Migration Study of Polypropylene (PP) Oil Blends in Food Simulants

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Summary: Migration study in aqueous and olive oil food simulants was carried out on PP and its blend with oil mixture. It was found that after 10 days at 44 °C PP with oil content up to 0.83% had overall migration into olive oil less than 10 mg/dm^2. However, under high temperature migration test (at 110–138 C for 4 hours), the overall migration into olive oil was large for both the virgin PP and all its blends. The overall migration in water, 10% ethanol, and 3% acetic acid was smaller than those in olive oil under both migration test conditions. DSC and density measurement showed that addition of oil in PP led to smaller spherulite size and increased degree of crystallinity in the pure PP part. Small decrease in tensile strength in the oil blends was also observed but there was no significant change in tensile strength after migration test.

Keywords: crystallinity; migration test; oil; PP

Introduction

Thermoplastic polymers have widespread applications in our daily life. In order to incorporate color in the polymer, several methods can be used. For example, the pigment and colorants can be directly mixed with polymer granular during polymer processing, which could result in non-homogeneous dispersion of colorant in the polymer matrix; high concentration pigment masterbatch is then a better material to mix with polymer granular to get universal dispersion. The third choice is to disperse pigment or colorant in liquid oil and then mix with polymer granular during processing, by which a fine dissolution or dispersion of colorant in oil can be reached before mixing and homogeneous distribution can be obtained in a large scale.[1] The disadvantage of the last method lies in that a relatively good compatability of oil with polymer must be obtained to realize the mixing process and the migration resistance of oil and colorants in the final product into different media could make some restriction on the amount of oil that can be used.

Polypropylene is an important commercial thermoplastic polymer. It can be compounded to different products by blending with other polymers and inorganic material to enhance its application area and replace some traditional polymers.[2–7] Since PP is a semicrystalline polymer, it has been found that the properties of these blends are very dependent on the crystallinity, crystalline morphology, and degree of dispersion of the blend. For example, the impact strength of elastomeric impact modifiers in PP blend was influenced by the incorporation of modifiers which change the superstructure of PP by decreasing the spherulites size.[7] The change in crystallization behaviour in different PP blends has been investigated by many research groups.[2–12] In addition, it is not only the mechanical properties but also the diffusion properties of small molecules in semicrystalline polymer and its blends that will be changed with different crystal morphology and superstructure. For example, Gedde and Hedenqvist et al. had studied the influence of chain branching, free volume, and crystal morphology on the diffusion property of polyethylene.[13,14]

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Paraffin oil and fatty acid esters have been used as lubricants for PP processing. They have good compatability with PP which can also be used as dispersing oil for pigment and colorants. In this work, the mixture of the above two oil components was blended with PP at different amount and the migration resistance of oils in different food simulants were tested. The changes in the tensile strength, the morphology of spherulite, and the degree of crystallinity were studied and compared in the blends.

Experimental

Materials

The PP granular (HH315 MO) was commercial product from Borealis. Edenol was polyunsaturated fatty acid esters. The PP, edenol and paraffin oil were provided from Controlled Polymers, Denmark. Triheptadecanoin (glyceryl trimargarate) (99.9%, Sigma Aldrich), trifluoroboron methanol solution for synthesis (20%, Merck) were used for fatty acid ester derivatization. All other chemicals used in migration test were of analytical grade.

Sample Preparation

Pre-weighed PP granular was mixed with defined amount of a 50:50 (v/v) mixture of paraffin oil and edenol. The mixture was then fed into the injection molding machine (Battenfeld BA 500/200 CD, Unilog 4000 B2 from Germany). The operating temperature for the three zones and die were 230, 220, 220, and 225 °C, respectively. The dumbbell shape bars with dimension of $14.7 \times 1 \times 0.2$ cm^3 and $14.7 \times 1 \times 0.3$ cm^3 were made for virgin PP, and PP blend with 0.53%, 0.96%, and 1.82% oil mixture. The oil content is the added oil mixture in the PP granular before feeding.

