

Influence of Surface Functionalized Waste Tire Powder on the Thermal and Rheological Properties of Polypropylene/Waste Tire Powder Composite

A.M. Shanmugharaj, Sung Hyo Lee*, Jin Kuk Kim*, and Sung Hun Ryu[†]

College of Environment and Applied Chemistry,

Kyung Hee University, Yongin Kyunggi-Do 449 701, South Korea

**Department of Polymer Science and Engineering*

Gyeongsang National University, Jinju, South Korea

(Received February 2, 2006, Revised & Accepted March 8, 2006)

표면기능화된 페타이어 분말이 PP/페타이어분말 복합체의 열 및 유변학적 성질에 미치는 영향

A.M. Shanmugharaj · 이 성 효* · 김 진 국* · 류 승 훈[†]

경희대학교 환경응용화학대학, *경상대학교 고분자공학과

(2006년 2월 2일 접수, 2006년 3월 8일 수정 및 채택)

ABSTRACT : The waste tire powder is modified with allylamine in the presence of ultraviolet radiation and the influence of surface modification on the thermal and rheological properties of polypropylene/waste tire powder composites was investigated. X-ray diffraction studies of PP/waste tire powder composite without compatibilizer, such as maleic anhydride-g-polypropylene (MA-PP), shows the increase in peak intensity of β crystalline peaks, whereas it completely disappears in the presence of the MA-PP. Differential scanning calorimetry results further supported the above fact. The melt viscosities and storage modulus of the composites with modified waste tire powder show higher value than that of composites with unmodified powder and it is attributed to the interaction between amine group on modified powder surface and maleic anhydride of MA-PP.

요 약 : Allylamine을 이용하여 UV하에서 페타이어 분말을 개질하였으며, 이를 이용한 PP/페타이어분말 복합체의 열적, 유변학적 성질을 분석하였다. X-ray 분석결과 무수말레 산이 그래프트된 폴리프로필렌과 같은 상용화제가 없는 경우 β 결정의 피크 강도가 증가한 반면 상용화제가 있는 경우 완전히 없어짐을 알 수 있었으며, DSC 결과에서도 이를 확인할 수 있었다. 개질된 페타이어 분말을 함유한 복합체의 용융점도와 탄성모듈러스는 개질되지 않은 분말을 함유한 복합체 보다 높은 값을 나타내었으며, 이는 개질된 분말 표면의 아민기와 말레이산이 그래프트된 PP의 상호작용에 기인하는 것으로 판단된다.

Keywords : waste tire powder, polypropylene, surface functionalization rheological property, thermal property

[†]대표저자(e-mail : shryu@khu.ac.kr)

I. Introduction

Thermoplastic elastomers unite the application properties for rubbers with the beneficial processing possibility of thermoplastics. The economic recycling of waste tire is a great challenge nowadays, because the land filling or incineration of the waste tires produces environmental problem. The finely ground waste tire powders (GRT) are being used in road construction (ground rubber tire modified bitumina), outdoor pavements, sport track and etc. Many researchers attempted to use the GRT with various thermoplastics and to produce economic polymeric materials that can be used for various applications.¹ In general, the resulting filled systems, however, exhibit poor mechanical properties due to the poor interfacial adhesion between GRT and the thermoplastics, which restricts its applications. To overcome this problem, the researchers have paid much attention to the thermoplastic elastomers, the so-called thermoplastic dynamic vulcanizates in which rubber phase is finely dispersed in the thermoplastic matrix.^{2,3} For GRT containing thermoplastic elastomers, additional small amount of pure elastomer is added to offset the decrease in the mechanical properties due to the loading of waste tire powder in the thermoplastics. In other way, the waste tire powder is subjected to devulcanization prior to use and the property improvement is dependent on the degree of devulcanization.

