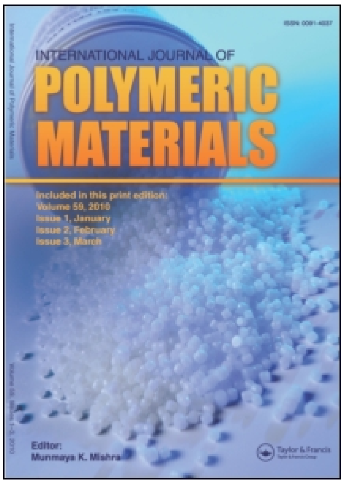

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Morphological Features of Poly (3-Hydroxybutyrate)/Low Density Polyethylene Blends

A. A. Ol'khov[a]; A. L. Iordanskii[a]; G. E. Zaikov[a]; L. S. Shibryaeva[a]; I. A. Litwinov[b]; S. V. Vlasov[c]
[a] Semenov's Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia [b] Topchiev's Institute of Petrochemical Synthesis, RAS, Moscow, Russia [c] Lomonov's State Academy of Fine Chemical Technology of Moscow, Moscow, Russia

To cite this Article Ol'khov, A. A. , Iordanskii, A. L. , Zaikov, G. E. , Shibryaeva, L. S. , Litwinov, I. A. and Vlasov, S. V.(2000) 'Morphological Features of Poly (3-Hydroxybutyrate)/Low Density Polyethylene Blends', International Journal of Polymeric Materials, 47: 2, 457 — 468

To link to this Article: DOI: 10.1080/00914030008035079

URL: http://dx.doi.org/10.1080/00914030008035079

Intern. J. Polymeric Mater., 2000, Vol. 47, pp. 457–468
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Morphological Features of Poly (3-Hydroxybutyrate)/Low Density Polyethylene Blends

A. A. OL'KHOV[a], A. L. IORDANSKII[a], G. E. ZAIKOV[a,*],
L. S. SHIBRYAEVA[a], I. A. LITWINOV[b] and S. V. VLASOV[c]

[a] *Semenov's Institute of Chemical Physics, Russian Academy of Sciences,*
4 Kosygin Str. Moscow, B-334, 117334, Russia;
[b] *Topchiev's Institute of Petrochemical Synthesis, RAS, 29 Leninskii Prospect,*
Moscow, 117912, Russia;
[c] *Lomonov's State Academy of Fine Chemical Technology of Moscow,*
86 Vernadskii Prospect, 117571, Moscow, Russia

(Received 5 May 1999)

In an effort to investigate the morphology of biodegradable films, the combination of DSC, SEM and FTIR polarization spectroscopy methods are used. The methods enable us to examine the structural and morphological peculiarities of extruded blend compositions on the base of PELD and poly(3-hydroxybutyrate) (PHB) at concentration of the latter ranges from 0 to 32 wt%. The blend components are thermodynamically incompatible and form morphological elements with good visible interfaces between disperse phase (PHB) and continuous matrix (LDPE). For film extrusion, blend components affect each other that is seen as the crystallinity drop for both PHB and LDPE. The dichroism measurements show that the axes of LDPE and PHB molecules are presumably located at right angle, therewith, the biggest axes of the PHB crysrtallites are oriented along the extrusion direction. The matrices at all blend ratios, besides 32 wt% composition, are reinforced by alternative band- and cylinder-like fibriles of PHB. The architecture of such morphological elements is carefully studied by SEM method.

Keywords: Low density PE; poly(3-hydroxybutyrate); blends morphology

---

*Corresponding author.

INTRODUCTION

For last two decades, both industrial and academic interest has been attracted by a novel family of microbial thermoplasts: poly-R-hydroxyakanoates (PHA) [1, 2]. The poly(3-hydroxybutyrate) (PHB) is one of the most abundant of this family that offers good physical-mechanical properties being close to propylene [3], effective biocompatibility [4], and microbial degradation in climatic/landscape environments [5].

