Polymer Bulletin 40, 787–793 (1998)

Polymer Bulletin

HDPE/ROSIN blends: I-Morphology, thermal and dynamic-mechanical behavior

R. S. Cardoso [1], A. L. C. Simões [1], L. C. Mendes [1,*], S. C. S. Teixeira [2], , A. A. Ferreira[3]

[1] Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal
do Rio de Janeiro, UFRJ, P.O. Box 68525, 21945-970 Rio de Janeiro, RJ, Brazil
[2] CENPES-PETROBRÁS, Ilha do Fundão, Rio de Janeiro, RJ, Brazil
[3] PETROFLEX COPERBO S/A, Campos Elíseos, Duque de Caxias, RJ, Brazil

Received: 7 May 1997/Revised version: 20 March 1998/Accepted: 14 April 1998

SUMMARY

Morphological and thermal studies on high density polyethylene (HDPE) / glycerol ester of partially hydrogenated rosin (ester gum) blends reveal phase separation. Both thermal and dynamic-mechanical tests showed no shift of the HDPE glass transition temperature while the HDPE α_c transition appeared. The presence of an additional transition was also noticed as the second component increased in blends; this was attributed to a rosin component. The peak ascribed to this transition became broader in blends enriched with oligomer; it moved toward lower temperatures due to the dissolution of low molecular weight HDPE. The melting temperature and crystallinity of HDPE varied slightly with the amount of amorphous oligomeric component in the blends.

INTRODUCTION

There are a lot of techniques to evaluate the homogeneity of a polymeric system. Usually, three criteria are used: thermodynamic, viscoelastic and optical (1-6). The thermodynamic assessment of polymer miscibility consists of state functions, interaction parameters and phase diagrams. At equilibrium, the mixture of two polymers can coexist as one phase or as two distinct phases. The viscoelastic response gives information of the elastic and loss modulus and tangent delta. The optical criterion comprises a range of observations (optical microscopy, refractive index, etc.) as regards the behavior of the mixture at defined temperatures. In previous papers (7-10) the morphology, thermal, dynamic-mechanical, tensile and crystallization behavior of high density polyethylene (HDPE) / oligo(cyclopentadiene) (HOCP), isotactic polypropylene (iPP) / HOCP and iPP / HDPE / HOCP systems were evaluated. The systems were partially miscible. The growth and shape of the polyolefins spherulites were influenced by HOCP. This component showed a compatibilizing action in the

---

[*] Corresponding author

ternary systems. Recently, we submitted an article (11) of HDPE / glycerol ester of partially hydrogenated Rosin blends focusing on morphology and tensile properties. All blends showed phase separation. In this work, we present the results of HDPE / rosin blends on morphology, thermal and dynamic-mechanical behavior.

EXPERIMENTAL

Materials, blend preparation, specimen preparation and SEM have been described (11).

Differential scanning calorimetry analysis (DSC)

The calorimetric study was performed over -150 to 0°C and 0 to 160°C under a nitrogen atmosphere using a Perkin-Elmer 7 Series Thermal Analysis Systems coupled with a low temperature cell. About 20 mg of sample was cooled from room temperature to -150°C at 200°C/min, and heated to 0°C at 20°C/min. Above 0°C the sample was heated to 160°C and cooled to 0°C at 50°C/min. After this, it was reheated to 160°C at 20°C/min. The glass transition temperature (T_g) and melting temperature (T_m) were registered. The T_g of the blends were determined from the thermograms by applying the first derivative procedure included in the software of the equipment. The T_m was taken from the maximum melting peak. The degree of crystallinity of the blend was calculated using the ratio of enthalpy measured by the equipment and enthalpy for 100% crystalline polyethylene ($\Delta H° = 290$ J/g) (12). The degree of crystallinity of HDPE in the blends was also calculated.

Dynamic-mechanical thermal analysis (DMTA)

Dynamic-mechanical thermal data were collected using a Polymer Laboratories DMTA equipment configured for automatic data acquisition at 1 Hz frequency, bending mode, 2°C/min, from -140 to 140°C, under nitrogen atmosphere employing a 3.0 x 1.0 x 0.15 cm sample.

RESULTS AND DISCUSSION

Figure 1 shows the first derivative traces of HDPE/Rosin blends applied the curves to evaluate the HDPE T_g . The HDPE trace presented inflections at -125°C, -106°C and -98°C. In the literature (13-18) the γ relaxation is the main glass transition of HDPE and is below -100°C. Other sub-transitions occur and are interpreted as superposed relaxations that have arisen from non crystalline domains. Surprisingly, the rosin trace revealed inflections at -125°C, -105°C and -105°C. All blends showed the same inflections as the individual components. The presence of rosin seems not shift the T_g of HDPE. This suggests that only a small amount of rosin was dissolved in the HDPE phase and that it was not able to change the T_g of HDPE. The calorimetric traces above 0°C are shown in Figure 2. The rosin trace showed a transition around 60 - 70°C and all blends presented the melting peak of HDPE.

