Design of Lubricating Grease Formulations Using Recycled Polypropylene from Postconsumer Films as Thickener Agent

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ABSTRACT: This work deals with the design of lubricating greases formulations based on blends of mineral oil and recycled polypropylene from postconsumer waste, coming from films with inks. In particular, the influence of polymer concentration on the rheological, mechanical, and thermal properties of recycled polymer/oil blends was characterized. From the experimental results obtained, it can be deduced that the evolution of recycled polymer/mineral oil formulations on linear viscoelasticity functions with frequency is quite similar to that found for traditional lithium greases. It is observed that these blends form systems with enhanced "plateau" modulus, G_N^o, with respect to industrial standard lubricating greases, which could be represent an important advantage, from an economic and environmental point of view. However, the influence of temperature on linear viscoelasticity functions is more pronounced than that found for traditional greases. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Population and economy growth worldwide have caused an enormous increase in waste production. To minimize this problem, some alternatives are being studied, such as, for instance, recycling of plastic materials.[1] According to the statistics of the Association of Plastics Manufactures in Europe, postconsumer waste reached 24.7 million tonnes, increasing by 2.5% from 2009 levels. Out of these, 10.4 million tonnes were disposed of and 14.3 million tonnes were recovered.[2] Waste is perceived as a major problem, especially for high-consumption plastics such as polypropylene (PP).[3] The recycling process of postconsumer waste involves several steps such as collection, washing, grinding, and extrusion. It has appeared to be complicated because of the necessity of materials separation as well as lower material properties (strength, stiffness, and stability) of recycled materials. This is a consequence of both environmental and thermomechanical degradations of its components because of its primary use and the recycling process itself. Recycled plastics can be used as raw materials by mixing with virgin polymers and subsequent coextrusion to produce multilayer films[4] or blended with stabilizers agents for other applications.[5] On the other hand, recycled plastics with degraded properties can be

eliminated by catalytic cracking,[6] energy recovery,[7] lubricating greases modification,[8] or landfilling.

One industrial application of these plastics waste is as a modifying agent for lubricating greases, as the resulting mixture may show similar or better performance to those containing virgin polymers.[9] Lubricating greases are generally considered complex colloidal system formed by a thickening agent dispersed in a viscous liquid medium. The physical, mechanical, and rheological properties of the lubricating greases depend basically on its colloidal structure, linked to the chemical composition, in particular to the proportion of thickening agent lubricant liquid and additive.[10] In general, virgin polymers because of their ability for swelling and gel formation in organic media might be used as thickening agents[11] or additives to other types of thickening agents[12] to either decrease the thickener content by keeping the constant consistency or increase the consistency of greases for some specific applications such as high-speed bearings where leakage and sealing are particular concerns.[13] Consequently, replacing virgin by recycled polymers in development of new lubricating grease formulations is a promising alternative that is environmentally favorable. In this sense, recycled polymeric materials based on commodity thermoplastics are
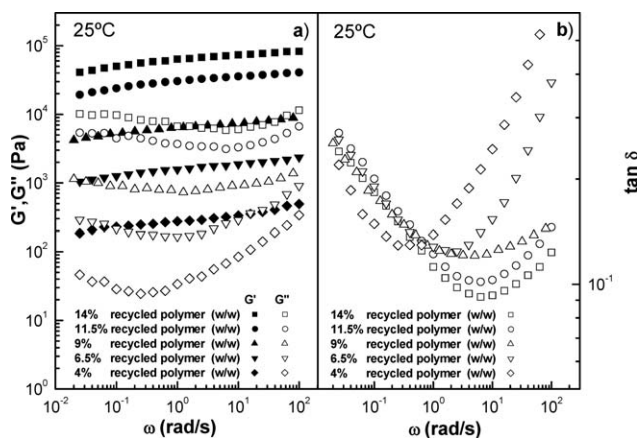
Figure 1. Frequency dependence of the storage and loss moduli (a) and tan δ (b) at 25°C in the linear viscoelasticity region for recycled PP/oil blend with different percentage of recycled polymer (filled symbols: G' and empty symbols: G'').

attractive for their technical performance and versatility of processing–transformation. In previous works, we have studied that recycled polyolefins from different plastics waste, such as low density polyethylene (LDPE), high density polyethylene (HDPE), copolymer of ethylene and vinyl acetate (EVA) and polypropylene (PP), can be satisfactorily used as additives in the lubricating greases formulation, acting as fillers in the soap-entangled microstructure, providing different rheological and mechanical responses as a function of the type of recycled polymer used.[8,14]

In this work, the potential use of recycled PP from postconsumer films, as thickener agent to formulate stable dispersions in mineral oil, is explored. The influence of recycled polymer concentration on the rheological and thermal properties as well as evaluation of some lubricant performance properties (mechanical stability) were carried out to investigate the potential applicability of these gel-like dispersions as lubricating greases.

