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The Role of Lubricants in Reactive Compatibilization of Polyolefin Blends

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Summary: Reactive compatibilization using liquid polybutadienes and dialkyl peroxides was studied in model low-density polyethylene/polystyrene (4/1) blends and the commingled waste of composition similar to these blends. The influence of three types of lubricants (Ca stearate, stearic acid - Loxiol G20 and paraffin - Loxiol G22) on the structure and toughness of these blends was determined. In spite of the fact that in the waste material, a coarse morphology and poor toughness were found in comparison with the blend of virgin polyolefins, reactive compatibilization has approximately the same effect in both types of the blends as far as the structure parameters and mechanical behaviour are concerned. This effect is enhanced by addition of lubricants, the most efficient being the paraffin in the model blends, probably due to its partial miscibility with LDPE. In the commingled waste, liquid polybutadienes supported on precipitated SiO_2 appear to be quite efficient. No influence of the reactive compatibilization on both the crystal modification and the crystalline content was observed in both types of these blends.

Introduction

The research results show that commingled plastics waste can give a material with relatively good end-use properties[1,2,3]. The key problem of the recycling of mixed plastics is the efficient compatibilization of polymer components. Besides additive compatibilization (incorporation of polymer compatibilizers), reactive blending is used. The latter procedure is based on the application of proper radical initiators which initiate grafting and/or crosslinking reactions. Compatibilization of polyolefins by both of the above mentioned procedures has been extensively studied[4-8].

An efficient reactive compatibilization system based on the combination of liquid polybutadienes and dialkyl peroxides has been developed[9]. This compatibilizer has been successfully tested on real commingled polyolefin waste[10-12]. In spite of achieving acceptable mechanical properties of the recyclate achieved, there are often problems with processability of such material. However, good processing properties

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of the recyclate are crucial for successful applications. The results from processing of commingled polyolefin waste showed that processability of these materials is mostly worse than is the case with virgin polymer blends.

Rheological behaviour of multiphase polymeric systems is very complex. Neither acceptable description of rheological behaviour of viscoelastic particles in viscoelastic liquid, nor generally valid empirical rule has been formulated so far. However, there are many papers in the literature describing specific systems of polyolefin blends13-18). It is proved that the dependence of viscosity on composition is affected by the ratio of component viscosities and by shear stress; consequently, it does not obey the additivity rule. Application of selected lubricants makes it possible to control rheological properties of the blended polyolefins, but the lubricants might also affect the structure of these blends on different dimensional levels.

The aim of this contribution is to determine how addition of lubricants can influence the blend morphology and the crystalline phase in polyolefins and thus, the end-use properties of these multiphase polyolefin blends. Two series of the blends were studied: (a) blends of virgin polyethylene and polypropylene and (b) commingled waste of composition similar to these blends.

Experimental

Materials

Low-density polyethylene (LDPE): Bralen RA 2-19, M_w = 120 000, Slovnaft a.s. Bratislava, Slovakia; high-density polyethylene (HDPE): Liten BB29, M_w = 420 000, Chemopetrol a.s. Litvínov, Czech Republic; polypropylene (PP): Mosten 52 592, M_w = 240 000, Chemopetrol a.s. Litvínov, Czech Republic. Liquid polybutadiene (1-PB): Krasol LB 3000, M_w = 3 100, development product of Kau uk a.s., Kralupy n/V, Czech Republic. Di-*tert*-butyl peroxide (TBP): Fluka, Switzerland. Ca stearate: Setuza Ústí n/L, Czech Republic. Loxiol G20: stearic acid, Henkel, Germany. Loxiol G22: Fischer-Tropsch paraffin, Henkel, Germany, Siloxyd: precipitated SiO_2, Tonaso Nešt mice, Czech Republic. Polyolefin waste: Scraps of agricultural polyolefinic films, Transform Ltd., Czech Republic. Composition of polymer blends is given in Table 1.