Recently, a surface-modification techniques have been adopted for recycling of waste tire powder by many researchers.^{4,5} The influence of various irradiation techniques on the effective reuse of the waste rubber have been extensively studied by many researchers.⁶ Ultraviolet (UV) energy has been extensively applied to modify the surface properties using monomers and photosensitizer such as benzophenone (BP). Lee and Ryu⁷ and Yu and Ryu⁸ used acrylamide and glycidyl methacrylate as a monomer to modify the surface characteristics of vulcanized styrene butadiene rubber (SBR) using UV. They found that photografting reaction with

functional monomer is an efficient way to modify the surface characteristics of vulcanized SBR, which is one of the major components of tire.

In this study, the surface functionalized rubber powder has been used to prepare the polypropylene/tire powder composite. The primary objective of this work is to understand the influence of surface functionalized tire powder and the concentration of the compatibilizer on the thermal and rheological processing characteristics of the PP/tire powder composite.

II. Experimental

1. Materials

Waste tire powder was obtained from Dong A Tire Co. Ltd. and allylamine and benzophenone used for the surface modification of tire powder was obtained from Kanto Chemical Co. Inc., Japan, and Aldrich Chemical Co.. Acetone was obtained from Duksan Chemical Co.. Polypropylene was obtained from Samsung General Chemicals and maleic anhydride grafted polypropylene (MA-PP, Polybond 3009TM) was obtained from Uniroyal Chemical.

2. UV photografting of waste tire powder

Allylamine solution of concentration (1.25 mol) was prepared by dissolving the allylamine in 1000 mL of acetone and 0.125 mol of benzophenone was added to the allylamine solution. Rubber powders were soaked in the allylamine solution for 3 hours followed by 3 hours drying at ambient temperature. The allylamine modified rubber powders were then subjected to the UV irradiation using 400 W medium-pressure mercury lamp. UV irradiation time was 30 min. The detailed characterization of grafted rubber powder can be seen elsewhere.⁹

3. Preparation of polypropylene/waste tire powder composites

PP with/without MA-PP was melted for 2 min at 200 °C followed by the addition of 40 wt% of

waste tire powder using Brabender plasticorder at the speed of 50 rpm and the mixing was continued for 5 minutes. It was then dumped out and molded at 200 °C for 2 minutes using Carver press to get 0.15 mm thick sheet. PP/waste tire powder is designated as PM_aA_{b/c}, where P represents tire powder, M represents MA-PP and suffix a represents the weight percent based on tire powder, A represents the allylamine solution and suffixes b and c represent allylamine concentration and UV radiation time, respectively.

4. Characterizations

X-ray diffraction studies of waste rubber powder/polypropylene have been done in the 2θ range of 10 to 50° using Mac Science X-ray diffractometer equipped with a monochromator operating at 40 KV and a copper cathode as the X-ray source (λ= 1.54 Å). Mean crystallite size L in the direction perpendicular to the (hkl) plane was determined using following Scherrer equation¹⁰:

$$L_{hkl} = (K\lambda / B\cos\theta) \tag{1}$$

where K is the crystallite shape constant (=0.89), λ is the wavelength of CuK_α radiation (1.541 Å), B is full width middle height (FWHM) of the peak for the (hkl) reflection. Eq. (1) was used to express the PP crystallite size, L₀₄₀, perpendicular to the (040) plane.

From WAXD pattern, α-phase orientation indexes of PP were determined by the following equations¹¹:

$$A_{110} = h_{\alpha 1} / (h_{\alpha 1} + h_{\alpha 4}) \tag{2}$$

$$A_{040} = h_{\alpha 3} / (h_{\alpha 1} + h_{\alpha 2} + h_{\alpha 3}) \tag{3}$$

where h is the peak height after background subtraction, α₁, α₂ and α₃ correspond to the (110), (040), (130) reflection respectively and α₄ corresponds to (111) and (131) reflections. The A₀₄₀ index is based on the extinction of the (hk0) reflections

relatively to the (0k0) reflections and gives an indication of a preferential orientation perpendicular to the b-axis of the crystallites.¹² Instead of A₁₁₀ from Eq. (3) a more general index, A_{hk0}, given by Eq. (4) is reported in this work since the validity of the A₁₁₀ index based on a constant ratio h_{α3}/h_{α1} is not observed in our samples.¹³

$$A_{hk0} = (h_{\alpha 1} + h_{\alpha 2} + h_{\alpha 3}) / (h_{\alpha 1} + h_{\alpha 2} + h_{\alpha 3} + h_{\alpha 4}) \tag{4}$$