Migration Test at Low Temperature

The migration test was carried out according to Danish/European standard DS/EN 1186. In each migration test glass tube, two pieces of injection molded bars with dimension $14.7 \times 1 \times 0.3$ cm^3 (surface area of 0.51 dm^2) and $14.7 \times 1 \times 0.2$ cm^3 (surface area of 0.48 dm^2) were immersed in 65 ml of food stimulant and sealed with glass stopper. The samples were inserted into glass beads that added at the bottom of the test tube in order to avoid sample floating up to the surface of the liquid. Four kinds of food simulants were used, which were olive oil, distilled water, 10% (v/v) ethanol, and 3% (w/v) acetic acid. Three replicates were made for each sample and in case of migration in olive oil, four replicates were made. The samples in the migration tube were then put into oven at 44 °C. After 10 days, the samples were taken out and weighed again. Blank run was done at the same temperature in the empty tube.

For the aqueous food simulants, the aqueous liquid was collected and evaporated by a water vacuum pump at 55 °C to get the weight of the migrated residue. For the migration test in olive oil, the samples were Soxhlet extracted with n-pentane, the dried extracts were then derivatized to get fatty acid methyl ester before GC/MS separation and quantification. GC/MS analysis was done on Varian 3800 GC coupled with Saturn 2000 MS detector and 8200 CX autosampler for sample injection (all from Varian Chromatography Systems Walnut Creek, CA, USA). The 50 m CP-select CB for FAME column (i.d. = 0.25 mm, d_f = 0.25 μm, Chrompack) was used. The GC temperature program was held at 160 °C for 1 min followed by increasing to 250 °C at 10 °C/min and held at 250 °C for 5 minutes. The injector temperature was 300 °C and helium flow of 1 ml/min was used. The mass spectroscopy detector was operated with EI ionization mode, and atomic mass range from 60 to 650 was collected. The myristic acid (C14 fatty acid), oil mixture and olive oil were derivatized for the calibration of oil mixture and olive oil.

The total migration into aqueous media ($M_{aqueous}$) and into olive oil (M_{oilve}) was calculated according to the following equations:

$$M_{aqueous} = \frac{(m_a - m_b) \times 1000}{S} \quad (1)$$

$$M_{olive} = \frac{[m_{a'} - (m_{b'} + m_d - m_c)] \times 1000}{S} \quad (2)$$

Where $M_{aqueous}$ (mg/dm^2) is the total migration into the stimulant; m_a (g) is the mass of the residue from test specimen after evaporation of the stimulant in which it had been immersed; m_b (g) is the mass of the residue from the blank stimulant; S (dm^2) is the surface area of the test specimen that come into contact with food simulant; M_{olive} (mg/dm^2) is the total migration into olive oil; $m_{a'}$ (g) is the initial mass of the test specimen before contact with olive oil; $m_{b'}$ (g) is the mass of the test specimen after contact with the olive oil; m_d (g) is the mean loss in mass of the test specimens in the empty tubes; m_c (g) is the mass of olive oil absorbed by test specimen.

Migration Test at High Temperature

The migration test at high temperature was done by using Kjeldatherm heating block (Gerhardt, Germany). The samples that immersed in the aqueous food simulants (200 ml) were heated up to boiling temperature and kept for 4 hours, while in olive oil the temperature range was from 110 to 138 °C. Blank run was done by putting the original samples in oven at 110 °C for 4 hours. Same treatment was done after the migration test as in the low temperature migration test.

Tensile Test

Tensile stress of the dumbbell bar was tested on Instron LR50K using a 5000 Newton load transducer with the crosshead speed of 60 mm/min. The deviation of the tensile strength measurement was lower than 3.5%.

Density Measurement

The density of the dumbbell bar was measured by immersing the bar into a mixture of ethanol and water solution. When the bar could stay in the mixture without moving up or moving down, the density of the liquid mixture was then measured and taken as the density of the bar. 3 to 5 replicates were made for each sample.

Polarized Light Microscopy (POM)

Thin piece of 1 μm was cut from the dumbbell bar and the spherulite was observed under an Olympus polarized light microscope with magnification of 400 times.

Differential Scanning Calorimetry (DSC)

The DSC was run on a Mettle Toledo DSC 822^e equipped with a sample robot TSO 801RO. One piece sample with thickness of 275 μm was cut and put into aluminum pan for the measurement. The temperature program was heating the sample from 25 to 200 °C at a rate of 10 °C/min. N_2 flow of 40 ml/min was used in all measurements.