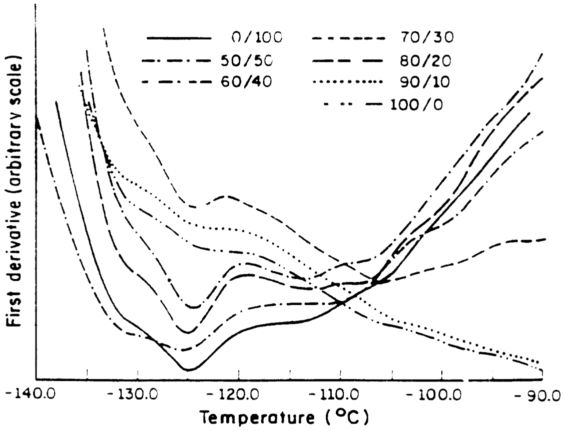


Figure 1 - First derivative traces of HDPE/Rosin blends

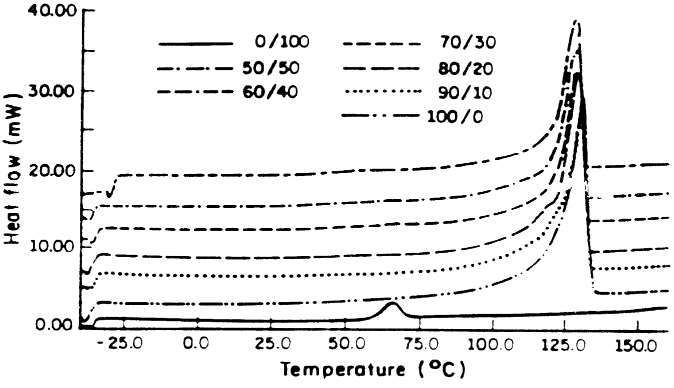


Figure 2 - DSC curves of HDPE/Rosin blends

The first derivative traces of blends are arranged in Figure 3. The rosin showed a peak with a maximum at about 63°C while HDPE presented a very slight inflection between 40 to 50°C, that can be attributed to HDPE α_c crystalline transition (19). The peak ascribed to the rosin transition became broader and moved toward lower temperatures in blends enriched with oligomer. This occurred due to the dissolution of low molecular weight HDPE. In Table 1 are arranged the calorimetric parameters. The HDPE crystallinity degree remained constant up to 30% oligomer and increased above this content; this can be attributed to crystallization of low molecular weight HDPE in the rosin phase. The HDPE melting temperature showed a slight decrease.

The DSC results suggested that the HDPE/Rosin blend shows phase separation. One of the phases is high molecular weight HDPE and a small amount of rosin, whereas the other is rosin and low molecular weight HDPE.

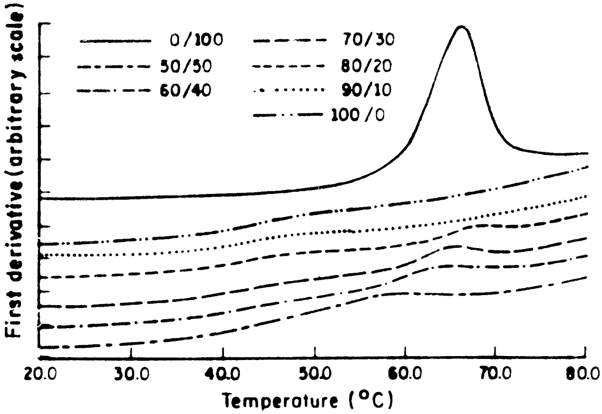


Figure 3- First derivative traces of HDPE/Rosin blends

TABLE 1 - CALORIMETRIC PARAMETERS OF HDPE / ROSIN BLENDS

BLEND	[a]X_b (%)	[b]X_{HDPE} (%)	[c]W_{HDPE} (%)	[d]W_{ROSIN} (%)	[e]T_m (°C)	[f]ΔH (J/g)
100/0	40	40	60	—	131	116
90/10	36	40	86	14	130	104
80/20	32	40	75	25	129	94
70/30	29	41	66	34	129	85
60/40	27	45	58	42	128	78
50/50	25	50	50	50	128	73