The relative content of the β-form, K_β, can be calculated according to Turner-Jones equation,¹⁴

$$K_{\beta} = I_{\beta} / (I_{\beta 1} + (I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3})) \tag{5}$$

where I_{β1} is the diffraction intensity of the β (300) plane at diffraction angle 16° and I_{α1}, I_{α2} and I_{α3} are the diffraction intensities of the α (110), α (040) and α (130) planes at diffraction angles 14.5°, 17.4° and 19.1°, respectively.

The melting behaviors of PP/waste tire blends were characterized using Perkin-Elmer DSC-7 differential scanning calorimeter. About 8 mg of sample was heated to 250° C at a heating rate of 10 °C/min, and cooled down to 30 °C. The samples were then subjected to second heating cycle with the heating rate of 10 °C from 30 to 250 °C. The enthalpy of fusion (ΔH_f⁰) can be used as a second quantitative assessment of crystallinity assuming the enthalpy of fusion ΔH_f⁰ of both 100 % crystalline α and β- phase is approximately the same.¹⁴ The crystallinity index, X_c (mass fraction) can be written as

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \tag{6}$$

where ΔH_f is the calibrated specific fusion heat of either the α or the β form using the method proposed by Li et al..¹⁴ ΔH_f⁰ is the standard fusion heat of α and β crystals of polypropylene, being 178 J/g and 170 J/g, respectively.¹⁵ The specific fusion heats for α and β phase were determined base on the following calibration method. The total heat of

fusion, ΔH , was integrated from 90 to 180 °C on the DSC thermogram. A vertical line was drawn through the minimum between α and β fusion peaks and the total fusion heat was divided into β component, ΔH_{β}^* and α component, ΔH_{α}^* . Since the less-perfect α crystals melt before the maximum point during heating and contributed to the ΔH_{β}^* , the true value of β -fusion heat, ΔH_{β} , has been approximated by a production of multiplying ΔH_{β}^* with a calibration factor A:

$$\Delta H_{\beta} = A \times \Delta H_{\beta}^* \quad (7)$$

$$A = [1 - (h_2 / h_1)]^{0.6} \quad (8)$$

$$\Delta H_{\alpha} = \Delta H - \Delta H_{\beta} \quad (9)$$

In Eq. (8), h_1 and h_2 are the heights from the baseline to the β -fusion peak and minimum point, respectively.

A Rheometric RMS 800 rheometer was used to determine the dynamic rheological properties. The viscoelastic properties of melt were measured in 25 mm parallel disk configuration with a fixed gap of 2 mm at 180° C in the frequency range of 1 to 50 Hz.

III. Results and Discussion

Figure 1 shows the wide angle X-ray diffraction peaks of pure polypropylene and its composites with waste tire powder with/without 25 parts of MA-PP. XRD of polypropylene is characterized by the presence of diffraction peaks at 14.6° (110), 17.4° (040), 19.1° (130), 21.7° (111) and 22.4° (131), which are attributed to the monoclinic α -crystal form of the crystalline phase. The small peak at 16.6° is due to the (300) reflection of β crystalline phase existing in the polypropylene. Furthermore a small hump at 20.5° is attributed to the γ -crystal of crystalline plane.¹⁶ Loading of waste tire powder slightly shifts the various crystalline peaks to the lower angle. The peak intensity of the β crystalline

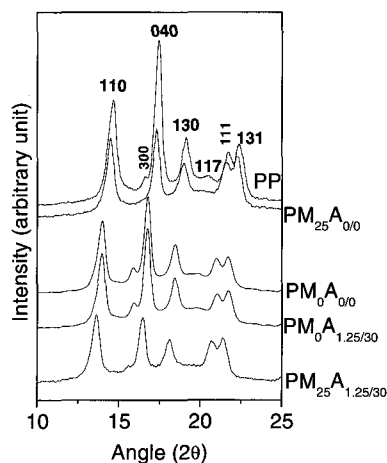


Figure 1. X-ray diffraction results of polypropylene based thermoplastic vulcanizates.