Samples

Table 1. Composition of samples (wt.-%)

	Virgin polyolefin blends					Commingled waste			
	R0	R1	R2	R3	R4	TR0	TR1	TR2	TR3
LDPE	80	78.0	77.8	77.8	77.8	-	-	-	-
PP	20	19.5	19.5	19.5	19.5	-	-	-	-
Transform	-	-	-	-	-	100	97.3	97.3	95.2
1-PB		2.3	2.3	2.3	2.3	-	2.3	2.3	2.3
TBP	-	0.2	0.2	0.2	0.2	-	0.2	0.2	0.2
Ca stearate	-	-	0.2	-	-	-	-	-	-
Loxiol G20	-	-	-	0.2	-	-	0.2	-	0.2
Loxiol G22	-	-	-	-	0.2	-	-	0.2	-
Siloxyd	-	-	-	-	-	-	-	-	2.1

Scanning and transmission electron microscopy (SEM, STEM)

Fracture surfaces were obtained from fracturing the samples in liquid nitrogen. Specimens for scanning electron microscopy (SEM) were sputter-coated with platinum film of 4 nm thickness. Micrographs were taken with a scanning electron microscope JSM 6400 (JEOL).

Low-voltage scanning transmission electron microscopy (STEM) was used at 25 V to observe ultrathin sections prepared at low temperature (-130 °C; ultramicrotome Ultracut UCT, LEICA; transmission adapter to scanning electron microscope JSM 6400, JEOL). No staining was applied[19].

Wide-angle X-ray scattering (WAXS)

X-ray intensities were measured on an automatic powder diffractometer HZG4A (Freiberg Praezisionsmechanik GmbH, Germany). CuKα radiation was registered with a scintillation counter and monochromatized with a Ni filter and pulse-height analyzer. Diffractograms were taken in the range of scattering angles 4–40°.

Small-angle X-ray scattering (SAXS)

SAXS measurements were performed using an upgraded Kratky camera with a 60 μm entrance slit and 42 cm flight path. Ni-filtered CuKα radiation (wavelength $\lambda = 1.54$ Δ) was used; it was registered with a position-sensitive detector[20] (Joint Institute for Nuclear Research, Dubna, Russia) for which the spatial resolution is approximately 0.15 mm. The intensities were taken in the range of the scattering vector $q = (4\pi/\lambda) \sin\theta$ from 0.006 to 0.2 Δ^{-1} (where 2θ is the scattering angle). The measured intensities were corrected for sample thickness and transmission, primary beam flux, and sample-detector distance.