[a] degree of crystallinity of blends, [b] HDPE degree of crystallinity, [c] Weight (%) of HDPE in amorphous phase, [d] Weight (%) of Rosin in amorphous phase, [e] HDPE melting temperature, [f] Mixture enthalpy

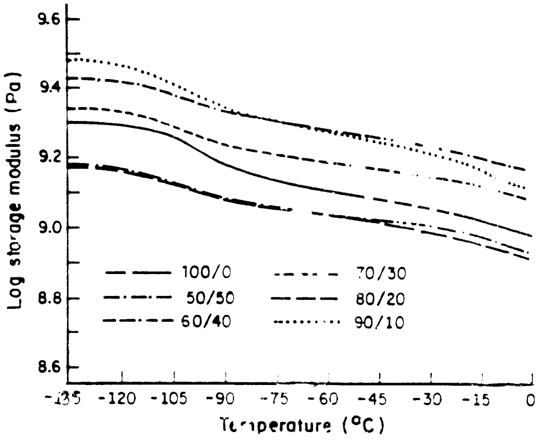


Figure 4 - Storage modulus *versus* temperature of HDPE/Rosin blends

Figure 4 shows the variation of storage modulus (E') versus temperature. As expected for HDPE all curves shows a slight decay around the T_g between -115°C and -90°C. The tan δ curves (Figure 5) shows a maximum at -108°C, attributed to the Tg of HDPE. The 50/50 mixture showed an abnormal additional peak. Above 0°C, the storage modulus (Figure 6) shows an intersection of curves at 62°C, except for the 90/10 mixture, and the HDPE line corresponded to a lower/upper limit. Up to this temperature the storage modulus of blends was similar to that of HDPE one while above it dropped progressively with rosin content.

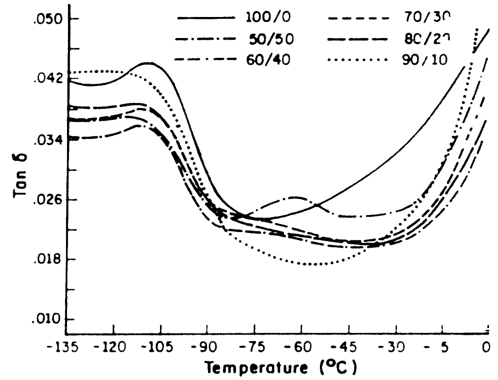


Figure 5 - Tan δ *versus* temperature of HDPE/Rosin blends

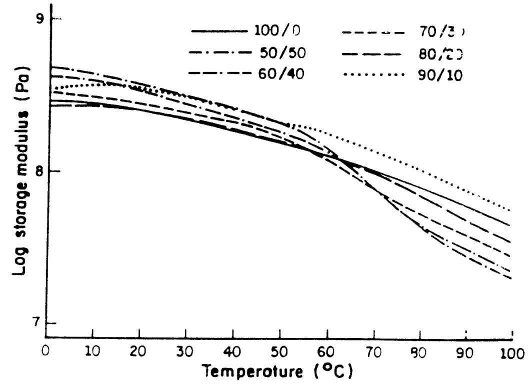


Figure 6 - Storage modulus *versus* temperature of HDPE/Rosin blends

The tan δ curves are shown in Figure 7. The 90/10 HDPE/Rosin tan δ curve was similar to that of HDPE. In blends with above 10% rosin the tan δ peak became higher and broader and moved toward lower temperatures. The 70/30 HDPE/Rosin tan δ curve showed also the HDPE α_c transition. These results are in agreement with those attained by DSC analysis. The HDPE/Rosin blends show phase separation. There is a phase rich in high molecular weigh HDPE with a small amount of rosin and an other phase rich in rosin with low molecular weight HDPE.

The presence of low molecular weight HDPE in the rosin phase was detected by etching.

