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A modified Polypropylene Resin for Food Packaging

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Abstract. The slip agents used to reduce coefficient of friction of polypropylene(PP) film, but it migrate brought the issue of food safety, to reduce of the corona effect and the peel strength of flexible film. We try another method to reduce the coefficient of friction. The result shown that the nano-modification not only reduces the coefficient of friction of PP, but also reduces the adsorption of volatile organic solvent in PP. The coefficient of friction of modified polypropylene was reduced by 50% when the concentration of nano-silica is between 1~2%. The final residues toluene in modified polypropylene was reduced to zero when the concentration of nano-silica in PP is between 1~3%. The modified polypropylene agrees quite well with food safety.

Introduction

The consumption of polypropylene flexible packaging in the field of food packaging increased year by year. But the pure PP film is not suitable for requirements of automatic packaging line because the coefficient of friction(COF) of polypropylene film is between 0.5~ 0.6 generally [1,2]. Now add the slip agent has been used way to reduce the friction coefficient of PP film [3,4]. Although slip agent can reduce the friction coefficient of PP's film to 0.2 ~0.3, but its migration brought the issue of food safety, at the same time reduce corona effect and the peel strength of dry lamination film. There is no other effective way to reduce the friction coefficient of film so far. Furthermore the Hansen Solubility Parameters (δ) of PP is similar with toluene and ethyl acetate, which are organic solvents in printing ink or laminating binder, it leads to high adsorption and difficult desorption[5,6] of solvent on the polypropylene films. The food safety incidents caused by the solvent residue occur sometimes.

Experimental Part

Materials

Nano SiO_2 agen:self-made by the criterion described in reference [7] and named as type NS-2.

Polypropylene powder: TC-0, standard of Q/HC001-1898, batch number:12148101, made by China National Bluestar Group Corporation Tianjin Branch.

1010 antioxidant: food-grade, made by CIBA Company.

168 antioxidant: food-grade, made by CIBA Company.

Calcium stearate(CaSt): food-grade, market buyed.

Equipments

High speed mixer: GH-50, manufactured by Beijing Yingte Plastic Machinery Co., Ltd.

Homodromous twin-screw compounding extruder:CTE35,screw diameter 35.6 mm,speed 600 r/min, aspect ratio L/D=28,Coperion（Nanjing）mechanics made.

Automatic video contact angle-meter: DSA100,Made by Germany Kruss Co.Ltd.

Differential scanning calorimeter:DSC-200PC,Netzsch company.

E3000 Test Iinstrument Electronic dynamic testing machines, Instron Corporation Manufacturing.

Slip and friction tester TMI 32-07, manufactured by USA TMI Testing Machines Inc.

Form Talysurf Intra, manufactured by Taylor Hobson Limited
CSPM 4000 Atomic Force Microscopy(AFM) made by Benyuan Co., Ltd.
FE-SEM S-4800 SEM made by Hitachi High Technologies America, Inc.

Sample Preparation

Table1. Raw material ratios of preparation of modified PP

Component of Modified PP(g)					
Sample	NS-2	1010	168	CaSt	PP
0	0	3	3	2	3000
1	15	3	3	2	3000
2	30	3	3	2	3000
3	90	3	3	2	3000
4	150	3	3	2	3000

PP resins were mixed with Nano SiO2 agent NS-2 (SiO2 content of 10%, the rest is EVA resin), antioxidant 1010, antioxidant 168 and Calcium stearate (CaSt) in high speed mixer for 5 minutes, the raw material ratios is shown in table 1.

The blended raw materials were melted and extruded in twin-screw compounding extruder and the details are shown in table 2.

Table 2. Melting blend conditions of modified PP

Each region temperatures of extruder/℃						
Heat region	1	2	3	4	5	6
T/℃	160	178	195	219	220	223

The modified PP materials were then put in plastic injection molding machines or plate vulcanizer to produce different samples for the following test.

Analytic Measures

Measure of COF. The static and dynamic coefficients of friction of plastic film tested in according with the standard ASTM D1894.

