Rheological Properties of Carbon Fiber and Carbon Black Filled Liquid Crystalline Polymer Melts

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Abstract:
The rheological properties of thermotropic liquid crystalline polymer (LCP) and its carbon fiber (CF) and carbon black (CB) filled composites in molten state were measured using a cone-plate rheometer. The measurements of the CF/LCP and CB/LCP melts were performed with carbon fiber contents of 5, 10 and 20 wt %, and carbon black contents of 1.5, 3, 5, 10 and 20 wt %. As expected, steady shear viscosity of the LCP, CF/LCP and CB/LCP melts in a low shear rate region (0.1 to 1 s^{-1}) decreased with an increase of temperature and increased with rise of filler content. In shear rate region of 1 to 50 s^{-1}, the LCP melt showed a unique viscosity behaviour with maximum and minimum values. The CF/LCP and CB/LCP melts showed disappearance of such a unique viscosity behaviour with an increase in the CF (CB) content and an increase of temperature. CB filler had a more pronounced effect on the disappearance of the unique viscosity behaviour in comparison with CF. Regarding apparent yield stress, the CF/LCP melts gave the same value as pure LCP, the CB/LCP melts showed an increase of yield with a rise of the filler content. In addition, the first normal stress difference of the LCP and CF/LCP melts are smaller than yield stress values, although the rate of increase with shear rate is higher in case of normal stress difference than in case of yield. The results of the dynamic shear oscillatory flow measurements of CF and CB based compounds at 300°C showed that both, the storage and loss moduli are more affected by carbon black filler. Complex viscosity values of the LCP and CF/LCP melts showed no such unique complex flow pattern as observed in the case of steady shear viscosity.

Zusammenfassung:
Die rheologischen Eigenschaften von thermotropischen flüssigkristallinen Polymeren (LCP) und der mit Kohlenstofffasern (CF) und Russ (CB) gefüllten Komposite wurden im geschmolzenen Zustand mit einem Kegel-Platte-Rheometer gemessen. Die Messungen der CF/LCP und der CB/LCP-Schmelzen wurden bei Kohlenstofffasergehalten von 5, 10 und 20 % und Russgehalten von 1.5, 3, 5, 10 und 20 wt % durchgeführt. Die stationäre Scherviskosiät der LCP-, CF/LCP- und CB/LCP-Schmelzen wird bei niedrigen Scherraten (0.1 bis 1 s^{-1}) bei Erhöhung der Temperatur erniedrigt und mit ansteigendem Füllgrad erhöht. Im Scherratenbereich von 1 bis 50 s^{-1} zeigte die LCP-Schmelze ein einzigartiges Viskositätsverhalten mit Maximal- und Minimalwerten. Dieses Verhalten verschwand bei den CF/LCP- und CB/LCP-Schmelzen mit zunehmendem Gehalt an CF (CB) und mit zunehmender Temperatur. Der Füllstoff CB hatte einen ausgeprägteren Einfluss auf das Verschwinden des einzigartigen Viskositätsverhaltens im Vergleich zu CF. Für die scheinbare Fliessgrenze ergab sich für die CF/LCP-Schmelzen dasselbe Resultat wie für die reine LCP-Schmelze, während die CB/LCP-Schmelzen mit ansteigendem Füllgrad ein Ansteigen der Fliessgrenze zeigen. Zusätzlich ist die erste Normalspannugsdifferenz der LCP und CF/LCP-Schmelzen kleiner als die Werte der Fliessgrenze, obwohl die Zuwachsrate bei Erhöhung der Scherrate im Falle der Normalspannungsdifferenz höher ist als bei der Fliessgrenze. Die Resultate oszillierender dynamischer Schermessungen der CF and CB Mischungen bei 300°C zeigte, dass sowohl der Speicher- als auch der Verlustmodul mehr vom Russ beeinflusst werden. Die Werte für die komplexe Viskosiät der LCP- and CF/LCP-Schmelzen zeigen kein so einzigartiges komplexes Fliessverhalten wie es im Falle der stationären Scherviskosität beobachtet wurde.

Key Words: thermotropic liquid crystalline polymer, carbon fiber, carbon black, filled systems, viscosity, viscoelastic properties, cone-plate rheometer

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The low-filled systems also show this unique viscosity pattern, while with an increase in the CF (CB) content and temperature this phenomenon disappears. The strengths of the fibre- and particle-filler in depriving this effect are not the same.

- The yield stress values were determined from the Casson plots for the unfilled LCP, CF and CB filled LCP systems. The apparent yield stress of the CF filled system gives almost the same value as that of the pure LCP, suggesting that CF contained in LCP has little contribution to its yield behavior. The yield stress of the CB filled LCP system, on the other hand, shows an increase in with rising of CB loading.
- CF (CB) filled LCP systems show large dependence of G' and G'' on the filler content and the relationship is more pronounced for CB than for CF. The $|\eta^*|$ curves of pure LCP and CF filled systems show no such dilatant flow pattern as observed in their η curves.

REFERENCES

[1] Jackson WJ, Kuhfuss HF: Liquid Crystal Polymers. I. Preparation and Properties of p-Hydroxy-benzoic Acid Copolyesters, J. Polym. Sci. Polym. Chem. 14 (1976) 2043-2058.

[2] Chung TS: The Recent Developments of Thermotropic Liquid Crystalline Polymers, Polym. Eng. Sci. 26 (1986) 901-919.