Determination of tensile impact strength

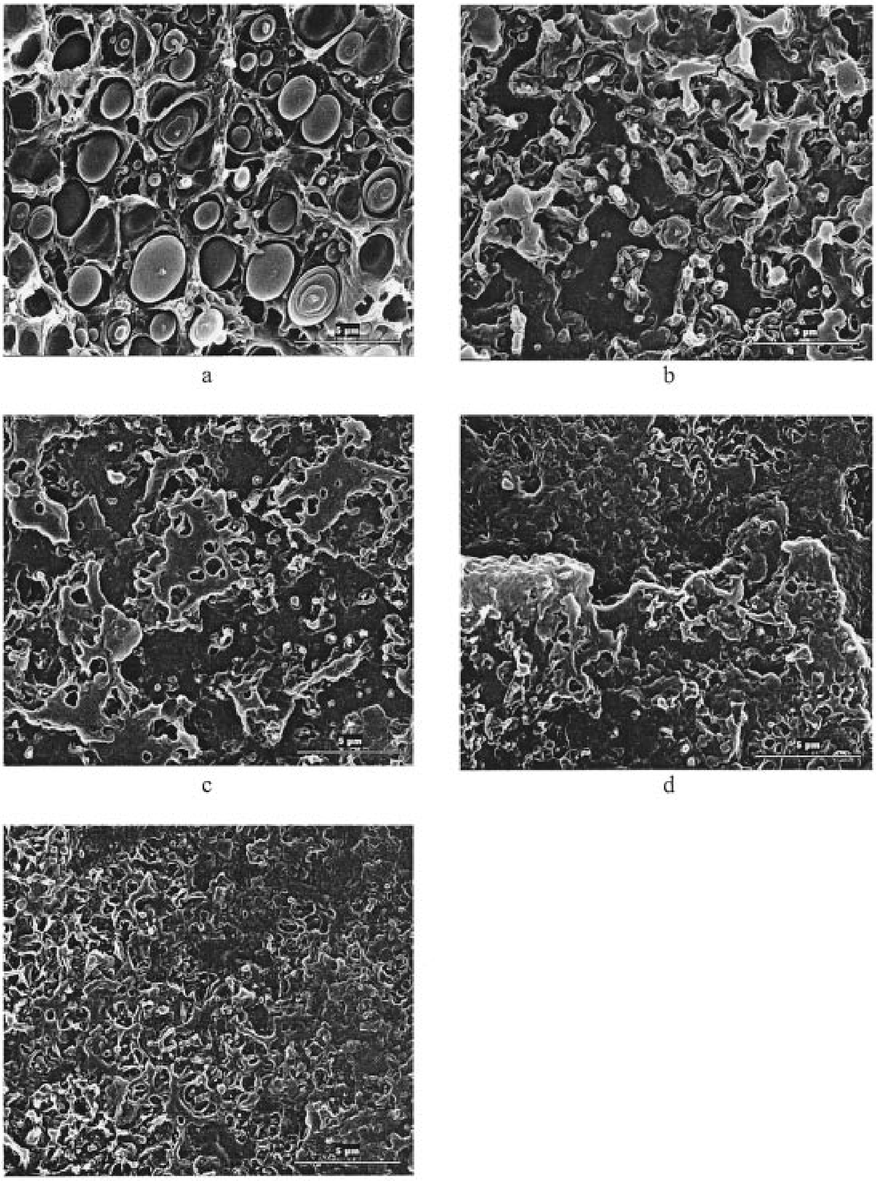
Tensile impact strength was measured at 23 °C using a Zwick tester which was equipped with a special fixture for test specimen according to DIN 53 448. The maximum energy of the pendulum was 2 J. Test specimens were cut from compression-moulded plates. The presented values are obtained from 10 measurements.

Results and Discussion

Electron microscopy

Particle sizes were evaluated from fracture surfaces and from ultrathin sections; interfacial adhesion was estimated from fracture surfaces. Both cryo-fracture surfaces and ultrathin sections reveal heterogeneous phase structure. PP particle sizes are substantially reduced in both systems of the compatibilized and lubricated blends.

The largest PP particles of the non-compatibilized model blend, up to 3 μm in size, (Fig. 1) are reduced to 0.6–1 μm in compatibilized and lubricated blends. Accordingly, very low interfacial adhesion observed in the non-compatibilized blend was enhanced on compatibilization. Differences in the phase structure between the compatibilized blends without other additives and lubricated blends are much lower than when compared with the non-compatibilized blends.