Measure of Roughness. The roughness of the PP sheets measuresed by Form Talysurf Intra, R/19×0.25mm/G/30/LS Line, 5.1mm/Admin/surface profiler.

Analysis of surface morphology. The surface morphology of the PP sheets measuresed by Atomic Force Microscope (AFM, CSPM5000 , made by Being Nano-Instruments) .The scanning size was 20μm×20μm, and the scanning frequency was set at 1.0 Hz.

Residual Toluene. Put PP sheets in 60°C oven and weighted after 24h drying in dryer. Then drop four toluene droplets on PP surface in different positions of the same side, weigh the PP sheets after 15 minutes in 25°C. The residual toluene in PP could be calculated relatively as the weight increase of PP sheets.

Results and Discussion

Effect of NS-2 on friction coefficient

The friction coefficient of ordinary unmodified polypropylene film is between 0.5~ 0.6 generally and not suitable for automatic packaging lines. To reduce PP's COF is achieved using slip agents such as silicone or fatty acid amides, which can modify the surface properties of the PP film. Stearamide, oleamide and erucamide are common slip agents used to reduce friction effects to 0.2~0.3 in polypropylene (PP) film processing.

Although there is no direct evidence that those slip agents are not harmful on the human body, we try to avoid pollution food contamination. Other methods to reduce the film COF have not been proposed. There are many reports that Nano-modification can reduce the size of PP's spherulites [8~11]. We had drawn the same conclusion when we used NS-2 to modify PP's spherulites indeed have become smaller [12]. With the increasing amount of NS-2, the spherulite's size decreases. In addition level 0.5% of NS-2, the spherulite size of PP falls within 50 ~ 500 nm and only a small amount of particle diameter of 50 microns, the diameter of most particles are more than 500 microns. In addition level 3% of NS-2, the proportion of particles of 50 microns in diameter is about 50%. In addition level 5% of NS-2, the spherulite's size of most fall the range of 50 ~ 100.

The smaller spherulite's size of modified PP, the outer surface of PP film is more smooth, COF of PP film is lower. As can be seen from fig. 2, the static and dynamic COF of unmodified PP were 0.35and 0.33 respectively, the static and dynamic COF of modified PP were much lower than unmodified PP. In particular 2# sheet with 1% of NS-2, its value of COF is lower than 50% compared to the 0# sheet .

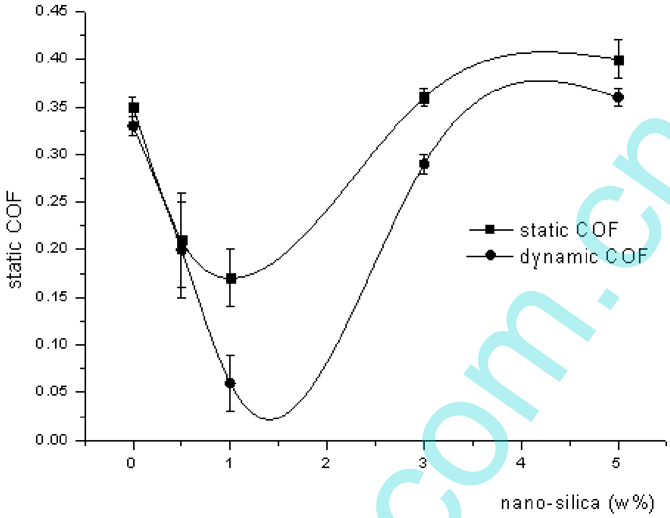

Fig. 2 The COF of modified PP

But when the concentration of NS-2 is 5% in the PP, the COF of modified PP's film has increased, instead. In order to discover the reasons for the above-mentioned changes in COF, the surface roughness analysis were measured by Form Talysurf Inductive, the testing results of unmodified and modified PP's sheets are listed in table 3. From the results, it can be seen the roughness parameters (Ra) of unmodified PP (0#) is 0.089, and the Ra of modified PP's film were greatly reduce, except the 4# sample.