Results and Discussion

Migration Test in Olive Oil

Figure 1 shows the GC/MS results on the derivatized extracts. In the virgin PP there was found fatty acid esters with carbon chain number of C14, C16 and C18, which indicates that fatty acid ester lubricant was present in the virgin PP granular. The derivatized oil mixture contains fatty acid with carbon number C14, C16, C18, and C18:1. In the olive oil there found fatty acid with carbon number of C16, C18, C18:1 and C18:2. Therefore, the C18:2 methyl ester peak was used for quantification of absorbed olive oil, while C14 methyl ester peak was used for oil mixture quantification. In case that the virgin PP contained C14 peak, the calculation of oil mixture content in the oil/PP blend sample was done by first subtracting the corresponding C14 content that found in the virgin PP (0.0068% by weight). The oil mixture content found in the oil/PP blend (Table 1) was lower than the added amount, some loss of the oil on the surface of the hopper could give the deviation. In order to check the extraction efficiency of oil mixture in the original PP and its blends, the injection molded bar was cut into 60 μm thin films before Soxhlet extraction and compared with those extracted directly from the 2 mm thick injection molded bars. It was found

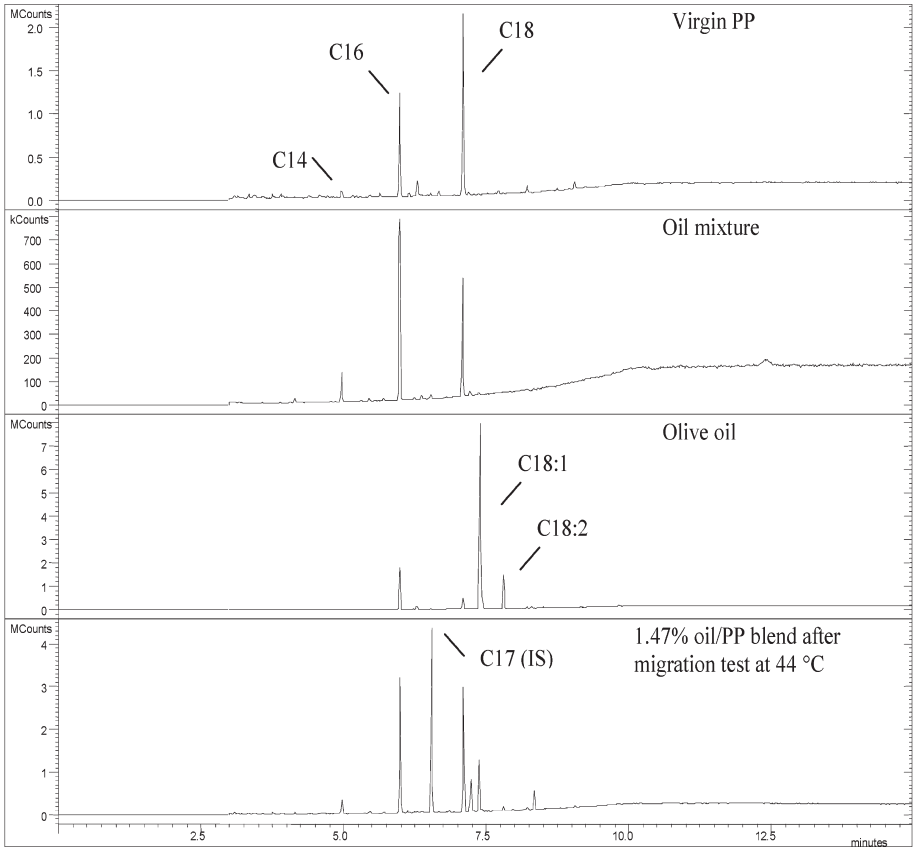

Figure 1.
The GC/MS chromatogram of the derivated extracts from virgin PP, oil mixture, olive oil, and 1.47% oil/PP blend after migration test in olive oil at 44 °C for 10 days.

that in case of 0.53% and 0.96% oil/PP blend the results were close, but in 1.83% oil/PP blend, the extracted oil from the 2 mm injection molded bar (1.28%) accounted for only 87% of those extracted from the 60 μm thin film (1.47%). However, after migration test, the extraction efficiency was similar for the thin film and 2 mm thick bar.