a

b

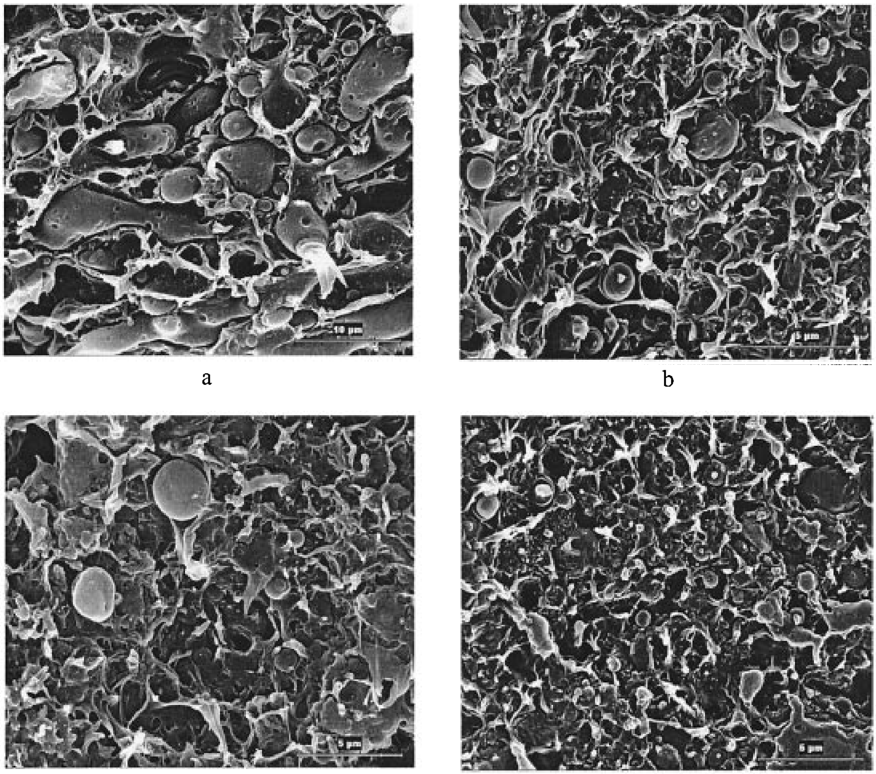
c

d

Fig. 1: Fracture surfaces of virgin polyolefin blends prepared at liquid nitrogen temperature (SEM). Blends R0 (a), R1 (b), R2 (c), R3 (d), R4 (e).

Similar trends are observed with the recycled polyolefin scrap - commingled waste (Fig. 2). Large particles of the dispersed (PP) phase in the non-compatibilized waste material (above 10 μm in size) are reduced about four times or more on compatibilization and lubrication.

The differences between the model system and the commingled waste, which can be observed from the particle size and their shape, refer to the differences in the material composition. Whereas the model systems comprise of relatively well-defined components, the recycled material contains various types of PE, the PP content is different from that in the model blends, and other impurities present in the systems have to be taken into account.



a b

c d

Fig. 2: Fracture surfaces of recycled polyolefin blends prepared at liquid nitrogen temperature (SEM). Blends TR0 (a), TR1 (b), TR2 (c), TR3 (d).

Tensile impact strength

Values of the tensile impact strength measured in both model blends and the waste material are shown in Fig. 3. In spite of the fact that the toughness of the waste material is much lower than that of the virgin polyolefins, due probably to a coarse morphology found in the waste material and also the presence of impurities, reactive compatibilization improves the tensile impact strength approximately twice in both types of blends. Positive influence on the mechanical properties can also be achieved through the addition of lubricants such as Ca stearate (blend R2), stearic acid - Loxiol G20 (blend R3) and paraffin - Loxiol G22 (blend R4). The improvement is most pronounced when the paraffin - Loxiol G22 is added into the virgin blend; in the waste material, addition of this lubricant has practically the same influence on toughness as the addition of Loxiol G20. Samples of the waste material with addition of Ca stearate are even useless from the point of view of mechanical properties; we did not include them in the structure research. On the other hand, toughness of the recycled waste material can be improved when a component taking part in the compatibilization process, SiO_2 is coated with liquid polybutadiene.

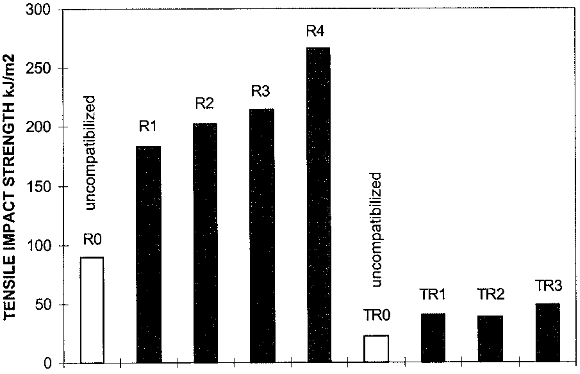


Fig. 3: Toughness of model polyolefin blends (R) and commingled waste (TR).