Table 1. Orientation indexes, mean crystallite sizes and relative content of β crystals calculated using XRD

Samples	A_{hk0}	A_{040}	Mean crystallite size L_{040} (nm)	K_{β}
PP	0.75	0.50	20.77	0.06
PM ₀ A _{0/0}	0.78	0.44	23.21	0.11
PM ₀ A _{1.25/30}	0.78	0.45	23.80	0.11
PM ₂₅ A _{0/0}	0.66	0.41	20.88	-
PM ₂₅ A _{1.25/30}	0.67	0.37	19.20	-

peak increases with loading of unmodified ($A_{0/0}$) and allylamine grafted waste tire powder ($A_{1.25/30}$) in the absence of compatibilizer (MA-PP). This is supported by the increase of K_{β} calculated using equation (5) from 0.06 (PP) to 0.11 (PM₀A_{0/0} and PM₀A_{1.25/30}). (see Table 1) However, it is interesting to observe the absence of β crystalline peak for PM₂₅A_{0/0} and PM₂₅A_{1.25/30}. Similarly, the absence of peak at 20.5° implies that there is no γ -crystals in the case of PM₂₅A_{0/0} and PM₂₅A_{1.25/30}, whereas a small hump is observable in pure PP, PM₀A_{0/0} and PM₀A_{1.25/30}. Earlier reports on PP crystallinity reveal that the formation of β crystal is associated with non-isothermal crystallization of polypropylene melt under compression. The polymer melts under compression experience the shear induced crystalliza-

tion. Varga¹⁷ and Wu¹⁸ explained the formation of β crystals under shearing conditions as follows: shearing the melts generates row nuclei of α modification (α row nuclei). At the surface of these α -row nuclei, the α -to- β transition, termed as $\alpha\beta$ secondary nucleation, occurs, which results in point-like β nuclei covering the surface of the α -row nuclei. In the present study, the generation of β crystals is being influenced by the preoriented molecules in the flow direction in the molten stage so as to form fibrillar bundles, which could crystallize easily under a certain degree of cooling¹⁷ and also due to the waste tire powder dispersion in the matrix. To understand the crystallite orientation in the PP/waste rubber blends, A_{hk0} and A_{040} have been calculated using the equations (3) and (4). In all the cases, the orientation index A_{hk0} lies in the range of 0.66 to 0.78, in agreement with values obtained by others for PP.¹⁹ Similarly, the orientation index due to (040) plane (A_{040}) doesn't vary significantly as observed by Perrin-Sarazin et al. in polymer blends.¹³ In case of $PM_0A_{0/0}$ and $PM_0A_{1.25/30}$, the presence of waste tire powder leads to faster cooling due to the transfer of heat energy through the thermally conductive carbon black filled waste tire powders that leads to the generation of imperfect α crystals, which is often interpreted as β crystals in the PP matrix. However, loading of small weight percentage of compatibilizer leads to form a thin film around the rubber powders that restricts its thermal energy dissipation through the waste tire powder. This is responsible for the formation of slow cooling rate and thereby results in well defined α crystals without imperfections (absence of β crystals).