While the high cost and rather high brittleness of PHB materials limit essentially the areas of their applications. Inserting in the macromolecule of PHB the entities of 3-hydroxybutyrate (~20 wt%) one enables to produce elastic material (*e.g.*, BIOPOL® Zeneka, the Netherlands) which is potentially applicable in medicine (surgical sutures, osteoprostheses), in the agricultural industry, in the preparation of biodegradable packing films and reservoirs. An alternative perspective approach to the upgrade of physical-mechanical parameters and to the suppression of the polymer cost is the blending of PHB with others more cheaper polymers such as starch [6, 7], cellulose [8], or its esters [9, 10], polypropylene [11], aliphatic polyethers [12] *etc.*

It is worth to note that the rate of degradation for immiscible blends is higher than for the miscible ones [13]. For design of biodegradable/bioerodable materials, hence, it needs to examine the structural features of blends combined on the base of thermodynamically incompatible components. This problem is very important for prognosis of exploitation parameters of blend materials.

This work is devoted to the study of morphological features of blends with different compositions for widespread low density polyethylene (LDPE) and PHB provided the base of a novel biodegradable material.

EXPERIMENTAL

Materials

The fine powdered PHB were provided by Biomer Co (Krailing, Germany). The chemical structure of PHD structure is well-established in the literature [2] and $M_\eta = 2.5\ 10^5$ was determined by intrinsic viscosimetry in chloroform solution [14]. The granulated LDPE is commercial product of SAFCT Moscow designated standart (15803-020) with following characteristics: $M_\eta = 2.5\ 10^5$ and specific density 0.92 g/cm^3.

Blending

All blends were made by melting in a single-screw extruder (ARP-20). Preliminary mixed compositions with different ratio components (PHB/LDPE): 2/98, 4/96, 8/92, 16/84, and 32/68 were loaded in the extruder. Temperature in a ringing heater head did not exceed 185°C and the frequency of the screw rotation was 100 min^{-1}. The factor of blowing (2.0) and drawing ratio (5.0) have controlled the production of the blend films with 40 – 50 mkm thickness. The unblended LDPE and PHB were also processes under identical extrusion conditions to undergo a thermal history similar to the history for the blends.

Methods

The thermal properties of the films were obtained from cooling and heating at the scanning rate 16°K/min by the DSC technique with differential calorimeter DSM-2 preliminary calibrated with In ($Tm = 156.6°\mathrm{C}$). Crystallinity was estimated knowing specific melting heats for LDPE (295 J/g) [15] and PHB (90 J/g) [16] with accuracy about 10%.

Orientation in LDPE and PHB components was monitored separately by FTIR dichroism measurements in range 700 – 1500 cm^{-1}. In a conventional manner, IR dichroism was recorded from the absorbance of appropriate bands (at 729 cm^{-1} for CH_2 groups of LDPE crystallites [17] and at 1228 cm^{-1} for CH_2 groups of PHB crystallites [18]) with radiation polarized parallel or normally to the extrusion direction. From the corresponding absorbances ($A_{=}$ and $A_{\perp}$) a dichroic ratio (DR) can be estimated as $DR = A_{=}/A_{\perp}$. As polarizer was used wire grid polarizer. The details of experimental procedures are reported elsewhere [19].

Scanning electron microscopy (SEM) has been used to characterize the morphology generated by melt extrusion. The circular extruded polymer blends were immersed in liquid nitrogen and then fractured. The fractured surfaces were coated with fine-dispersed Au. The areas of blends were viewed end-on by scanning electron microscope "Tesla BS 301" at magnification from 100 to 10000. More comprehensively the sample preparation and measurement procedure have been published in [20].