Table 3 The surface roughness of modified PP's film

samples	0#	1#	2#	3#	4#
Ra [um]	0.089	0.050	0.071	0.057	0.088
Sa [nm]	22.8	6.2	2.3	2.5	21.9
Sq [nm]	30.8	8.8	3.1	3.4	27.8
Sy [nm]	240.8	87.5	29.4	31.8	204.1
Sz [nm]	219.9	87.2	28.3	30.1	197.4
Sds [1/um^2]	2.52	3.7	23.8	16.4	1.95

Furthermore the visual surface topographies are given by AFM analysis. There are many peaks and troughs on the surface of unmodified PP's film. The following parameters,such as Sa, Sq, Sy and Sz, were obtained through AFM analysis. The *Sa* is roughness average, the *Sq* is the root mean square (RMS) parameter of roughness average. The peak-peak height, are denoted by two parameter names *Sz* and *Sy*, according to ISO and reference [13]. They are defined as the height difference between the highest and lowest pixel in the image: $S_z=S_y=Z_{max}-Z_{min}$. The Density of Summits, Sds is a parameter of spatial properties, is the number of local maximums per area。

The surface of 0# is very rough, the Sy (peak-peak) reached 240.8 nm on average, the Sz (Ten Point Height), Sa(Roughness Average), Sq(Root Mean Square) reached 219.9 nm, 21.9 nm, 27.8 nm, respectively. The Sds of 0# is low which shows that there is a few of peaks on the surface of 0#, but the *Sz* and *Sy* are high, the peaks have big drop. The 2# and 3#, samples of modified PP, have low Sa, Sq, Sy and Sz, but their Sds are greater values which shows that there are a lot of peaks of low peak-peak height. From Fig.3 can be found that the surface of 2# and 3# is very smooth, their spherulite's sizes is small, the large crystal is disappeared. The COF of 2# and 3# samples is significant declined. Compared with 0#sample, the rolling peaks are split into separate peaks on the surface of 1#, the Sy and Sz values increase, it makes the COF higher than 2# and 3# sample. The numbers of flat peaks are reduced on the surface of 4#, the Sds of 4# is smallest, but its COF is higher than 2# and 3# samples that may be caused by the surface of 4# sample is too smooth lead to increasing of stickky led to increase the friction between two surfaces of films 4#. From the view of COF value, the 1# and 4# samples are relatively high, but the reasones of increasing of COF are essentially different. There are many sharp and steep peaks on the suface of 1# sample. The Sa, Sq, Sy, Sz, Sds all have increased since the addition of 0.5% NS-2, but the COF is still lower than unmodified PP, only is higher than 2# and 3# samples.

Results discussed above can prove that nano-modification reduce COF of PP film that has been well proven through analysis of surface morphology by AFM and Form Talysurf.

The effect of NS-2 on solvent residue in the films

The toluene and ehtyl acetate were normally applied as solvent in printing ink and multi-laminated binder. When the flexible packaging films have been printed or multi-laminated, it is often occurs that the residue of used organic solvents in the flexible packaging films is more than the standart requirements, even more when such methods were used as increasing air flow, temperature and length of the oven, so it is difficult to lower the value of the organic solvents residue less than the standart requirements. This phenomenon can be explaned by the theory that like dissolves like where one molecule is defined as being 'like' another if it bonds to itself in a similar way. The toluene (ehtyl acetate) and PP have similar Hansen Solubility Parameters (HSP) which is reason to lead to absorption of toluene easily on the surface or in the amorphous areas of PP film, and desorption difficult.

The SiO_2 has a higher polarity than PP resion or toluene. The polarity of modified PP by nano-SiO_2 is increased which will create up the difference of HSP between toluene and modified PP.