This is further supported by the differential scanning calorimetric results. Figure 2 shows a few DSC data of melt crystallized PP/waste tire powder composites. The endothermic thermal transitions centered at around 145 and 165 °C provide evidences of melting of PP crystals with different perfections. These crystals are developed due to the non-isothermal cooling of PP sheets. According to the literature, the two melting peaks centered around

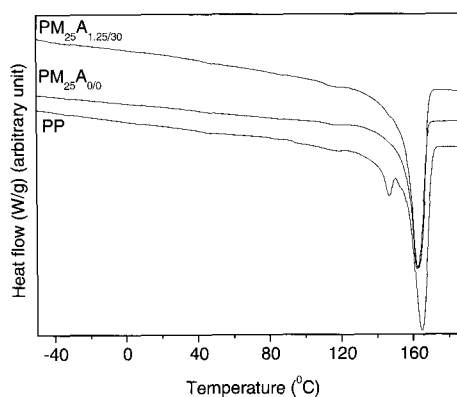


Figure 2. Differential scanning calorimetry results of thermoplastic vulcanizates.

Table 2. Differential scanning calorimetric results of PP/waste rubber powder

Samples	Crystalline peaks	Melting temperature (°C)	Heat of fusion (J/g)	Relative content of each phases
PP	α	164.2	-45.4	0.61
	β	146.8	-29.5	0.39
$PM_0A_{0/0}$	α	163.9	-22.1	0.46
	β	148.9	-25.4	0.54
$PM_0A_{1.25/30}$	α	164.6	-23.1	0.42
	β	149.5	-32.2	0.58
$PM_{25}A_{0/0}$	α	163.1	-34.3	1.0
$PM_{25}A_{1.25/30}$	α	163.1	-39.5	1.0

159 and 163.5 °C corresponds to the α crystalline form of PP and two small peaks centered around 143.3° and 150.8° C corresponds to the β crystalline form of PP.²⁰ However, in our case, the respective α and β crystalline peaks merged together to give two individual peaks centered at 145 and at 165 °C. Loading of waste tire powder and allylamine grafted waste tire powder in the absence of compatibilizer shifts the melting endothermic peak values of β crystals to higher temperature of the PP (Table 2). However, it is interesting to observe the melting peak endotherms due to the β crystalline forms completely vanishes in the case of waste tire powder

and allylamine grafted waste tire powder loaded PP in the presence of compatibilizer. The relative content of β crystalline peaks increases from 0.39 (PP) to 0.54 ($PM_{0}A_{0/0}$) on loading waste tire powder. Similarly it increases to about 0.58 on loading allylamine grafted waste tire powder supporting the X-ray diffraction results.

The viscoelastic properties of pure PP and its blends with waste tire powder are included in Figure 3. Figure 3 shows the variation of storage modulus (G') for pure PP and PP/waste tire powder composites with various MA-PP concentrations. It is clear that the storage modulus (G') increases with increasing frequency, which is undoubtedly due to the decrease in time available for molecular relaxation. Loading of waste tire powder ($A_{0/0}$) decreases the storage modulus over the range of the frequency compared to pure PP and it further decreases with increasing compatibilizer concentration from 10 ($PM_{10}A_{0/0}$) to 25 % ($PM_{25}A_{0/0}$). However, the storage modulus doesn't vary significantly with increasing compatibilizer concentration in the case of PP/allylamine modified tire powder powder over the range of frequency. Also, it is interesting to note storage modulus is high for the PP/functionalized rubber powder blends ($PM_{10}A_{1.25/30}$, $PM_{25}A_{1.25/30}$) compared to its unmodified counterpart ($PM_{25}A_{0/0}$) at low frequency. This is due to the interaction between MA-PP and functionalized rubber powder. This pronounced elastic properties and very long relaxation process of the immiscible polymer blends were also reported in the PS-PMMA blend.^{21,22} The slopes of $\log G'$ vs. $\log \omega$ in the terminal zone (low frequency region) is found to be in the range of 0.74 to 0.81 for PP/waste tire powder blends confirming phase separation due to immiscibility between PP and waste tire powder.²³

Figure 4 shows the plot of complex viscosity vs. frequency for all the systems. The complex viscosity decreases with increase in frequency indicating the pseudoplastic or shear thinning behavior. However, loading of unmodified tire powder decreases the complex viscosity over the range of frequency and