RESULTS AND DISCUSSION

Figure 1 (curves a and b) shows endotherms of melting for PHB/LDPE blend with composition 8/92 wt%. For original heating the thermal curve gives two peaks which were found to belong to individual components PHB and LDPE respectively. In Table I the thermal parameters of blends with different ratios of components are presented. As evident from the table, the melting temperatures of all blends are little different from these parameters for the origin polymers. It is important to note that on cooling of blends down to room temperature only one peak is shown in the thermogram that is possessed by LDPE. The remelting causes the appear of one peak too. The occurrence of the second peak for PHB component can be seen only after storing for 60 hours at room temperature. Analyzing thermal data it may be deduced that both polymers form the proper phases affecting weakly each other. Nearly constant temperature of crystallization for LDPE together with WAXS data [21] show stability of its crystalline parameters (elementary cell parameters and a means of arranging for segments in crystallites). The crystallinity degrees for both components in blends drop remarkably as compared with the pure origin polymers. The drop of crystallinity allows to propose the availability of both steric hindrances realized already in melts and kinetic-relaxation problems due to quiet fast rate of the melt cooling as compared with the rate of crystallization.

Supplementary information on molecular orientation in extruded blend films would be obtained by FTIR polarized spectroscopy. Since such orientation includes the alignment of structural/morphological elements in particular crystallites, estimation of such orientation is performed by dichroism. As pointed out above in methodical part, a plane of polarizer was directed either with the extrusion direction or normally to the one. The dichroism dependences of structure-sensitive group bands for PHB (methylene groups, 1228 cm^{-1}) and LDPE

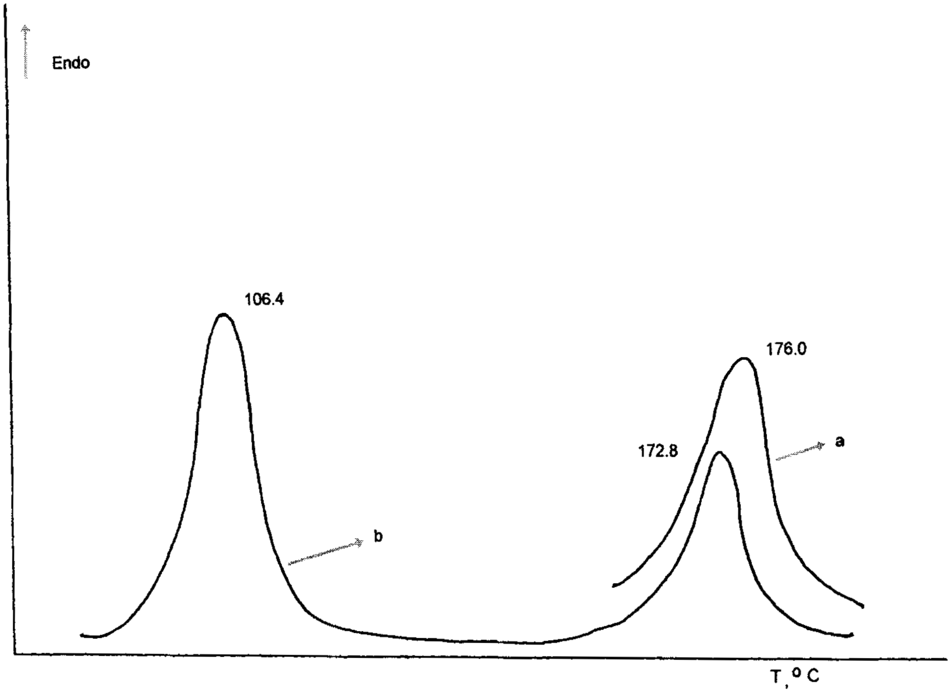

FIGURE 1 Endotherms of melting for PHB (a) and LDPE-PPHB blends (b).

TABLE I Thermal properties of LDPE/PHB blended films

Blend content, %	*Melting point T_m, °C*		*Melting heat, ΔH_m, J/°C*		*Crystallinity X,% (*)*		*Crystallisation temperature °C*
PE/PHB	ПЭ	ПГБ	ПЭ	ПГБ	ПЭ	ПГБ	ПЭ
100/0	107,0	–	70,0	–	40	–	89,6
98/2	106,4	172,0	58,0	58,0	35	42	89,8
96/4	106,3	172,6	55,0	38,0	29	45,4	89,4
92/8	106,5	171,8	70,0	44,0	30,5	47	89,5
84/16	106,8	173,2	60,0	40,0	28	49	89,7
68/32	105,9	173,2	35,0	48,0	25	55	89,5
0/100	–	175,4	–	61,9	–	68,8	85,0 + 78,6

(*) – DSC data.