EXPERIMENTAL

Materials
A naphthenic oil (SR-10) from crude distillation (110 cSt at 40°C, kindly supplied by Verkol Lubricantes, Spain) was used as base oil for gel-like formulations studied. Recycled PP ($M_w = 4.03 \times 10^5$; $M_w/M_n = 6.08$; $\rho = 0.910$ g/cm^3; and melt flow rate of 3.96 g/10 min refer to ASTM D 1238 2.16 kg load at 190°C) from postconsumer waste in the form of pellets, coming from films with inks and provided by Eslava Plásticos, S.A (Spain), was used as thickener agent.

Preparation of Recycled Polymer/Oil Blend Formulations
Binary blends of recycled polymer and oil were prepared in a laboratory scale in an open vessel by stirring with an IKA RW-20 mixer (Germany) with a four-blade propeller to disperse the thickener agent. Batches of 600 g were processed for 60 min in the molten state at 170°C and rotational speed of 150 rpm. Then, the solution was cooled down to room temperature to induce gelification. Cooling was carried out by placing the solution on steel sheet having a thickness of 3–5 mm. A final homogenization treatment (rotational speed: 4000 rpm and

homogenization time: 5 min), using a rotor-stator turbine (Ultra Turrax T-50, Ika, Staufen, Germany), was applied at room temperature. Recycled polymer contents in the blends were 4, 6.5, 9, 11.5, and 14% (w/w).

Characterization
Rheological measurements were carried out in both controlled-stress (PHYSICA MCR-301, Anton Paar, Austria) and controlled-strain (ARES, Rheometric Scientific, UK) rheometers using plate–plate (25 and 50 mm diameter and 1 mm gap) geometry. Small-amplitude oscillatory shear (SAOS) measurements, inside the linear viscoelasticity regime, were performed in a frequency range between 10^{-2} and 10^2 rad/s, and temperatures ranged between 0 and 75°C. Strain sweep tests, at the frequency of 1 Hz, were previously performed on each sample to determine the linear viscoelasticity region. Viscous flow measurements were performed at 25°C in a shear rate range of 10^{-4}–10^2 s^{-1}. A serrated plate–plate (25 mm diameter and 1 mm gap) geometry was used to avoid wall slip effects usually observed during the flow of these materials.[15] All the samples had the same recent past thermal history. At least two replications were performed on fresh samples.

Differential scanning calorimetry (DSC) measurements were performed with a Q-100 TA instrument using 5–10 mg samples sealed in hermetic aluminum pans. The sample was purged with nitrogen at a flow rate of 50 mL/min. Calibration of temperatures and enthalpy was performed with standard indium using the thermal software version 4.0. Heat flow curves were obtained by applying a temperature program of −85 to 170°C/170°C to −85°C/−85 to 170°C, with all ramps conducted at 5°C/min for polymeric materials. The melting and glass transition temperatures and the fusion enthalpy were calculated for samples from the calorimetric data obtained during the second heating ramp.