X-ray structure analysis

WAXS diffractograms of the polyolefin blends differ only slightly in the case of both model samples (R) and waste materials (TR). Hence, we have chosen for the demonstration of the character of the crystalline phase in these blends only 4 samples:

uncompatibilized model blend (R0), uncompatibilized waste material (TR0), compatibilized model blend R4 with addition of Loxiol G22 as a lubricant, which has the highest value of toughness, and corresponding waste material TR2 (Fig. 4). A comparison of the diffraction curves of compatibilized and uncompatibilized samples in both the model system and the waste material points to the fact that not even the reactive compatibilization influences the crystalline modification and the degree of crystallinity in these polyolefin blends.

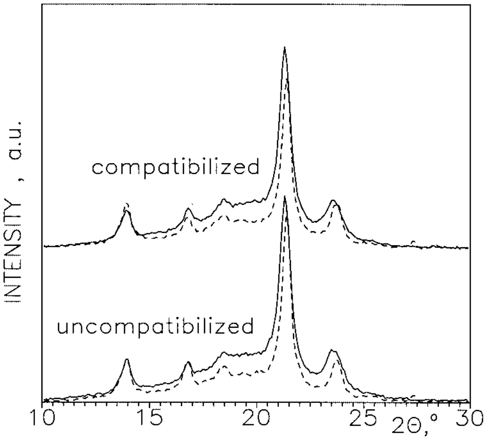


Fig. 4: WAXS diffractograms of model blends (solid lines) and waste material (dashed lines).

Profile analysis of the WAXS diffractograms, using the program FIT[21], is shown in Fig. 5 for the R4 sample. Parameters obtained on the basis of the profile analysis of this sample and the corresponding waste material TR2 are given in Table 2. In spite of the fact that separation of the PE and PP contributions from the whole diffraction curve is difficult, as the strong (110) PE reflection is superimposed onto (111), (131) and (041) -relatively weak reflections of PP- it is clear that compositions of the model blend and the waste material differ significantly.

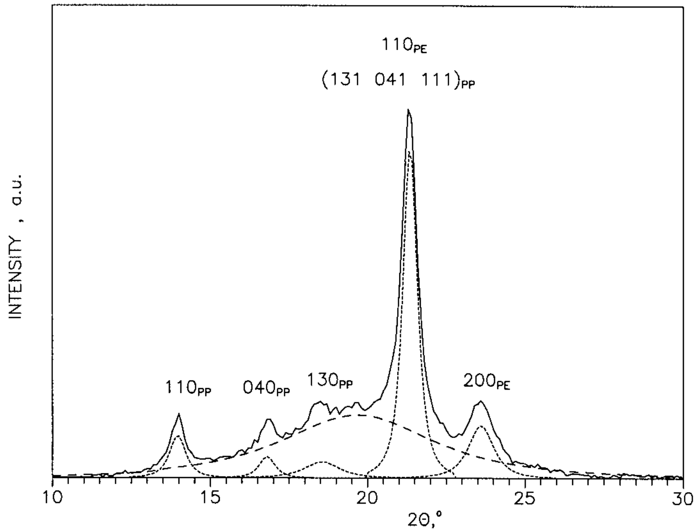


Fig. 5: Profile analysis of the uncompatibilized model blend R4: —— experiment; - - - - common amorphous halo of PE and PP; "‥‥" profiles of PE and PP reflections.

The relative increase in the integral intensity of the selected PP reflections found in the diffractograms of the waste material in comparison with this value in the model blend, points to a higher amount of PP in the waste material than it was expected. The decrease in the half-widths of the PE reflections points to better ordering of the crystalline phase and larger size of crystallites, which is typical of high-density polyethylene (HDPE). Hence, it appears that also the character of the polyethylene component in the waste material is not the same as it is in the model blends, in spite of the fact that the model blends were prepared to match the most common composition of the waste material.