(methylene groups, 729 cm^{-1}) on the blend compositions are presented in Figures 2a and 2b, respectively. FTIR dichroism functions indicate that the polymer orientation behavior of both methylen groups are related to PHB content in blends. Dichroism of either depends extremely on PHB concentration. It is notable that an inversion of dichroism for PHB is observed.

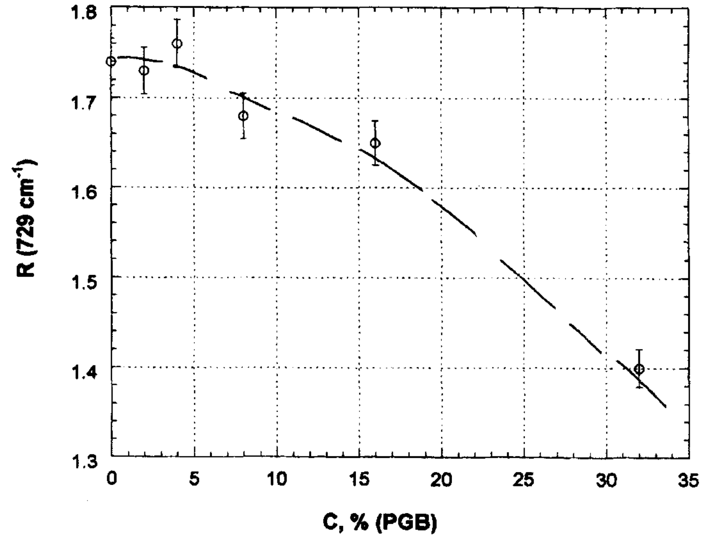

FIGURE 2 Dependence of dichroism on PHB concentration at 729 cm^{-1} (LDPE) (a) and 1228 cm^{-1} PHB (b).

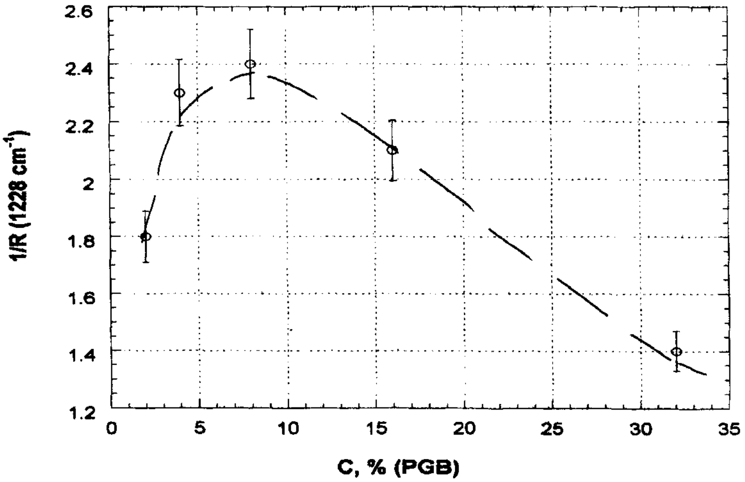

FIGURE 2 (Continued).

The increase of the PHB content in blends causes a desorientation of LDPE segments (decreasing crystallinity) that was characterized by monotonously scaled-down dichroism ratio (curve 2a). But this inverted function for PHB fragments has a maximum at 8 wt%. The reason of maximum occurrence in the curve "dichroism-content" could be explained by superposition of two opposite processes affecting segmental orientation realized during the film formation. With increasing PHB content, on the one hand, the tendency of order for rigid and semi rigid chains of macromolecules is increased due to the flow of melt through the extruder slit. On the other hand, the viscosity of the blend melts is increased with PHB content and hence the relaxation time for structural elements does too. At constant rate of the melt cooling, the effective time of structural reorientation may exceed the time it takes for crystallization/solidification of PHB phase. Hence, incomplete orientation will be 'frozen'. Preliminary results for both FTIR dichroism orientation and DSC crystallization testify that only after 60 h storing of blend films at ambient temperature, the orientation function and the crystallinity begin to restore nearly to the origin equilibrium values. At low PHB concentrations (< 8% wt.) dominates the orientation of PHB segments but at higher concentrations begin to dominate viscosity-relaxation effect and we see more disordered structural organization. The decrease of crystallinity counts in favour of above hypothesis.