Thermogravimetric analyses were carried out by using a Q-50 TA Instrument under N$_2$ purge. Approximately 15 mg of each sample was placed on a Pt pan and heated from 30 to 600°C at 10°C/min. Morphological characterization of samples was carried out by means of atomic force microscopy (AFM), with a
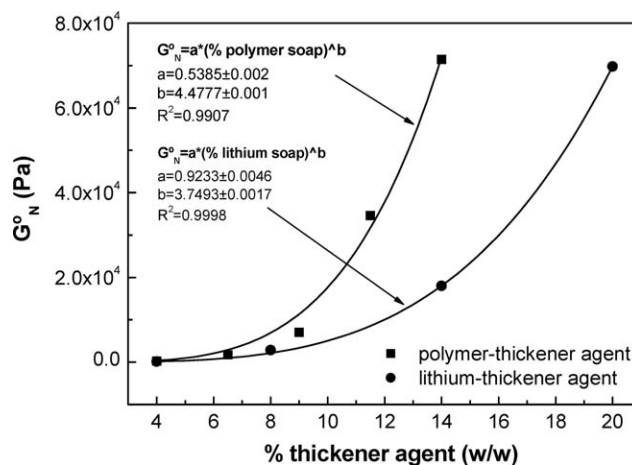
Figure 2. Evolution of the plateau modulus with percentage of recycled polymer (square symbols) and lithium soap (circles symbols).
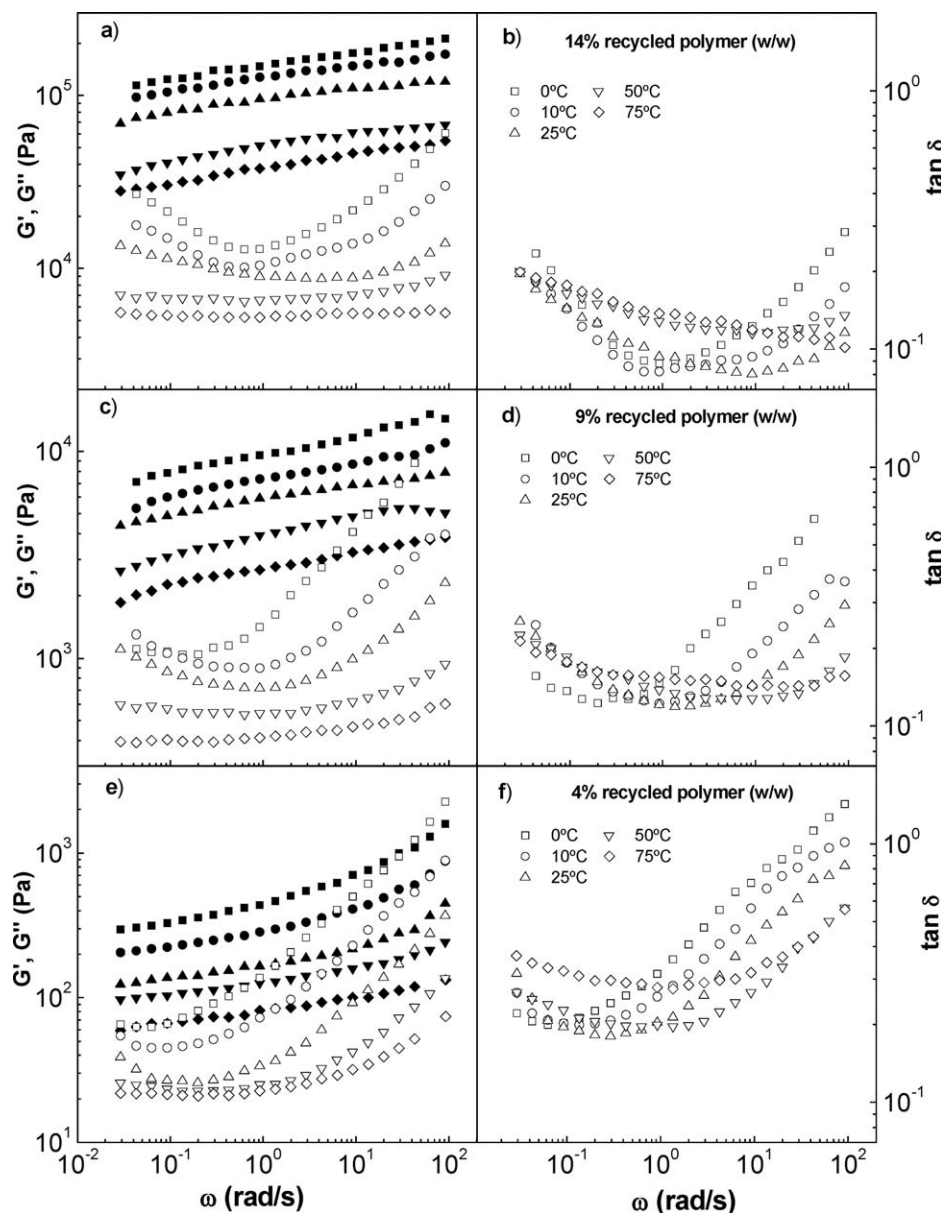
Figure 3. Frequency dependence of the storage and loss moduli (a, c, e) and tan d (b, d, f) in the linear viscoelasticity region for selected recycled polymer/oil blend at different temperatures (filled symbols: G' and empty symbols: G'').

Multimode apparatus connected to a Nanoscope-IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., USA). All images were acquired in the tapping mode, using Veeco NanoprobeTM tips.

Penetration and Mechanical Stability Tests. Both unworked and worked penetration indexes of lubricating greases were determined according to ASTM D 1403 standard using the Seta Universal penetrometer, model 17000-2 (Stanhope-Seta, UK), with a one-quarter cone geometry. The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values following ASTM D 217 standard. The samples were worked in a Roll Stability tester, model 19400-3 (Stanhope-Seta, UK), according to ASTM D 1831 standard.

RESULTS AND DISCUSSION

Rheological Characterization: Linear Viscoelastic Behavior

Figure 1 shows the mechanical spectra in the linear viscoelasticity range of polymer-based greases as a function of recycled polymer concentration. As can be observed, the linear viscoelasticity response is qualitatively similar for all the greases studied and also similar to that found with other commercial lubricating greases.[16] The evolution of the storage and loss moduli with frequency for these lubricating greases (higher values of the storage modulus and a minimum in the loss modulus at intermediate frequencies) is characteristic of polymeric systems with physical entanglements.[17] As can be observed in Figure 1(a), a significant increase in both SAOS functions and a shift of the minimum in G'' to higher frequencies are noticed with
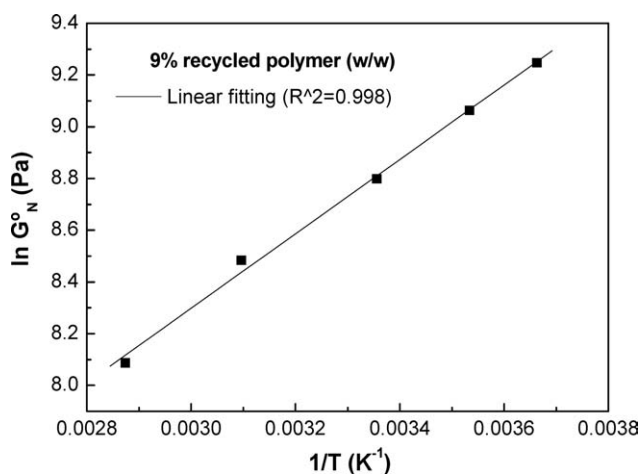
Figure 4. Evolution of the plateau modulus (square symbols) with temperature, and Arrhenius' fitting (solid line), for a selected recycled polymer/oil blend.

