Rheology of LCP/PET Blends at Solid and Molten States of LCP

S.A.R. Hashmi* and Takeshi Kitano [1]

Regional Research Laboratory (CSIR), Hoshangabad Road, Bhopal 462026, India
[1] Polymer Centre, Tomas Bata University in Zlin, T.G.M 275, 762 72 Zlin, Czech Republic

* Email: sarhashmi@rediffmail.com
Fax: x91.755.2488323

Abstract:

Liquid crystalline polymer (LCP) and polyethylene terephthalate (PET) were blended in an elastic melt extruder to make samples having different volume fractions of constituent polymers. Shear stress, shear viscosity, first normal stress difference at different shear rates under steady state conditions of these blends were evaluated at two different temperatures 265 and 285°C. The LCP was in solid state at 265°C and in melt state at 285°C and was dispersed in molten matrix of PET at both temperatures. Shear viscosity of blend increased with addition of LCP in PET matrix. A maxima was observed in viscosity versus composition plot. Blends containing more than 50 vol. % of LCP in the blend show higher viscosity as compared to the constituent polymers. First normal stress difference, N_1, increased with LCP content in the blend at 285°C when ploted against shear stress whereas at 265°C this trend was opposite. The increased value of N_1 with shear rate was explained assuming a tendency of asymmetric particles to rotate under velocity gradient of suspending medium. At 285°C N_1 varied with shear stress in two stages. First stage was characterized with high sensitivity of N_1 with shear stress, which reduced in second stage on plastic deformation of LCP droplets.

Zusammenfassung:

Flüssigkristalline Polymere (LCP) und Polyethylenterephthalat (PET) wurden in einem elastischen Extruder für Schmelzen geblendet, um Proben mit unterschiedlichen Volumenanteilen der Blendkomponenten herzustellen. Scherspannung, Scherviskosität und erste Normalspannungsdifferenz bei verschiedenen Schergeschwindigkeiten im stationären Bereich dieser Blends wurden bei zwei unterschiedlichen Temperaturen (265 und 285°C) ausgewertet. Das LCP war bei 265°C fest und flüssig bei 285°C und war bei beiden Temperaturen in der PET-Schmelze dispergiert. Die Scherviskosität des Blends nahm mit LCP-Gehalt in der PET-Matrix zu. Ein Maximum wurde in dem Viskositäts-Kompositionsdiagramm beobachtet. Die Blends, die mehr als 50% LCP enthielten, wiesen eine höhere Viskosität im Vergleich zu den Blendkomponenten auf. Die erste Normalspannungsdifferenz N_1 nahm mit LCP-Gehalt in dem Blend bei 285°C zu, wenn sie als Funktion der Scherspannung geplottet wurde, wohingegen dieser Trend bei 265°C umgekehrt verlief. Der durch die Schergeschwindigkeit erhöhte N_1-Wert wurde durch die Annahme einer Tendenz der asymmetrischen Teilchen zur Rotation durch den Geschwindigkeitsgradienten des suspendierenden Mediums erklärt. Bei 285°C treten bei der Scherspannung zwei Regime auf. Der erste Bereich wurde durch eine hohe Abhängigkeit von N_1 mit der Scherspannung charakterisiert, die im zweiten Bereich durch eine plastische Deformation der LCP-Tropfen abnahm.

Résumé:

Un polymère cristal liquide (LCP) et un téréphtalate de polyéthylène (PET) ont été mélangés dans une extrudeuse pour fondu élastique afin de fabriquer des échantillons possédant différentes fractions volumiques de polymères constituants. La contrainte de cisaillement, la viscosité de cisaillement, la première différence de contraintes normales de ces mélanges ont été mesurées pour différentes vitesses de cisaillement et sous conditions stationnaires, à deux températures différentes, 265 et 285°C. Le LCP est à l'état solide à 265°C et à l'état fondu à 285°C, et a été dispersé dans la matrice fondue aux deux températures. La viscosité de cisaillement du mélange augmente avec l'addition de LCP dans la matrice PET. Un maximum est observé quand on représente la viscosité en fonction de la composition. Les mélanges contenant plus de 50% en volume de LCP présentent une viscosité supérieure à celle des polymères constituants. La première différence de contraintes normales, N_1, augmente avec la quantité de LCP dans le mélange, lorsqu'elle est représentée en fonction de la contrainte de cisaillement à 285°C, tandis qu'à 265°C cette tendance est à l'opposé. La valeur croissante de N_1 avec la vitesse de cisaillement a été interprétée en supposant que les particules asymétriques ont une tendance pour se tourner sous un gradient de vitesses présent dans le milieu qui les suspend. A 285°C, N_1 varie avec la contrainte de cisaillement suivant deux étapes. La première est caractérisée par une grande sensitivité de N_1 à la contrainte de cisaillement, tandis qu'elle est réduite dans la deuxième étape correspondant à la déformation plastique des gouttelettes de LCP.