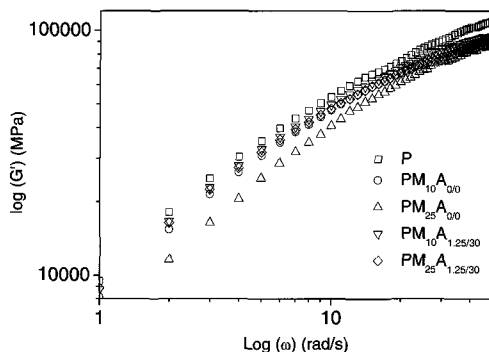


Figure 3. Variation of storage modulus with frequency for PP/waste tire powder blends

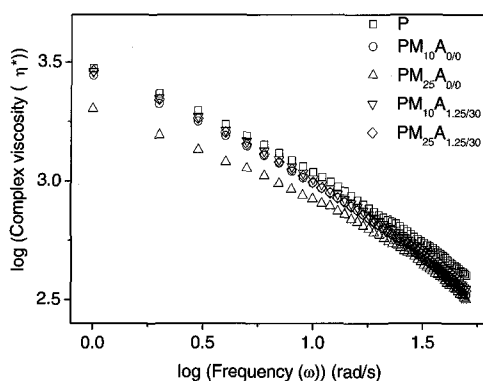


Figure 4. Variation of complex viscosity with frequency for PP/waste tire powder blends.

it decreases with increasing compatibilizer concentration ($PM_{10}A_{0/0}$ and $PM_{25}A_{0/0}$) and it can be attributed to the low viscosity of MA-PP itself. However, viscosity does not change much by increasing compatibilizer concentration for surface functionalized rubber powder ($PM_{10}A_{1.25/30}$ and $PM_{25}A_{1.25/30}$) composites. The interaction between the surface of functionalized tire powder and MA-PP disturbs the flow of composite and it increases the viscosity of composites. Within our experimental range the degree of interaction increases with compatibilizer concentration and it compensates the reduction of viscosity due to MA-PP. This supports the above discussion on the surface interaction between functionalized tire powder and MA-PP.

IV. Conclusions

In the present investigation, the influence of allylamine modified rubber powder on the thermal and rheological properties of PP/waste tire powder blends were studied and following conclusions were drawn. Loading of waste tire powder in polypropylene increases the amount of β crystals in the absence of compatibilizer. However, generation of β crystals is totally absent in the presence of compatibilizer in PP/waste tire blends. This is supported by the X-ray diffraction and differential scanning calorimetric results. PP/allylamine functionalized rubber powder blends exhibits higher storage modulus over the measured frequency range compared to its unmodified counterpart. This is being explained due to the chemical interaction between the allylamine and maleic anhydride of MA-PP. Complex viscosity decreases with increase in frequency for all the blends indicating the pseudoplastic or shear thinning behavior.

Acknowledgement

The authors are thankful to the Industrial Waste Recycling R&D Center, KOREA, for providing fund to carry out research.