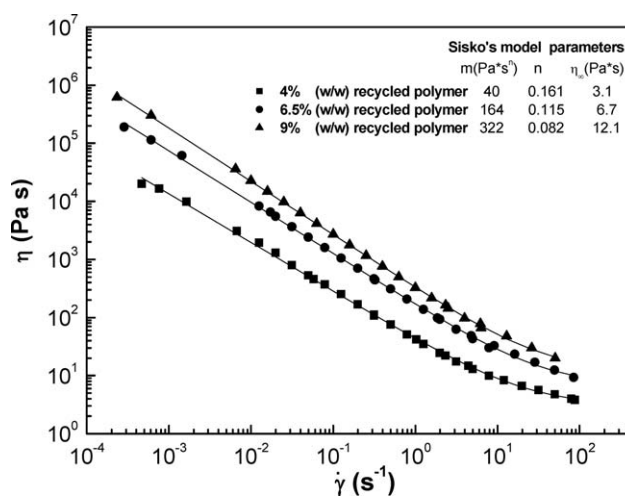**Figure 5.** Flow curves for selected recycled PP/oil blends.

increased recycled polymer concentration. The aforementioned increase in both linear viscoelasticity functions is similar in the low frequency range, and, consequently, the relative elastic characteristics of these gel-like dispersions are not significantly affected, as can be observed in Figure 1(b) where the loss tangent (G''/G') is plotted versus frequency. However, these differences increase with frequency. In this sense, formulations containing high recycled polymer concentration show minimum loss tangent values at large frequencies. The characteristic parameter of this region, the plateau modulus, G_N^o, defined for polymers as the extrapolation of the contribution of the entanglements to G' at high frequencies,[18] may be considered as a measure of the density of physical entanglements, and consequently, it is related to the strength of the microstructural network. The variation of G_N^o, as a function of recycled polymer concentrations, is represented in linear plots in Figure 2 for samples studied. It is observed that the samples form polymer/oil gels with enhanced G_N^o, with respect to industrial standard lithium lubricating greases. These results are also displayed[19] for comparison purposes. These evolutions can be fitted to power-law tendencies:

$$G_N^o = a \cdot C_{thickener}^b. \quad (1)$$

Corresponding potential factors of this power-law equation are $b = 4.183$ and $b = 3.794$ for polymer/oil gels and lithium lubricating greases, respectively. Figure 3 shows the evolution of the

Table I. Activation Energy Values, from eq. (2), for the Different Recycled PP/Oil Blends Studied

% Recycled polymer	E_a (KJ/mol)
14 (w/w)	2.69 ± 0.16
11.5 (w/w)	2.84 ± 0.13
9 (w/w)	2.87 ± 0.15
6.5 (w/w)	3.02 ± 0.16
4 (w/w)	3.12 ± 0.14