An inverted dichroism function is realized for the extruded PHB films (curve 2b) and may reveal the electric moment orientation of CH_2 groups normally to the extrusion sense and the polarization plane. In accordance with WAXS/SAXS data obtained recently [22], the both PHB and LDPE crystallites form *a*-textured morphology in the extruded blends (axial texture along *a*-axes of elementary cells) and change their direction relative to film plane being aligned parallel to both this plane and extrusion direction, in contrast to the solvent casting films of PHB where those fragments oriented normally to the film plane (*c*-textured morphology) [23]. Such arrangement of crystallies is typical for all blend ratios. The combination of diffraction data obtained before and ir polarization spectroscopy allow to suggest that the reason of inversion of dichroism is a difference of transition moment angles of methylene groups belonging to LDPE ($\approx 0°$) [19] and PHB ($\approx 90°$) [17, 18].

SEM photographs of fracture surfaces for PHB/LDPE blends are shown in Figure 3 both normally and parallel the extrusion direction.

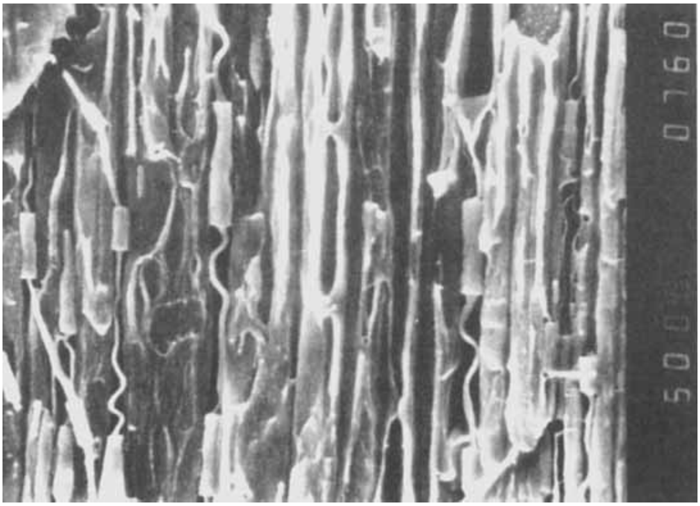

FIGURE 3 SEM photomicrographs of fractured surfaces normally and parallel the extrusion direction. a – along fractured sample: 8/92 PHB/LDPE blend, b – cross section fractured sample 16/84, and c – the same procedure for 32/68 PHB/LDPE blend.