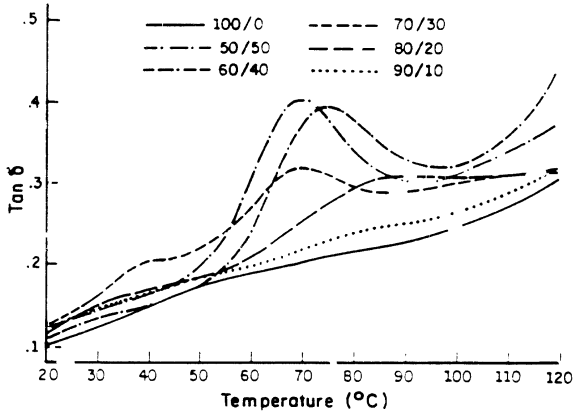
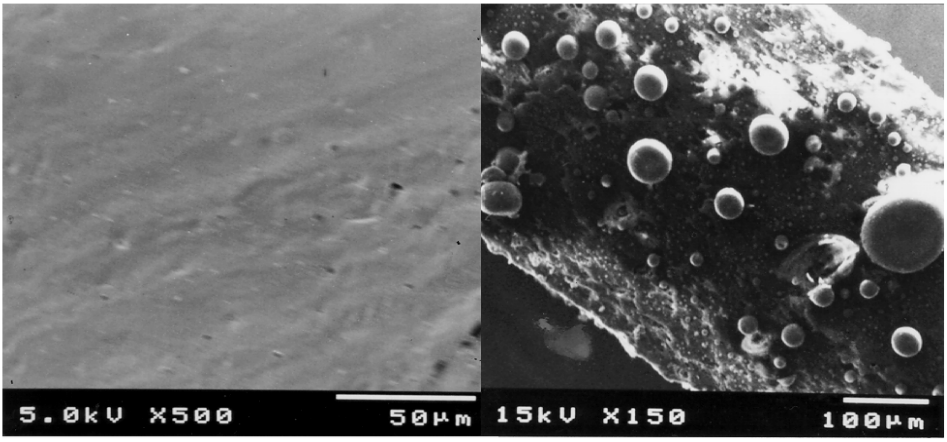


Figure 7 - Tan δ *versus* temperature of HDPE/Rosin blends

Figure 8 shows the photomicrograph of the 50/50 HDPE/Rosin blend before and after etching. The rosin was extracted by n-heptane and the suface revealed the presence of spherical domains of different sizes emerging from the matrix, attributed to low molecular weight HDPE.



before etching

after etching

Figure 8 - SEM photomicrograph of 50/50 HDPE/Rosin blend before and after etching

CONCLUSION

Thermal and morphological studies with HDPE / glycerol ester of partially hydrogenated rosin blends revealed phase separation. In both DSC and DMTA experiments the glass transition temperature of HDPE did not change. The presence of an additional transition was noticed which was attributed to the rosin component. This transition moved toward lower temperatures. After etching, SEM analysis showed the presence of spherical domains of HDPE in the rosin phase.

Acknowledgements

The authors thank to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) for support this research.

REFERENCES

1. Plochocki A (1972) J.Appl.Pol.Sci. 16:987
2. Paul DR, Barlow J, Keskkula H (1988). In Mark HF, Bikales NM, Overberger CG, Menges G (ed) Encyclopedia of Polymer Science and Engineering. John Wiley New York 12:399
3. Sanches IC (1987). In Meyers RA (ed) Encyclopedia of Phisical Science and Technology Academic Press Orlando 11: 1
4. Carpenter DK (1970). In Mark HF, Gaylord NG, Bikales NM (ed) Encyclopedia of Polymer Science and Technology. John Wiley New York 12:655
5. Liberman AS (1984) D.Sc.Thesis, Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro
6. Stein AS (1978). In Newman S (ed) Polymer Blends Academic Press New York 1:393
7. Cimmino S, Pace EDi, Martuscelli E, Mendes LC, Silvestre C (1994) J Polym Sci Part B Polym Phys 32: 2025
8. Cimmino S, Pace EDi, Martuscelli E, Silvestre C, Mendes LC, Bonfanti G (1995) J Polym Sci Part B Polym Phys 33: 1723
9. Mendes LC, Tavares MIB, Mano EB (1996) Polymer Testing 15: 53
10. Mendes LC, Mano EB, Martuscelli E, Cimmino S (1995)Polymer Bulletin 35: 237
11. Cardoso RS, Simões ALC, Diez Filho MA, Mendes LC HDPE/Rosin Blends: I - Morphology, mechanical and rheological properties submitted to Polymer Bulletin
12. Quirk RP, Alsamarraie MAA (1989). In Brandrup J, Immergut EH (ed) Polymer Handbook John Wiley New York V:15
13. Sakagushi F, Mandelkern L, Maxfield J (1976) J.Pol.Sci. Pol.Phys. 14:2137
14. Stehling FC, Mandelkern L (1970) Macromolecules 3(2):242
15. Beatty CL, Karasz FE (1979) J.Macrom.Sci. C17(l):37
16. Alberola N, Cavaille JY, Perez J (1992) Eur.Pol.J. 28(8):935
17. Alberola N, Cavaille JY, Perez J (1992) Eur.Pol.J. 28(8):953
18. Fischer EW, Kloos F (1970) J.Pol.Sci. Pol.Letters 8(1):685
19. Doak KW (1986). In Mark HF, Bikales NM, Overberger CG, Menges G (ed) Encyclopedia of Polymer Science and Engeneering. John Wiley New York 6:410