Our assumption about the presence of HDPE in the waste material instead of LDPE was confirmed also by SAXS. In Fig. 6, SAXS curves of both model blends, R, and recycled waste material, TR, are plotted as $I \times q^2$ vs. q. On SAXS curves of the recycled material, an increase in the intensities for $q \rightarrow 0$ is observed in comparison with those of the virgin blends (indicating the presence of impurities in the waste) and also a shift of the interference maximum corresponding to the long period, L_P, typical of semicrystalline polymers. From the position of this maximum, the long period for blends R4 and TR2 was determined to be 110 and 160 Δ, respectively (see Table 2). This corresponds with the results of WAXS as higher values of L_P are usually found for HDPE than for LDPE, due to the better development of the crystalline phase.

Table 2. Parameters of the crystalline phase in the PE/PP blends

Blend	$(w_{cr})_{tot}$	$I(110)_{PP}/I(200)_{PE}$	$I(040)_{PP}/I(200)_{PE}$	$(h_{sum})_{PE+PP}$ deg	$(h_{200})_{PE}$ deg	L_p Δ
R4	0.46	0.69	0.30	0.56	0.92	110
TR2	0.48	1.06	0.43	0.47	0.59	160

Total degree of crystallinity, $(w_{cr})_{tot}$, is given by the ratio of integral intensities of the sum of PE and PP crystalline reflections and the overall scattered intensity; h_i is the half-width of the i-th reflection in deg; $(h_{sum})_{PE+PP}$ is the half-width of the strong complex peak at $2\Theta = 21.3°$, where the contribution of the 110_{PE} reflection is dominant; long period, L_p, corresponds to alternation of crystalline and amorphous regions in semicrystalline polymers.

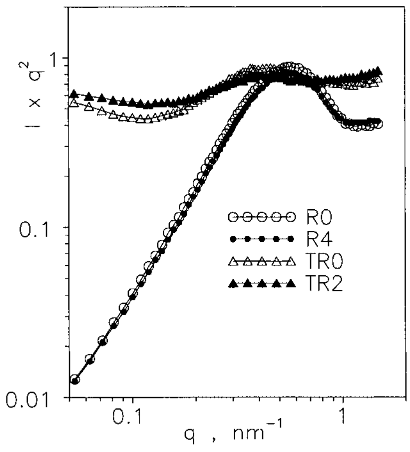


Fig. 6: SAXS curves of model blends (R) and waste material (TR).

It is practically impossible to find structural changes of the blends after addition of such a small amount of a lubricant as 0.2 wt.-%. In order to explain the remarkable increase in toughness of model polyolefin blend with addition of the Loxiol G22 lubricant (R4), we prepared mixtures of the components of these blends, PP or LDPE, with 10 wt.-% of the used lubricants: Ca stearate, stearic acid (Loxiol G20) or paraffin (Loxiol G22) and we studied the structure of these blends.

Though the WAXS curves point out to a decrease in the overall degree of crystallinity in both PP/lubricant and LDPE/lubricant blends with an exception of LDPE/Loxiol G22 sample, this evidence is not very pronounced. Nevertheless, it seems that the paraffin lubricant is miscible with this component of the model LDPE/PP blends. We verified this assumption also by means of SAXS experiments (Fig. 7). It is clear that the SAXS curves of all mixtures are composed of independently scattered components, LDPE + lubricants and PP + lubricants, with the exception of LDPE + paraffin (Loxiol G22). As the curves of LDPE and LDPE/Loxiol G22 (9/1) are virtually the same, we suppose that this lubricant is miscible in this concentration range with LDPE and cocrystallization of these two components occurs. Thus, the paraffin Loxiol G22 acts as a low-molecular-weight lubricant in a melted blend but in the solid state it does not form an additional phase in the blend lowering its toughness, as it is in the case of Ca stearate and stearic acid.