Table 1 lists the migration results for PP and its blends carried out at different temperatures. Fatty acid ester lubricant was migrated out from the virgin PP and the sample absorbed similar amount of olive oil as that of 0.39% oil/PP blend. It can be seen that after low temperature migration test the amount of migrated oil mixture is higher than the total migration into olive oil. Since only the fatty acid ester in the oil mixture can be quantified, the high amount of migrated oil mixture that found after migration test accounted most probably for the migration of fatty acid ester into olive oil, where more fatty acid ester could locate at the surface of the sample. On the other hand, the paraffin oil could act as a better internal lubricant and disperse more at the inside of the sample and be more resistant to migration. When the samples were tested at high temperature, all the oil mixture migrated out together with some other additives. Again it can be seen that relatively less amount of olive oil was absorbed in the 0.39% oil/PP blend than those in the sample with higher oil mixture content.

Table 1.
The oil mixture and absorbed olive oil contents before and after the migration tests.

Sample	Absolute C14 acid content (wt% × 10^2)	Oil mixture content (%)	Absorbed olive oil[a] (mg/dm^2)	Total migration into olive oil[b] (mg/dm^2)
Virgin PP	0.68	/	/	/
0.53% oil blend	1.21	0.39	/	/
0.96% oil blend	1.85	0.85	/	/
1.83% oil blend	2.43	1.47	/	/
Virgin PP[c]	0.50		6.25 (0.083)	1.15 (0.015)
0.53% oil blend[c]	1.07	0.28	6.46 (0.085)	2.91 (0.039)
0.96% oil blend[c]	1.66	0.72	9.48 (0.125)	9.27 (0.122)
1.83% oil blend[c]	2.28	1.17	12.3 (0.162)	17.3 (0.228)
Virgin PP[d]	0.25		123 (1.55)	31.6 (0.422)
0.53% oil blend[d]	0.48		136 (1.69)	46.7 (0.616)
0.96% oil blend[d]	0.39		197 (2.45)	57.0 (0.751)
1.83% oil blend[d]	0.60		270 (3.36)	118 (1.561)

[a] The value in parenthesis is the corresponding wt% of oil mixture in the sample calculated according to the absorbed olive oil.
[b] The value in parenthesis is the wt% of the total migrated residue into olive oil.
[c] The samples were immersed in olive oil at 44 °C for 10 days,
[d] The samples were immersed in olive oil between 110 to 130 °C for 4 hours.

Migration Test in Aqueous Media

Table 2 shows the migration results in different aqueous media for the PP and its blends. The migration into different aqueous media at 44 °C for all samples are quite low with maximum value of 2.4 mg/dm^2, which corresponds to about 0.1 % of the total weight of the sample. However, the ingredients migrated out at 100 °C for 4h was about two orders higher than those at low temperature ranging from 7 to 28 mg/dm^2. The derivatization on the migrated residue from 0.85% oil/PP blend in ethanol solution followed by GC/MS analysis shows that fatty acid esters is present in the residue.

Polarized Light Microscopy and Density of PP and its Blends

Figure 2 shows the polarized light microscopy of PP and its oil blends. Comparing the spherulites in different samples, it can be seen that the virgin PP has relatively larger spherulites and the size of the spherulites varied in a big range. Very small spherulites were formed when 0.39% of oil mixture was added, the spherulites size increased but still smaller than the large ones in the virgin PP with increasing oil content in the blend. Since more fatty acid ester seems to disperse at the surface of sample bar, whether it took the role as weak nucleating agent is not clear in this case.

Table 2.
The total migration into different aqueous media at different temperatures.

sample	Distilled water (mg/dm^2)	10% ethanol (mg/dm^2)	3% acetic acid (mg/dm^2)
Virgin PP[a]	0.1	0.5	0
0.39% oil blend[a]	1.4	0.3	0.1
0.85% oil blend[a]	2.4	0	0.47
1.47% oil blend[a]	0.4	0.3	1.2
Virgin PP[b]	11.4	9.8	7.0
0.39% oil blend[b]	27.9	10	14.0
0.85% oil blend[b]	8.6	12.8	23.2
1.47% oil blend[b]	10.3	11.5	27.6

[a] the samples were immersed in the media at 44 °C for 10 days.
[b] the samples were immersed in the media at boiling temperature for 4 hours.