[3] Voss H, Friedrich K: Influence of Short-Fiber Reinforcement on the Fracture Behavior of a Bulk Liquid Crystal Polymer, J. Mater. Sci. 21 (1986) 2889-2900.

[4] Iimura K, Ashada T, Abe A: Ekisho-Koubunshi, Shiguma Press, Japan (1988).

[5] Wu JS, Friedrich K, Grosso M: Impact Behavior of Short Fiber/Liquid Crystal Polymer Composites, Composites 20 (1989) 223-233.

[6] Kitano T, Kataoka T: The Effect of the Mixing Methods on Viscous Properties of Polyethylene Melts Filled with Fibers, Rheol. Acta 19 (1980) 753-763.

[7] Sakai S, Kitano T, Nishimura T: Rheological Properties of Polyethylene Melt Filled with Metal and Carbon Fiber, Kobunshi Ronbunshu 45 (1988) 123-131.

[8] Araki K, Nakamura K: Melt Flow Properties of Fiber Reinforced Nylon and Polycarbonate, J. Text. Machinery Soc. Japan 41 (1988) 89-97.

[9] Araki K, Nakamura K: Flow Properties of Fiber-Reinforced Nylon, Polyethyleneterephtalate and Polybuthyleneterephtalate Melts, J. Text. Machinery Soc. Japan 42 (1989) 47-59.

[10] Araki K, Nakamura K: Melt Flow Properties of Whisker Reinforced Nylon, J. Text. Machinery Soc. Japan 42 (1989) 99-112.

[11] Chuang HK, Han CD: Rheological Behavior of Polymer Blends, J. Appl. Polym. Sci. 29 (1984) 2205-2229.

[12] Min K, White JL, Fellers JF: High Density Polyethylene/Polystyrene Blends: Phase Distribution, Morphology, Rheological Measurements, Extrusion and Melt Spinning Behavior, J. Appl. Polym. Sci. 29 (1984) 2117-2142.

[13] Carley JF, Crossan SC: Viscosities of Molten Polymer Blends, Polym. Eng. Sci. 21 (1981) 249-258.

[14] Utracki LA: Melt Flow of Polymer Blends, Polym. Eng. Sci. 23 (1983) 602-609.

[15] Nishimura T: Capillary Flow Behavior of Bicomponent Polymer Blends, Rheol. Acta 23 (1984) 617-626.

[16] Utracki LA, Sammut P: Rheological Evaluation of Polystyrene/Polyethylene Blends, Polym. Eng. Sci. 28 (1988) 1405-1415.

[17] Hong SM, Kim BC, Kim KU, Chung IJ: Rheology and Physical Properties of Polysulfone In-situ Reinforced with a Thermotropic Liquid-Crystalline Polyester, Polym. J. 23 (1991) 1347-1357.

[18] Driscoll P, Fujiwara K, Masuda T: The Effect of Temperature on Optical and Viscoelastic Properties of a Homogeneous Thermotropic Liquid Crystalline Polymer, Polym. J. 20 (1988) 351-356.

[19] Blumstein A, Vilasagar S, Ponrathnam S, Clough SB, Blumstein RB, Maret G: Nematic and Cholesteric Thermotropic Polyesters with Azoxybenzene Mesogenic Units and Flexible Spacers in the Main Chain, J. Polym. Sci. Phys. Ed. 20 (1982) 877-892.

[20] Kim C, Allcock HR: A Liquid Crystalline Poly(organophosphazene), Macromolecules 20 (1987) 1726-1727.

[21] La Mantia FP, Valenza A: A Comprehensive Experimental Study of the Rheological Behaviour of HDPE. I. Entrance Effect and Shear Viscosity Results, Rheol. Acta 22 (1983) 299-307.

[22] Kitano T, Kataoka T: The Rheology of Suspensions of Vinylon Fibers in Polymer Liquids. I. Suspensions in Silicone Oil, Rheol. Acta 20 (1981) 390-402.

[23] Mikami Y, Matsumoto T, Onogi S: Rheological Properties of Suspensions of Titanate Fibers in Polystyrene Solution, Nihon Reoroji Gakkaishi 4 (1978) 86-89.

[24] Japan Industrial Standard Handbook, Plastics, Japanese Standard Association (1991).

[25] Kambara S: Koubunshi Handbook, Asakura Press, Japan (1982).

[26] Kitano T, Nagatsuka M, Lee MW, Kimijima K, Ohyanagi Y: A Method for the Production of Randomly Oriented Fiber Reinforced Thermoplastic Composites and Their Mechanical Properties, J. Japan Soc. Polym. Process 6 (1994) 905-915.

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http://www.appliedrheology.org

[27] Cogswell FN: Recent Advance in Liquid Crystalline Polymers, Chapman and Hall Press, London (1983).
[28] Krigbaum WR, Liu CK, Yang DK: Fiber Spinning from the Nematic Melt (V), Flow Instabilities in the 75:25 Copolyester of p-Hydroxybenzoic Acid and 2-Hydroxy-6-naphthoic Acid, J. Polym. Sci. Polym. Phys. 26 (1988) 1711-1725.
[29] Lakdawala K, Salovey R: Rheology of Polymers Containing Carbon Black, Polym. Eng. Sci. 27 (1987) 1035-1042.
[30] Hausnerová B, Sáha P, Kubát J: Capillary Flow of Hard-Metal Carbide Compounds, J. Polym. Proc. Soc. 3 (1999) 254-260.
[31] Casson N: Rheology of Disperse Systems, Pergamon Press, London (1959).

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