shear stress can be observed in Figs 13 and 14. When LCP is in molten state the addition of LCP in the blend increased N_1 as shown in Fig 14. A careful inspection of the curve reveals that these curves have two stages. In first stage slopes of curves are high as compared to those of second stage. First stage is characterized with high sensitivity of N_1 with shear stress, which reduced in second stage. Slope of first stage curve increased with LCP loading. First stage may be attributed to dominant elastic deformations of LCP droplets under applied shear that increased with the volume fraction of LCP or the number of droplets in the blend. The deformed droplets stored large amount of surface energy and consequently increased N_1. On further increase in shear stress the plastic deformation of LCP droplets took place and molecules aligned in flow direction and possibly energy is spend on fibrillation of droplets resulting in reducing the sensitivity of N_1 on shear stress. It is generally believed that droplet deformation is controlled by two important parameters; the viscosity ratio and interfacial tension between the two fluids. When interfacial tension is negligible compared to viscosity effect, the deformed droplet in the form of spheroid shall align in flow direction. In case of polymer blend processing low viscosity ratios and large capillary numbers, which develop fibrillation of domains, are encountered. Mathematically droplet deformation criteria have been evolved and can be summarized as follows [8, 24]:

- If $Ca^* < 0.1$, droplets deform slightly (negligible deformation)
- If $0.1 < Ca^* < 1$, droplets deform without break
- If $1 < Ca^* < 4$, droplets deform but break conditionally
- If $Ca^* > 4$ droplets deform affinely with the rest of matrix and extend into long stable filaments

Here the reduced capillary number is given by $Ca^* = Ca/Ca_c$ where Ca is the ratio of hydrodynamic stress to interfacial stress, i.e. $Ca = \eta_m \dot{\gamma} R/\sigma$ where η_m is the matrix viscosity, R the drop radius and σ the interfacial tension. Ca_c is critical capillary number beyond which the droplet can no longer sustain further deformation and breaks.

Experimental and theoretical analysis on dependence of N_1 and σ_{12} on γ suggest that at low shear rates σ_{12} is proportional to $\dot{\gamma}$ and N_1 is proportional to $\dot{\gamma}^2$ (Eqs. 4, 5, 7). As the rate of shear increases both N_1 and σ_{12} increase but rate of increase of N_1 is faster and therefore it crossover σ_{12}. The relation between N_1 and σ_{12} becomes quadratic and some times even higher near the forced-rubbery state region [25,26]. Czarnecki and White [27] reported increased normal stress difference of melts containing flexible particulates such as cellulose fibre and Kevlar fibres, which depend on fibre length to diameter ratio. It implies that LCP droplets were deformed on shearing and resulted in increased N_1 with shear stress. On the other hand blends at 265°C showed decreasing trend indicating non-deformed LCP droplets (particles) in the shear field.

4 CONCLUSIONS

Shear depend viscosity and first normal stress difference of LCP/PET blends at solid and molten states of LCP were investigated. Blends with more than 50% of LCP displayed high shear viscosity than that of either LCP or PET at low shear rates. LCP was found more shear sensitive as compared to PET. A maxima was observed in viscosity versus composition plot. First normal stress difference increased with LCP content in the blend at 285°C whereas at 265°C this trend was opposite. The value of N_1 increased with shear-rate as well as with shear stress indicating increase in recoverable elastic strain with shear. At 285°C N_1 varied with shear stress in two stages. First stage was characterized with high sensitivity of N_1 with shear stress, which reduced in second stage on plastic deformation of LCP droplets.

REFERENCES

[1] Kiss G: In situ composites: Blends of isotropic polymers and thermotropic liquid crystalline polymers, Polym. Eng. Sci. 27 (1987) 410.
[2] Tjong SC: Structure, morphology, mechanical and thermal characteristics of the in situ composites

based on liquid crystalline polymers and thermoplastics, Mater. Sci. Eng. Rev. 41 (2003) 1.