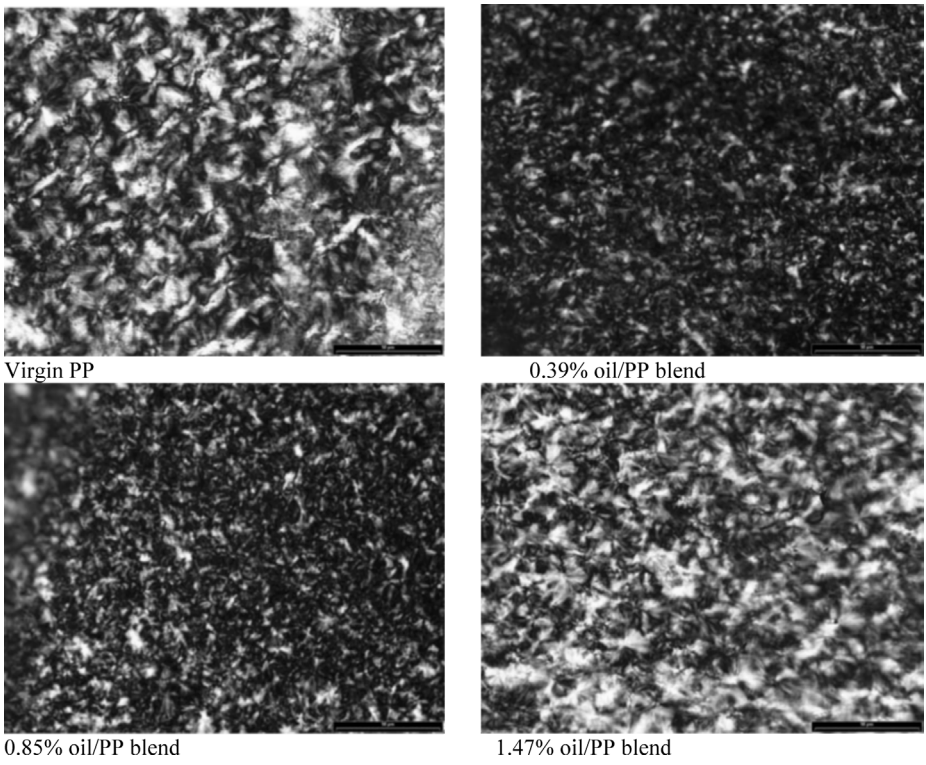

Figure 2.
The polarized light microscopy of PP, 0.39% oil blend, 0.85% oil blend, 1.47% oil blend.

Similar decreased spherulite size were also found in the PP and elastomer (EPM, SBS) blend.[7] Results from density measurement were listed in Table 3, where the density of pure PP part was calculated according to the PP amount in the blend. Oil mixture has lower density (0.8546 g/ml) than that of virgin PP and the density of the blends should decrease with increasing oil content by assuming no change in the volume and the density of each component after blending. The density measurement indicates that except for the 0.85% oil/PP blend, the overall degree of crystallinity in the blend kept nearly the same (0.39% oil) or slightly higher (1.47% oil) than that of the virgin PP.

DSC Study on PP and its Blends before and after Migration Test

The melting temperature and melting enthalpy of different samples was measured on DSC. The results shown in Table 3 indicate that the 0.39% oil blend have slightly higher melting enthalpy than the virgin PP, which is in agreement with the density measurement (the density for the pure PP part was calculated to be 0.9096 g/cm^3). The 1.47% oil blends had slightly higher PP density (0.9106 g/cm^3) than that of the 0.39% oil blend from the density measurement, but the melting enthalpy for pure PP in this sample from DSC study was slightly lower than the 0.39% oil blend. Therefore, it is assumed that there exists much more free volume in the 1.47% oil blend, which could be due to the increased spherulite size and more free volume created between the bigger spherulites and in the amorphous phase where oil locate. In case of the 0.85% oil blend, the smallest density and melting enthalpy was found, it is unclear whether the small value is caused by the small spherulite size and