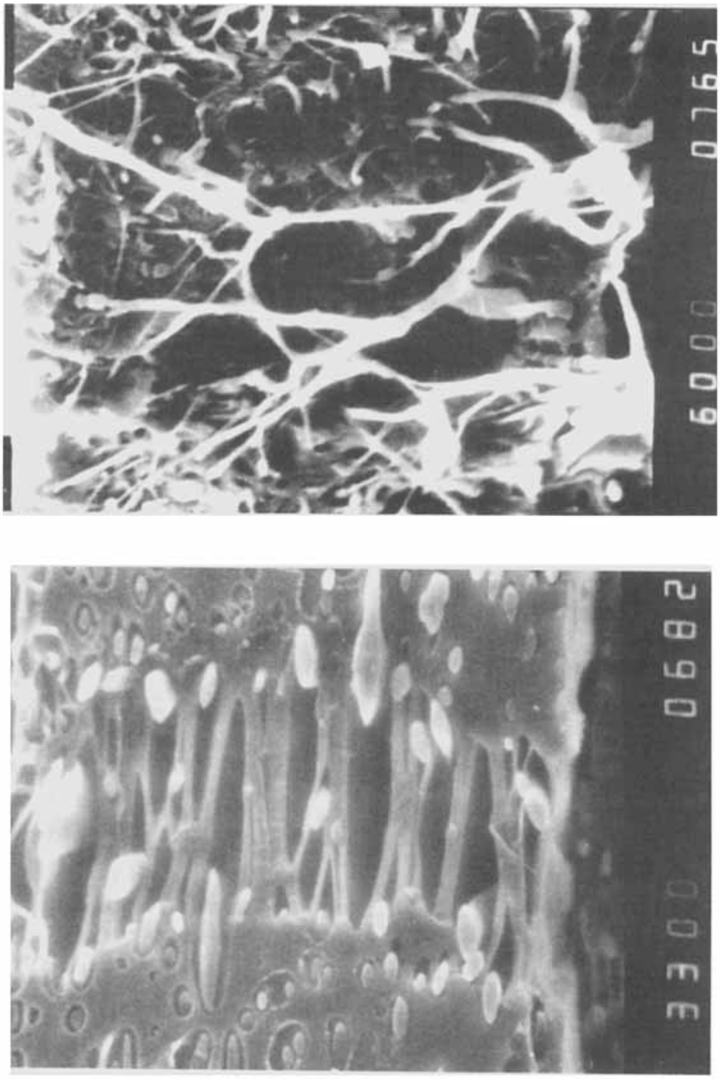

FIGURE 3 (Continued).

In Figure 3a the dispersion phase of PHB is clearly visible as alternate band-like and cylinder-like morphological elements. Averaged cross section diameters of the cylinder-like elements are about 0.35 mkm, averaged widths of the band-like ones ranged between 0.09 and

2.0 mkm and their lengths are varied from 3 to 15 mkm. These lengths are in excess of the averaged lengths of the cylinders roughly by 10. Cross sections of fracture relative to extrusion direction is shown in Figure 3b. It is worth to note, in LDPE matrix, there are cylindrical pores where all above elements have been located or are locating.

A different picture arises with blend composition picture shown in Figure 3c. Here we can see the along-extrusion deformation of PHB fibriles formed as cylyndroid elements imbedded in microholes located presumably in interface between PHB and LDPE. The sizes of such microholes are ranged from 2 to 20 mkm in length and from 1 to 3 mkm in cross-section. The origin of the microholes likely to be conditioned by the exfoliation of PHB elements from LDPE matrix due to mechanical forces realized at extrusion [24]. Generally, a comparison of parallel or normally directed fractures enables to estimate the geometry of morphological elements of PHB and LDPE.

CONCLUSIONS

The combined study of PHB/LDPE blend compositions with SEM, DSC and FTIR polarized spectroscopy shows

(1) blend-formation components are thermodinamically noncompatible and form the proper morphological elements with good visible interfaces between disperse phase (PHB) and dispersive matrix (LDPE);
(2) during film extrusion, blend components affect each other that shows as the crystallinity drop for both PHB and LDPE because of rheology and structural relaxation attended by extrusion;
(3) the axes of LDPE and PHB molecules are presumably located at right angle, therewith, the biggest axes of the PHB crystallites are oriented along the extrusion direction with the design of axial texture [23].

The special morphological features of the blends implies that the matrices at all blend ratios, besides 32 wt% composition, are reinforced by band/cylinder-like fibriles of PHB. On the one hand, owing to this morphology the blend films are superior to the origin polymer films (PHB or LDPE) in some mechanical characteristics (ultimate tensile strength, elastic modulus) [25]. On the other hand, heterogenity of such compositions enhances the rate of degradation under artificial climatic conditions and under thermooxidation [26]. The following search of the relationship between transport phenomena and morphology is a necessary step for design of biodegradable/bioerosive materials on the base of petro and green polymer blends.

Acknowledgements

This research was generously supported by the Russian Academy of Sciences (RFFI 99-0332078) The authors would like to thank to Biomer Company, Kraisling Germany and personally Dr. U. Hanggi for providing the PHB powder.