[3] Lin YG, Lee HW, Winter HH, Dashevsky S, and Kim KS: Miscibility and viscoelastic properties of blends of a liquid-crystalline polymer and poly(ethylene terephthalate), Polymer 34 (1993) 4703.

[4] Shimizu H, Kitano T, Nakayama K: Morphological control of LCP/PET blends using a melt mixer equipped with a milling part, Mater. Lett. 58 (2004) 1277.

[5] Kyotani M, Kaito A, Nakayama K: Structural, mechanical, and thermal properties of extruded sheets of a liquid crystalline copolyester, J. Appl. Polym. Sci. 47 (1993) 2053.

[6] Congswell FN in Lawrence Chapoy L (Ed): Recent Advances in Liquid Crystalline Polymers Elsevier, New York (1985) 172.

[7] Marrucci G. in Mantia, La FP (Ed.): Thermotropic Liquid Crystal Polymer Blends, Technomic, Lancaster (1993) 43.

[8] Song CH, Isayev AI: LCP droplet deformation in fiber spinning of self-reinforced composites, Polymer 42 (2001) 2611.

[9] Nguyen TN, Geiger K, Fritz H-G: Rheological Properties and Shear Induced Texture Development of Thermotopic Liquid Crystalline Polymer Melts, Appl. Rheol. 12 (2002) 142.

[10] Araki K, Kitano T, Hausnerova B: Rheological Properties of Carbon Fiber and Carbon Black Filled Liquid Crystalline Polymer Melts, Appl. Rheol. 11 (2001) 188.

[11] Kröger M: Simple models for complex nonequilibrium fluids, Physics Reports 390 (2004) 453.

[12] Kröger M, Loose W, Hess S: Rheology and structural changes of polymer melts via nonequilibrium molecular dynamics, J. Rheol. 37 (1993) 1057.

[13] Kataoka T, Ohnishi S, Kitano T, Nakama K, Takayama H: Mixing effect of filler and polymer by an elastic melt extruder, Rheol. Acta 15(1976) 268.

[14] Meitz DW, Yen L, Berry GC, Markovitz H: Rheological Studies of Dispersions of Spherical Particles in a Polymer Solution, J. Rheol. 32 (1988) 309.

[15] Araki T, White JL: Shear viscosity of carbon black filled polypropylene at very low shear stresses, Polym. Eng. Sci. 38 (1998) 616.

[16] White JL: A plastic-viscoelastic constitutive equation to represent the rheological behavior of concentrated suspensions of small particles in polymer melts, J. Non-Newtonian Fluid Mech. 5 (1979) 177.

[17] Onuki A: Viscosity enhancement by domains in phase-separating fluids near the critical point: Proposal of critical rheology, Phys. Rev. A 35 (1987) 5149.

[18] Ferry J.D: Viscoelastic Properties of Polymers, Wiley, New York (1980).

[19] Takahashi Y, Noda, M, Ochiai, N, Noda I: Shear rate dependence of first normal stress difference of polyisoprene-b-styrene) in solution near the order-disorder transition temperature, Polymer 37 (1996) 5943.

[20] Goddard JD, Miller C: Non-linear effects in the rheology of dilute suspensions, J. Fluid Mech. 28 (1967) 657.

[21] Han CD: Multiphase Flow in Polymer Processing, Academic Press, New York (1981)

[22] Tanaka H, White JL: Experimental investigations of shear and elongational flow properties of polystyrene melts reinforced with calcium carbonate, titanium dioxide, and carbon black, Polym. Eng. Sci. 20 (1980) 949.

[23] Lin Li: Viscoelastic properties of particle filled polymers in the molten state, Ph.D. thesis, Kyoto University, Japan, (1989).

[24] Huneault MA, Shi ZH, Utracki LA: Development of polymer blend morphology during compounding in a twin-screw extruder. Part IV: A new computational model with coalescence, Polym. Eng. Sci. 35 (1995) 115.

[25] Brizitsky VI, Vinogradov GV, Isaev AI, Podolsky Yu Ya: Polarization-optical investigation of normal and shear stresses in flow of polymers, J. Appl. Polym. Sci. 20 (1976) 25.

[26] Vinagrodov GV, Malkin A Ya: Rheology of Polymers, Mir Publishers, Moscow (1980) 324.

[27] Czarnecki L, White JL: Shear flow rheological properties, fiber damage, and mastication characteristics of aramid-, glass-, and cellulose-fiber-reinforced polystyrene melts J. Appl. Polym. Sci. 25 (1980) 1217.