Table 3.
The density and melting enthalpy of PP and its blends.[a)]

Sample	PP	0.39% oil	0.85% oil	1.47% oil
Density (g/cm^3)	0.9096	0.9095 0.9096[b)] 0.9094[c)]	0.9088 0.9093[b)] 0.9091[c)]	0.9097 0.9106[b)] 0.9088[c)]
ΔH (J/g)	88.4	89.2 89.6[b)]	80.6 81.2[b)]	87.4 88.7[b)]
ΔH[d)]	93.2	92.2	93.8	91.4
ΔH[e)]	99.1	96.6	94.8	102.4

[a)] The estimated error in the density and melt enthalpy measurement is $\pm$ 0.0001 g/cm^3 and $\pm$ 3.0 J/g, respectively. The relative standard deviation with 5 replicates is lower than 5%.
[b)] The calculated value is the density or the melt enthalpy of pure PP part in the sample.
[c)] The density is calculated by assuming no change in the volume and density of PP and oil mixture after mixing.
[d)] The melt enthalpy of the sample after staying at 44 °C for 10 days.
[e)] The melt enthalpy of the sample after staying at 110–138 °C for 4 hours.

big free volume in the sample or some fault in the sample preparation during the injection molding.

The above results indicate that there was more free volume in the virgin PP, the PP blend with 0.85% and 1.28% oil. The free volume in these samples could make the sample absorb more olive oil. For example, the virgin PP absorbed similar amount of olive oil as that of the 0.39% oil/PP blend even though there was no oil added in the sample, and in spite of the fact that there existed both large and small spherulites in the virgin PP which could make the absorbance of olive oil more difficult than those of 0.39% oil blend in which there were more smaller spherulites.[13,14] With increasing amount of oil (0.85% or more), more free volume could be generated and facilitate the absorbance of olive oil into the sample and more oil migrated out from the sample.

The melting temperature doesn't deviate so much. The degree of crystallinity increased also after both low and high temperature migration test, which indicate crystal perfection in the sample.

Changes in the Tensile Strength before and after Migration Test

The change in tensile strength for different samples is shown in Figure 3. The tensile strength of PP/oil blend decreased by 0.33%, 1.12%, and 5.6% with increasing oil content, respectively.

Blank test of PP and its blends at low and high temperature migration conditions lead to increased tensile strength for all the samples due to the crystal perfection at increased temperatures. No significant decrease in tensile strength in PP and its oil blend samples was found after low and high temperature migration test either in olive oil or aqueous media.

Conclusion

Migration test in olive oil shows that at 44 °C the fatty acid ester near the surface of the blends accounted for the most part of migration into olive oil. The 0.39% oil/PP

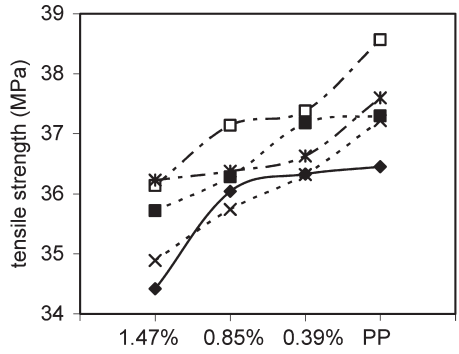

Figure 3.
The change in tensile strength after migration test in olive oil. (◆) original, (■) blank after 10 days at 44 °C, (□) blank after 4h at 110 °C, (×) after 10 days in olive oil at 44 °C, (*) after 4h in olive oil at ≥110 °C.

blend showed small absorption of olive oil as that of virgin PP due to the densely packed small crystals in the sample. Increased amount of oil in PP lead to slightly increased spherulite size but larger free volume and resulted in the increased amount of absorbed olive oil after migration test. Migration test at high temperature showed similar tendency, and in addition, all the added oil mixture migrated out together with other additives. The oil/PP blend had nearly no migration into different aqueous media at 44 °C. The tensile strength decreased a little with the addition of oil mixture, no significant decrease in tensile strength was observed after migration test under both high and low temperatures.

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