linear viscoelasticity functions with frequency, as a function of temperature, for three selected samples, containing 4, 9, and 14% (w/w) recycled polymer, respectively, over a temperature range between 0 and 75°C. As can be observed, all the samples show a gel-like behavior over the whole range of temperature studied, with the storage modulus (G') being higher than the loss modulus (G''). Also, a well-developed plateau region was displayed over the whole range of frequency studied. At lower temperatures, the loss modulus becomes strongly dependent on frequency. This can be observed in Figure 3(b,d,e), where the values of the loss tangent (tan $\delta = G''/G'$) versus frequency have been plotted. Thus, there is a clear tendency to a crossover between both viscoelasticity functions at high frequency and low temperature (beginning of the transition to the glassy region of the mechanical spectrum). In fact, a crossover between G' and G'' is found at 0°C and high frequencies [Figure 3(e)]. This behavior with the temperature is similar to that shown by traditional lithium lubricating greases previously studied[20] and as, in the case of other copolymers, the ability of the polyolefin to form physical networks can explain the gel-like mechanical behavior shown by these materials over a wide range of
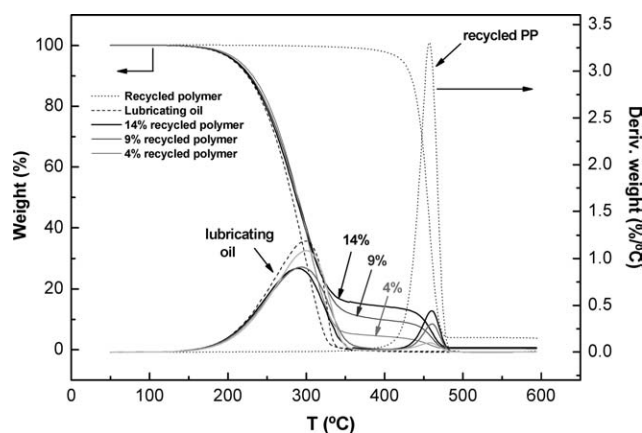
Figure 6. TGA thermograms for selected recycled polymer/oil blend [9% (w/w)].
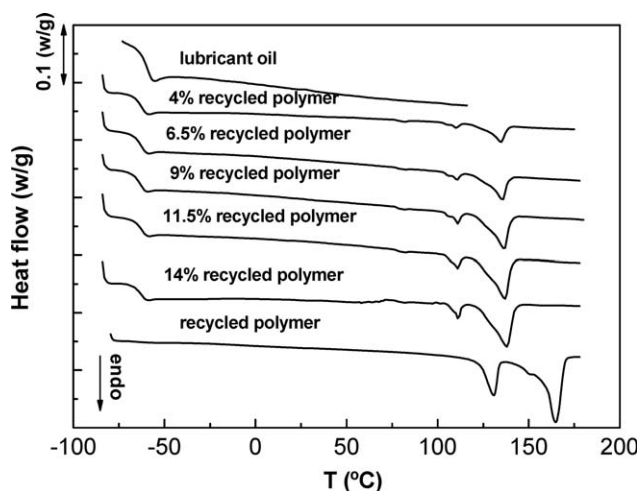
Table II. Characteristic Parameters Obtained from TGA Measurements

Samples	T_{onset} (°C)	Decomposition temperature range (°C)	T_{max} (°C)	W^{600} (%)
Lubricating oil	207	207–344	299.3	0.102
Recycled PP	422	422–483	457.1	3.964
4	213	213–390/390–500	295.1/457.4	0.246
6.5	210	210–388/388–498	296.8/460.4	0.238
9	210	210–391/391–494	293.8/460.5	0.369
11.5	205	205–390/390–504	286.7/462.1	0.713
14	208	208–391/391–500	289.1/460.2	0.732
Standard lithium grease	202	202–341/341–490	294.9/463.1	1.330

temperature and frequencies.[21,22] These samples are not thermo-rheologically simple materials and, therefore, it was not possible to apply the time–temperature superposition principle to the experimental linear viscoelasticity data.[17] This fact may be due to the development of multiphase domains depending on the temperature and polymer concentration. Such domains interact leading to the different mechanical responses with time and temperature. This means that the value of the plateau modulus is not unique for a given system but a function of temperature. Thus, the evolution of G_N^o with temperature has been fitted successfully (see Figure 4 for a selected formulation) to an Arrhenius-like equation ($R^2 > 0.991$):

$$G_N^o = A \cdot e^{\frac{E_a}{R}\left(\frac{1}{T}\right)},\qquad(2)$$

where E_a is the activation energy (J/mol), R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa). Table I shows eq. (2) fitting parameters for the greases studied. The sample containing lower recycled polymer content shows slightly the highest activation energy. In this sense, these polymer/oil gels show a higher thermal susceptibility than formulations containing higher polymer content.

Rheological Characterization: Viscous Flow Behavior

From a rheological point of view, lubricating grease formulation development needs the characterization of both viscous flow and linear viscoelastic behaviors. Figure 5 shows polymer/oil gels viscous flow curves as a function of recycled polymer concentrations. A shear-thinning behavior with a slight tendency to a high-shear rate-limiting viscosity, η_∞, is observed. Shear rates larger than those shown in Figure 5 produce the fracture and/or sample expelling, as previously reported.[15,23] Sisko's model fits this flow behavior fairly well ($R^2 > 0.995$):