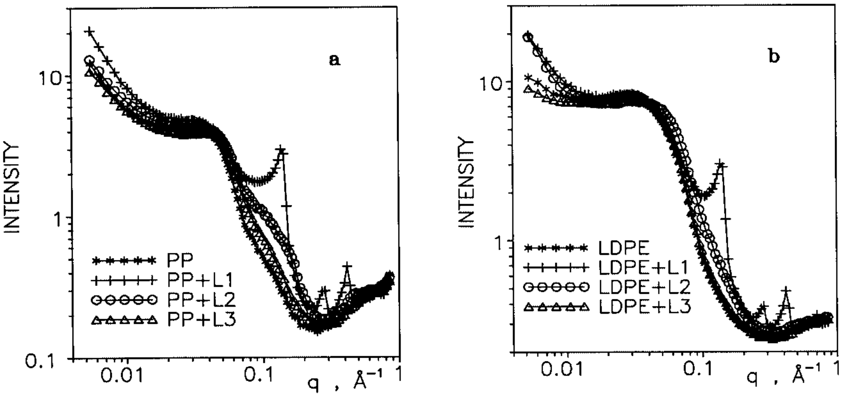


Fig. 7: SAXS curves of PP (a) and LDPE (b) with addition of 10 wt.-% of lubricants: L1-Ca stearate, L2-Loxiol G20, L3-Loxiol G22.

Due to the finding that in the waste material HDPE prevails instead of LDPE, we have also prepared blends of HDPE (Liten BB29) with paraffin (Loxiol G22) and the SAXS curves of both HDPE and HDPE/paraffin (9/1) were measured (Fig. 8). It is evident that, unlike the case of LDPE, paraffin is not miscible with this type of polyethylene. Here, the SAXS curve of Loxiol G22 is superimposed on the curve of HDPE as it was observed in blends of other lubricants with LDPE and for all three lubricants with PP.

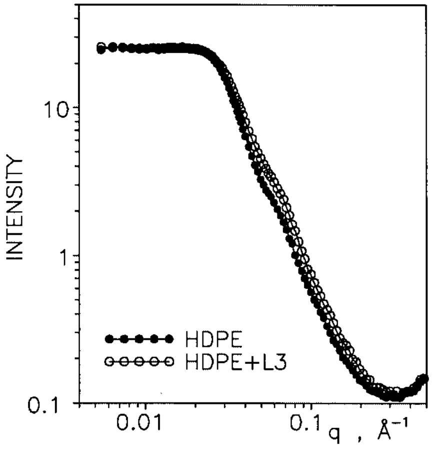


Figure 8: SAXS curves of HDPE + 10 wt % lubricant L3-Loxiol G22.

Different miscibility of paraffin Loxiol G22 with LDPE and HDPE might be the reason why addition of this lubricant to the model polyolefin blends containing LDPE improves both phase dispersion and toughness, but it has no effect if added to the waste material, where the polyethylene component was found to be predominantly HDPE.

Conclusions

In spite of the fact that analysis of WAXS data shows that the PP content in the waste material is higher (~30%) than in the model blends and that the waste material contains predominantly HDPE instead of LDPE (in contrast to the model blends), the reactive compatibilization improves both particle dispersion and the tensile impact strength approximately twice in both types of the blends. The compatibilization efficiency is enhanced by addition of lubricants. The most effective lubricant in the model LDPE/PP blends appears to be paraffin Loxiol G22 as it is miscible with the polyethylene component of these blends. This lubricant is not effective in the transform (waste) material due to the presence of another type of polyethylene here. For the waste material, the best compatibilization results were obtained with liquid PB anchored on SiO_2.

Although the reactive compatibilization in the presence of lubricants leads to much finer morphology (a remarkable decrease in the particle size), no changes of the PP or PE crystalline phase were observed in both types of the compatibilized blends in comparison with the uncompatibilized ones.

An important conclusion should be made on the basis of the results obtained: the composition of the commingled waste is variable and hence, this material has to be carefully characterized before starting compatibilization, especially with respect to the choice of a proper lubricant.

Acknowledgement

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