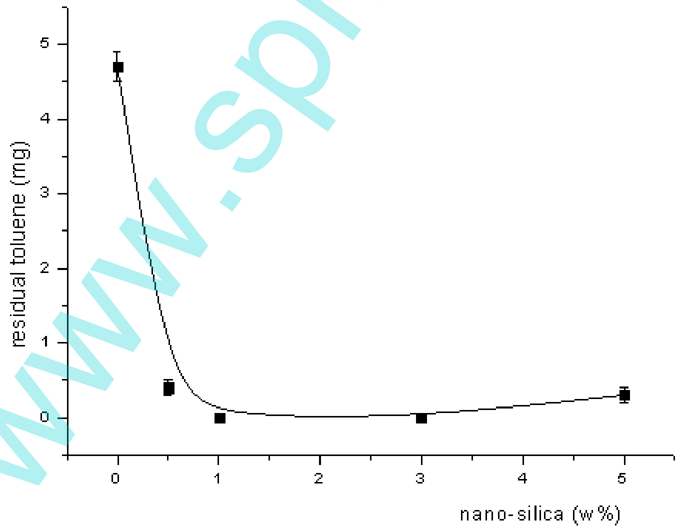

Fig. 4 The residual solvent of Toluene in modified PP

The increasing polarity of modified PP films leads to a dramatically decrease of absorption of toluene on PP, thus the toluene residue reduced greatly(Fig. 4.). It is shown in Fig. 4 that the result of toluene absorption experiment is almost zero value when the content of nano SiO_2 is in range of 1～3% which can solve exceeding the genereal problem of organic solvents residue on flexble packaging

Conclusion

PP flexible packaging materials were modified by self-made nano-SiO_2 agent (NS-2), which improved obviously the polarity , spherulite size, suface morphology of PP. Only a low addition of SiO_2 can make a great improvement of PP'mechanic properties, printability and composite properties, and also a reduce of COF and organic solvent residue. The namo-modification is a new method of reducing COF and organic solvent residue that enhances the overall performance of PP as food flexible packaging materials.

Acknowledgments

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References

[1] Cai Mingchi, Proceddings of National Plastic Packaging Materials and New Technology Workshop. 3,1 **(2007)** In Chinese.

[2] Eric So; Melik C Demirel, Mechanical anisotropy of nanostructured parylene films during sliding contact. J. Phys. D: Appl. Phys. 43, 45403 **(2010)**

[3] Su, Tien-kuei; Reprocessed polyhydroxy amino ether coated polypropylene film. US Patent 7666518. Feb. 23 **(2010)**

[4] Sun, Likuo, Articles and film of poly-alpha-olefin having reduced coefficient of friction. US Patent 20030134965. July 17 **(2003)**.

[5] Yanli Zhang; Dongguang Li, Polypropylene Fibre Grafted Styrene-divinylbenzene Copolymers Post-cross-linked with Cyanuric Chloride. Iranian Polymer Journal. 18,617 **(2009)**

[6] Muwamba A; Nkedi-Kizza P; Rhue RD, Use of mixed solvent systems to eliminate sorption of strongly hydrophobic organic chemicals on container walls. Journal of environmental quality. 38,1170 **(2009).**

[7] Li Dongli, Xu Wencai, A kind of additive for polyolefin packaging materials. CN Patent 200810171239.X. Oct. 27(2008) In Chinese

[8] Ke Wang, Jingshen Wu, Hanmin Zeng, Microstructure and fracture behavior of polypropylene/barium sulfate composites. Journal of Applied Polymer Science. 99,1207 (2005)

[9] Chailier Yves, Production of Polypropylene Having Improved Properties. EP1038893A1. Sep. 27(2000)

[10] Kelusky, Eric Charles, Manufacture of Modified Polypropylene Using non Intermeshing twin screw extruder. EP0370735A2. May 30 (1990)

[11] Kelusky, Eric Charles, Method for the Manufacture of Modified Polypropylene Compositions. EP0370736A2. May 30 (1990)

[12] Wencai Xu, Dongli Li , Yabo Fu. Study on Preparation and Properties of Nano-Modified Polypropylene. Advanced Materials Research. 152-153,465 (2011)

[13] K. J. Stout, P. J. Sullivan, W. P. Dong, E. Mainsah, N. Luo, T. Mathia, H. Zahouani, The development of methods for the characterization of roughness on three dimensions. Publication no. EUR 15178 EN of the Commission of the European Communities, Luxembourg. (1994)