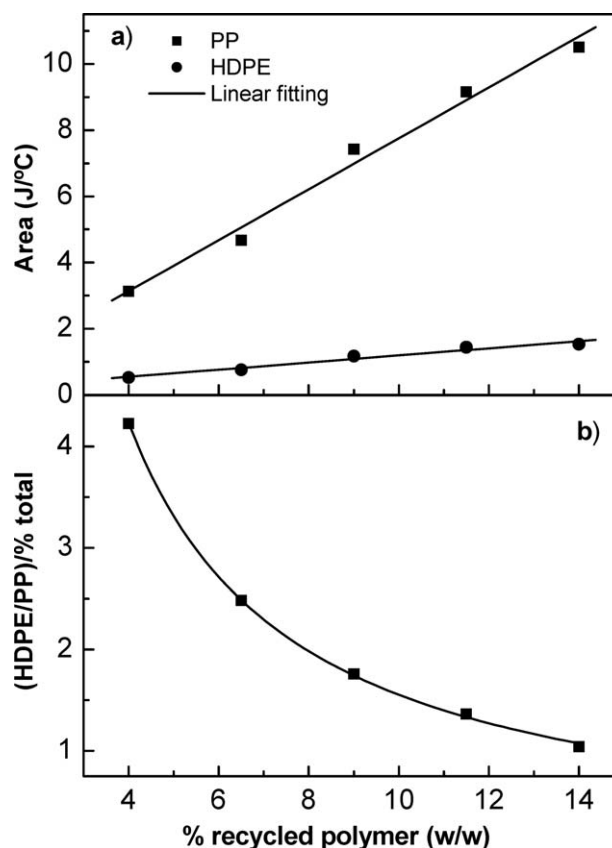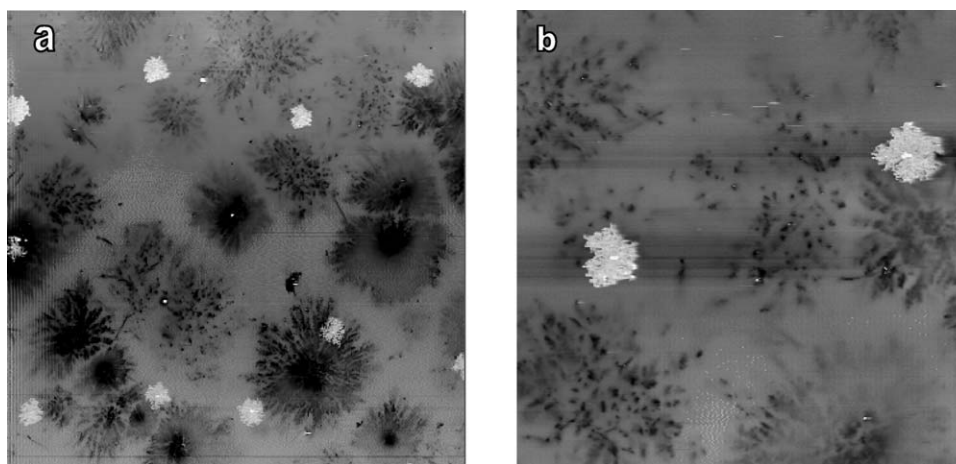$$\eta = m\dot{\gamma}^{n-1} + \eta_\infty,\qquad(3)$$

Figure 7. DSC heat flow curves for lubricant oil, recycled polymer used as thickener agent, and recycled polymer/oil blends. The curves have been shifted in the y-direction to make them distinguishable.

Figure 8. Evolution of melting peak area values and the ratio of areas divided by the polymer fraction with recycled polymer concentration.

Figure 9. AFM observations [window size corresponds to (a) 50 μm and (b) 20 μm] for a selected recycled polymer/oil blend [14% (w/w)].

where m is a parameter related to the consistency of the sample, n is the slope of the shear thinning region, and η_∞ is the high-shear rate-limiting viscosity. The values of these parameters for the aforementioned samples are shown in Figure 5. As can be observed, viscosity clearly increases with recycled polymer concentrations, yielding higher values of the consistency index, m. On the other hand, the flow index, n, decreases by increasing the thickener concentration, being quite close to zero for the highest concentration studied, which is representative of the typical yielding behavior shown by these materials.[8,14]

Thermal Characterization

Figure 6 shows the themogravimetric analysis curves, using N_2 flux, for a selected polymer/oil gel [9% (w/w)], lubricating oil, and recycled polymer. In general, thermal decomposition takes place in just two stages, which is identical for all the blends studied. The first step, obtained in the temperature range (205–388°C), is attributed to the departure of the lubricating oil from the sample. The second step occurs between 388 and 504°C and exhibits a total weight loss, in this case of 8.95% (w/w) (depending on polymer content), which corresponds to the recycled polymer degradations. It should be added that the characteristic temperatures for the greases change in comparison with those for each component (Table II). Lubricant oil decreases their thermal stability as can be concluded from the shift to T_{max} toward smaller values (Table II), whereas for the polymer, this temperature increases. On the other hand, DSC measurement has also been used for samples characterization. As can be seen in Figure 7, the heat flow curve of the recycled polymer used shows several melting peaks, giving clear indication that the material is a mixture of different polymers.[24] Thus, the two major melting peaks (at about 130.9 and 164.9°C) are attributed to the HDPE and PP, respectively. This result is not surprising, because, for industrial products, PP is usually blended with HDPE to improve its stability, and, during the recycling process, it is not easy to separate different types of plastics.[25] The samples show two main thermal events. The first one occurs in the low temperature region, at around −60°C, and corresponds to the glass transition of the naphthenic oil.[26] The second one takes place in the high-temperature region and