References

1. J.K. Kim and R.P. Burford, "Study on powder utilization of waste tires as a filler in rubber compounding", *Rubber Chem. Technol.*, **71**, 1028 (1998).
2. S.K. De and A.K. Bhowmick, "Thermoplastic elastomers from rubber-plastic blends", Ellis Horwood, 1990.
3. J. Karger-Kocsis, "Polymer blends and alloys", ed. by G.O. Shonaie and G.P. Simon, p. 125, Marcel Dekker, New York, 1999.
4. E.L. McInnis, B.D. Bauman and A. Williams, "Higher modulus compositions incorporating particulate rubber", U.S. Patent 5506283 (1996).
5. B. Adhikari, D. De and S. Maiti, "Reclamation and recycling of waste rubber", *Prog. Polym. Sci.*, **25**(7), 909 (2000).
6. C. Peter, "Free radicals in diene polymers induced by ultraviolet irradiation I, An ESR study of cis-1,4-poly(isoprene)", *Rubber Chem. Technol.*, **45** (4), 918 (1972).
7. K.I. Lee and S.H. Ryu, "Ultraviolet Photografting reaction of acrylamide onto styrene-butadiene rubber", *Elastomer*, **33**, 363 (1998).
8. J.J. Yu and S.H. Ryu, "Ultraviolet-initiated photografting of glycidyl methacrylate onto styrene-butadiene rubber", *J. Appl. Polym. Sci.*, **73** (9), 1733 (1999).
9. A.M. Shanmugaraj, J.K. Kim and S.H. Ryu, "UV surface modification of waste tire powder: Characterization and its influence on the properties of polypropylene/waste powder composites", *Polymer testing*, **24**, 739 (2005).
10. S. Hambir, N. Bulakh and J.P. Jog, "Polypropylene/Clay nanocomposites: Effect of compatibilizer on the thermal, crystallization and dynamic mechanical behavior" *Polym. Eng. Sci.*, **42**, 1800 (2002).
11. R.A. Kalgaonkar and J.P. Jog, "Copolyester/layered silicate nanocomposites: The effect of the molecular size and molecular structure of the intercalant on the structure and viscoelastic properties of the nanocomposites", *J. Polym. Sci., Part B: Polym. Phys.*, **41**, 3102 (2003).
12. P.W. Zhu and G. Edward, "Studies of Injection-Molded Isotactic Poly(propylene) by Synchrotron WAXD/SAXS: Effects of Nucleating Agent on Morphological Distribution" *Macromol. Mater. Eng.*, **288**, 301 (2003).
13. F. Perrin-Sarazin, M.T. Ton-That and J.B. Denault, "Micro- and nano-structure in polypropylene/clay nanocomposites", *Polymer*, **46**, 11624- (2005).
14. J.X. Li and W.L. Cheung, "On the deformation mechanisms of β -polypropylene: 1. Effect of necking on β -phase PP crystals", *Polymer*, **39**, 6935 (1998).
15. J.X. Li, W.L. Cheung and D. Jia, "A study on the heat of fusion of β -polypropylene", *Polymer*, **40**, 1219(1999).
16. A. Turner-Jones, J.M. Aizlewood and D.R. Beckett, "Crystalline forms of isotactic polypropylene", *Makromol Chem.*, **75**, 134 (1964).
17. J. Varga and J. Karger-Kocsis, "Rules of super-

- molecular structure formation in sheared isotactic polypropylene melts”, *J. Polym. Sci. Polym. Phys.*, **34**(4), 657 (1996).
18. C.M. Wu, M. Chen and J. Karger-Kocsis, “The role of metastability in the micromorphologic features of sheared isotactic polypropylene melts”, *Polymer*, **40**(15), 4195 (1999).
 19. J.P. Trotignon and J. Verdu, “Skin-core structure-fatigue behavior relationships for injection-molded parts of polypropylene. I. Influence of molecular weight and injection conditions on the morphology”, *J. Appl. Polym. Sci.*, **34**, 1 (1987).
 20. J. Scudla, K.J. Eichhorn, M. Raab, P. Schmidt, D. Jehnichen and L. Haußler, “The effect of specific nucleation on molecular and supermolecular orientation in isotactic polypropylene”, *Macromol. Symp.*, **184**, 371 (2002).
 21. H. Gramespacher and J. Meissner, “Interfacial tension between polymer melts measured by shear oscillations of their blends”, *J. Rheol.*, **36**, 1127 (1992).
 22. D. Graebbling, R. Muller and J.F. Paliarne, “Linear viscoelastic behavior of some incompatible polymer blends in the melt. Interpretation of data with a model of emulsion of viscoelastic liquids”, *Macromolecules*, **26**, 320 (1993).
 23. J.H. Lee, M.L. Ruegg, N.P. Balsara, Y.Q. Zhu, S.P. Gido and R. Krishnamoorti, “Phase Behavior of Highly Immiscible Polymer Blends Stabilized by a Balanced Block Copolymer Surfactant”, *Macromolecules*, **36**, 6537 (2003).