References

[1] Seebach, D., Brunner, A., Bachmann, B. M., Hoffman, T., Kuhnle, F. N. M. and Lengweier, U. D. (1996). Biopolymers and -oligomers of (R)-3-Hydroxyalkanoic Acids-Contributions of Synthetic Organic Chemists. Zurich: Edgenossische Technicshe Hochschule.

[2] *International Symposium on Bacterial Polyhydroxyalkanoates '96*. Davos, Switzerland, 18–23 August 1996.

[3] Babel, W., Riis, F. and Hainich, E. (1990). *Plaste und Kautschuk*, **B.37**(N4), S. 109–115.

[4] Lafferty, R. M. and Korsatko, B. (1988). Biotechnology Ed. by Rehm, H. J., *Weinheim*: VCH, **6b**, 135.

[5] Gilmore, D. F., Antoun, S., Lenz, R. W. *et al.* (1992). *J. Ind. Microbiol*, N **10**, 199–206.

[6] Tanna, S. T., Gross, R. A. and Mc Carthy, S. P. (1992). *Polym. Mater. Sci. Eng.*, **67**, 294–295.

[7] Willett, J. L. and O'Brien, G. (1997). Novel Uses and Processes (Eds., Campbel, G. M., Webb, C. and Mckee, S. L.) Plenum Press, New York.

[8] Gatenholm, P. and Mathiasson, A. (1994). *J. Appl. Polym. Sci.*, **51**, 1231–1237.

[9] Lotti, N. and Scandola, M. (1992). *Polym. Bull.*, **29**, 407–413.

[10] Scandola, M., Ceccorulli, G. and Pizzoli, M. (1992). *Macromolecules*, **25**, 6441–6446.

[11] Patent, U. S. 5.135.966. 4 August (1992).

[12] Gussner, F. and Owen, A. J. (1992). *Polymer*, **35**, 2233–2236.

[13] Verhoogt, H., St-Pierre, N., Truchou, F. S. *et al.* (1995). *Can. J. Microbiol.*, **41**, 323–328.

[14] Iordanskii, A. L., Kamaev, P. P. and Zaikov, G. E. (1998). *J. Intern, Polymeric Mater.*, **41**, 55–63.

[15] Godovskiy, Yu. K. (1982). *Thermophysics of Polymers*, Moscow Chemistry.

[16] Koyama, N. and Doi, Y. (1995). *Can Microbiol.*, **41**, 316–322.

[17] Dechant, I. and Danz, R. (1972). u.a. Ultrarotspektroskopische Untersuchuugen an Polymeren Berlin: Academie-Verlag.

[18] Labeek, G., Vorenkamp, E. J. and Schouten, A. J. (1995). *Macromolecules*, **28**(N6), 2023–2032.

[19] Elliott, A. (1969). Infra-red Spectra and Structure of Organic Long-chain Polymers London, Edward Arnold (publishers) LTD.

[20] Yoshie, N., Azuma, Y., Sacurai, M. and Inoue, Y. (1995). *J. of Applied Polymer Science*, **56**, 17–24.

[21] Lauzier, Ch. A., Monasterios, C. J., Saracovan, I., Marchessault, R. H. and Ramsay, B. A. (1993). **76**(5), 71–77.

[22] Ol'khov, A. A., Vlasov, S. V., Iordanskii, A. L., Shibryaeva, L. S., Tarasova, N. A. and Hanggi, U. J. (1998). *18th Discussion Conference "Mechanical Behaviour of Polymeric Materials"*. Prague 20–23 July 1998 P71.

[23] Krivandin, A. V., Shatalova, O. V. and Iordanskii, A. L. (1997). *J. Polymer Science Ser*, **B.39**(3–4), 102–105.

[24] Fisher, E. G. (1970). Extrusion of Plastics New York.

[25] Ol'khov, A. A., Vlasov, S. V. and Iordanskii, A. L. (1998). No. (3), pp. 14–16.

[26] Ol'khov, A. A., Ivanov, V. B., Vlasov, S. V. and Iordanskii, A. L. (1998). Plast Massy No. (6), pp. 19–21.