is a double endothermic melting peak corresponding to different types of crystals of HDPE and PP that becomes more apparent as polymer concentration increases, as can be observed. Thus, the melting peaks of the two polymers crystalline phases move to lower temperatures, as a consequence of the increased effective volume of the polymer (polymer swelling) in the oil medium.[27] However, no significant shifting in oil T_g is observed, which indicates that the amorphous part of the recycled polymer and the oil show a large degree of incompatibility, from a thermodynamic point of view, in this range of concentration. From a thermodynamic point of view, the partial compatibility between the recycled polymer and lubricant oil can also be assessed by the heat fusion of melting for the crystals of HDPE and PP, respectively. As can be seen in Figure 8(a), the enthalpies of these events always increase by the addition of recycled polymer, and larger differences between melting peak area values are noticed as polymer concentration increases. In this sense, this influence is illustrated in Figure 8(b), where the evolution of the ratio of areas divided by the polymer fraction with the content of polymer is shown. As can be observed, asymptotic values are obtained by increasing the addition of recycled polymer. Thermal behavior influences how polymers are dispersed in the oil medium and, therefore, grease morphology. Figure 9(a,b) shows some AFM observations for a selected system [14% (w/w) recycled polymer]. A homogeneous polymer/

Table III. Penetration Values and Mechanical Stability for Recycled PP/Oil Blends

Samples	Unworked penetration (dmm)	NLGI	Worked penetration (dmm)	Penetration change (dmm)
4% (w/w)	>475	>000	–	–
6.5% (w/w)	429	00	495	66
9% (w/w)	387	00-0	429	42
11.5% (w/w)	263	1-2	323	60
14% (w/w)	210	2-3	257	47
Standard lithium grease	367	0-00	390	23
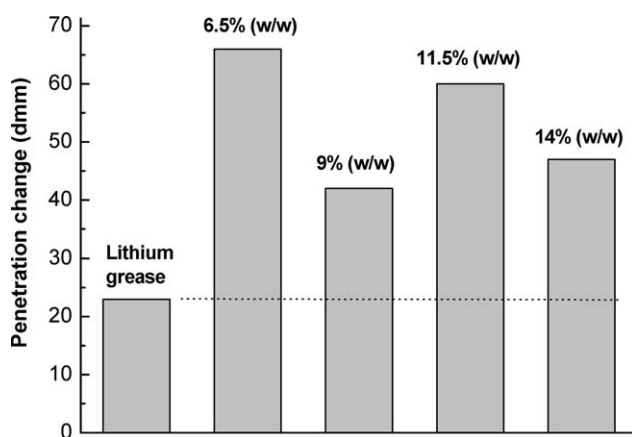
Figure 10. Evolution of penetration increment obtained after working with percentage of recycled polymer.

oil blend was obtained in all cases. However, at the microscopic scale, both crystalline and amorphous fractions dispersed in the oil medium can be distinguished, mainly corresponding to HDPE and PP fractions, respectively, in the recycled material. In this morphology, a swollen fraction in the oil media is perfectly detected as soft regions (dark zones) in the phase AFM image. On the other hand, not swollen crystalline particles appears as hard regions (light zones) in the phase AFM image.

Mechanical Stability

Mechanical stability of lubricating greases is important for controlling the "in-service" performance and the relubrication periods. In many bearing applications, grease can be subjected to high mechanical shear stresses or high loading conditions. Hence, from a tribological point view, lubricating greases must be physically and chemically stable during operation. In this work, grease mechanical stability has been simulated by performing the traditional penetration measurements before and after the standardized roll-stability test. Table III and Figure 10 collect the penetration values obtained for unworked and worked samples and the penetration increment obtained after working, respectively. A lubricating grease is usually considered stable to the continuous shear of rolling elements when its penetration variation before and after the roll-stability test is around zero. In this research, significant differences in mechanical stability have been found depending on sample composition. As expected, and in concordance with the rheological results, an increase in polymer concentrations yields a decrease in the penetration values, because of the increase in viscosity previously mentioned. Similarly, the values of the penetration after working decrease with polymer concentration in the sample. However, samples containing large polymer concentrations show a lower positive increment of the penetration index.

CONCLUSIONS

The ability for swelling and gel formation of recycled PP from postconsumer waste, coming from films with inks in mineral lubricating oil, to evaluate its applicability as thickener agent for lubricating greases, was investigated. From the result obtained, it can be deduced that recycled PP can be potentially used as an effective thickener agent for lubricating greases. The evolution of the linear viscoelasticity functions with frequency is qualitatively similar to that found for traditional lithium lubricating grease. It is observed that recycled PP/oil blend formulations form lubricant greases with enhanced "plateau" modulus, with respect to industrial standard lithium lubricating greases, being the corresponding potential factors of the scaling law G_N^o α $soap^b$ are, respectively, $b = 4.183$ and $b = 3.794$ for recycled polymer and lithium lubricating greases, which may represent an important advantage, from an economic and environmental point of view. The systems studied are thermorheologically complex materials, because of the complex structure developed as a function of polymer concentration. An Arrhenius-type equation can be used to quantify the thermal dependence of the "plateau" modulus. Thermal susceptibilities are lower for gels containing higher polymer content in the formulation. From a thermodynamic point of view, amorphous part of the recycled polymer and oil used in these blends show a large degree of incompatibility. However, the oil influences recycled polymer thermal behavior, lowering its melting point and increasing the ratio of HDPE crystallites. Thermal decompositions of these systems take place in two stages, showing slightly higher thermal stabilities and maximum decomposition rate temperatures than traditional greases based on lithium soap. In general, the samples formulations studied show slightly lower mechanical stability tendency, mainly at lower polymer content, than traditional lubricating greases.

