**, *35*(1), 128.

[26] A. M. C. Souza, N. R. Demarquette, *Polymer* **2001**, *43*, 1313.