REFERENCES

1. Heller, M.; Keoleian, G.; Volk, T. *Biomass Bioenergy* **2003,** *25*, 147.

2. Association of Plastics Manufactures in Europe. Plastics the Facts 2011. An Analysis of European Plastics Production, Demand and Recovery for 2010, Brussels, Belgium, **2011;** p 1.

3. Papaspyrides, C. D.; Poulakis, J.G. In The Polymeric Materials Encyclopedia; Salomone, J. C., Ed.; CRC Press: New York, **1996;** p 7403.

4. Dintcheva, N. T.; La Mantia, F. P.; Cascone, M.; Balloni, A. *J. Appl. Polym. Sci.* **2011,** *119*, 1986.

5. Vasconcelos Barbosa, R.; Baumhardt-Neto, R.; Santos Mauler, R.; Perez Gorga, C. J.; Tedesco, A. *J. Appl. Polym. Sci.* **2002,** *84*, 1544.

6. Aguado, J.; Serrano, D. P.; Escola, J. M. *Ind. Eng. Chem. Res.* **2008,** *47*, 7982.

7. Fricke, K.; Bahr, T.; Bidlingmaier, W.; Springer, C. *Waste Manage.* **2006,** *31*, 644.

8. Martín-Alfonso, J. E.; Valencia, C.; Sánchez, M. C.; Franco, J. M.; Gallegos, C. *Ind. Eng. Chem. Res.* **2009,** *48*, 4136.

9. Martín-Alfonso, J. E.; Valencia, C.; Sánchez, M. C.; Franco, J. M.; Gallegos, C. *Polym. Eng. Sci.* **2008,** *48*, 1112.

10. Mas, R.; Magnin, A. *J. Rheol.* **1994,** *38*, 889.

11. Martín-Alfonso, J. E.; Valencia, C.; Sánchez, M. C.; Franco, J. M.; Gallegos, C. *Mater. Chem. Phys.* **2011,** *128*, 530.

12. Hassan, A. M.; Shahba, R. M. A.; Youssif, M. A.; Mazrouaa, A. M.; Youssif, M. A. E. *J. Appl. Polym. Sci.* **2011,** *119*, 1026.

13. NLGI. Lubricating Greases Guide; National Lubricating Greases Institute: Kansas City, MO, **1994.**

14. Martín-Alfonso, J. E.; Valencia, C.; Sánchez, M. C.; Franco, J. M.; Gallegos, C. *Eur. Polym. J.* **2007,** *43*, 139.

15. Balan, C.; Franco, J. M. *Tribol. Trans.* **2001,** *44*, 53.

16. Madiedo, J. M.; Franco, J. M.; Valencia, C.; Gallegos, C. *J. Tribol.* **2000,** *122*, 590.

17. Ferry, J. D. In Viscoelastic Properties of Polymers; 3rd ed.; John Wiley & Sons: New York, **1980.**

18. Baumgaertel, M.; De Rosa, M. E.; Machado, J.; Masse, M.; Winter, H. H. *Rheol. Acta* **1992,** *31*, 75.

19. Delgado, M. A.; Valencia, C.; Sánchez, M. C.; Franco, J. M.; Gallegos, C. *Ind. Eng. Chem. Res.* **2006,** *45*, 1902.

20. Delgado, M. A.; Valencia, C.; Sánchez, M. C.; Franco, J. M.; Gallegos, C. *Tribol. Lett.* **2006,** *23*, 47.

21. Barral, M. S.; Lizaso, I.; Muñoz, M. E.; Santamaría, A. *Rheol. Acta* **2001,** *40*, 193.

22. Laurer, J. H.; Mulling, J. F.; Khan, S. A.; Spontak, R. J.; Lin, J. S.; Bukovnik, R. *J. Polym. Sci. Part B: Polym. Phys.* **1998,** *36*, 2513.

23. Moreno, G.; Franco, J. M.; Valencia, C.; Gallegos, C. *J. Appl. Polym. Sci.* **2010,** *118*, 693.

24. Man, H. H.; Byung, K. K. *Polym. Eng. Sci.* **2004,** *44*, 1858.

25. Dintcheva, N. T.; Jilov, N.; LaMantia, F. *J. Polym. Degrad. Stab.* **1997,** *57*, 191.

26. Masson, J. F.; Polomark, G. M.; Bundalo-Perc, S.; Collins, P. *Thermochim. Acta* **2006,** *440*, 132.

27. Garcia-Morales, M.; Partal, P.; Navarro, F. J.; Martinez-Boza, F.; Gallegos, C. *Energy Fuels* **2004,** *18*, 357.