IMPREGNATION OF FIBROUS MATERIALS WITH LC POLYESTERS AND BLENDS ON THEIR BASE

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ABSTRACT

Impregnation and infiltration of fibrous materials by LC copolyester melts and the blends with viscous thermoplastic polysulphone were quantitatively described as unsteady and steady stages in terms of rheological characteristics of the melts using an equivalent capillary model. Addition of LC polyester to viscous thermoplastic melt noticeably enhances impregnation condition. Study of the melt flow through various capillaries demonstrated a development of the melt slippage at high shear rate along the capillary walls. Slippage phenomena may be important at the initial stage of impregnation but can be neglected for final stage due to low shear rate in the last case. On the other hand, at those conditions a yield stress of the melt may considerably complicate the impregnation process due to a drastic viscosity increase.

ZUSAMMENFASSUNG

Die Imprägnierung und Infiltration von faserigen Materialien durch Polyesterschmelzen und Mischungen aus viskosem, thermoplastischem Polysulfon wurden quantitativ unter Verwendung eines „Equivalent Capillary Model" beschrieben. Die Zugabe von Polyester zu einer viskosen, thermoplastischen Schmelze erhöht die Imprägnierwirkung merklich. Die Untersuchung des Schmelzflusses durch verschiedene Kapillaren zeigte, dass die Schmelze bei hohen Schergeschwindigkeiten entlang der Kapillarwände abgleitet. Diese Abgleitphänomene können im Anfangsstadium der Imprägnation wichtig sein, sind aber im Endstadium wegen der tiefen Schergeschwindigkeit vernachlässigbar. Auf der anderen Seite könnte bei diesen Bedingungen die Fließgrenze der Schmelze die Imprägnation wegen eines drastischen Anstiegs der Viskosität wesentlich erschweren.

RÉSUMÉ

L'imprégnation et l'infiltration de matériaux fibreux par des fondus de copolyester cristaux liquides et les mélanges avec des polysulfones thermoplastiques visqueux sont décrites quantitativement comme des étapes stables et instables en termes de charactéristiques rhéologiques des fondus, en utilisant un modèle capillaire équivalent. L'addition de polyester cristal liquide à un fondu thermoplastique visqueux augmente de façon remarquable la condition d'imprégnation. L'étude de l'écoulement de fondu dans différentes capillaires, révèle le développement du glissement du fondu le long des parois de la capillaire, pour des grandes vitesses de cisaillement. Les phénomènes de glissement pourraient être importants au stade initial de l'imprégnation, mais peuvent être négligés à l'étape finale, à cause de la faible vitesse de cisaillement. D'autre part, dans ces conditions, une contrainte seuil du fondu peut compliquer considérablement le procédé d'imprégnation, suite à l'augmentation sévère de la viscosité.

1 INTRODUCTION

Impregnation of reinforcing material (*i.e.* glass, carbon and aramid fibers) by liquid polymeric matrix is an important stage in the reinforced thermoplastics technology. When using advanced thermoplastics (aromatic polysulphones, polyetherketones, polyesterimides) as matrices, the main difficulty is to provide a sufficient impregnation rate for highly viscous melts of these polymers. Possible increase of impregnation temperature is restricted by thermal decomposition of polymers.

Nematic melts of liquid-crystal (LC) polymers have much lower effective viscosity and flow activation energies than most of commer-
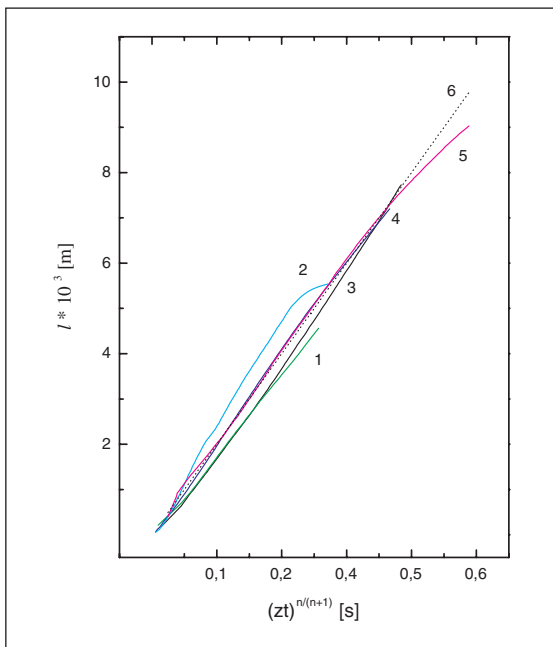
In this equation dl/dt is the impregnation rate, k and n are parameters of the power law (3). Integration of this equation gives

$$l^{\frac{n+1}{n}} = \frac{n+1}{3n+1}\left(\frac{P}{2k}\right)^{\frac{1}{n}} R_e^{\frac{n+1}{n}} t$$

(12)

Assuming factor $\dfrac{n+1}{3n+1}\left(\dfrac{P}{2k}\right)^{\frac{1}{n}} R_e^{\frac{n+1}{n}}$ in this relationship to be constant during experiment and denoting it as z, we get

$$l^{\frac{n+1}{n}} = zt$$

(13)

or

$$l = (zt)^{\frac{n}{n+1}}$$

(14)

It is obvious from the last equation that impregnation kinetics curves for power-law liquids should be straight lines with a slope equal to unity regardless of temperature and pressure. For theoretical prediction of impregnation depth (or time) it is necessary to know parameters of power law equation for liquid, equivalent capillary radius for fibrous material and pressure drop. It should be mentioned that z value is extremely sensible to errors in viscosity data. Fig. 13 represents the impregnation curves for the blend PES-2 (25 %)-PSF at different pressures and temperatures. The experimental dependencies coincide fairly well with the calculated curves, even at the initial stage of impregnation (~ 10 seconds in time or ~ 1 mm thickness), and the difference does not exceed 20 %. Some of possible reasons

for the deviation are errors in estimation of the equation parameters (14), neglecting the viscoelastic nature of liquid and slippage effect.

Dependencies of effective viscosity on shear stress for PES-2 melt and its blends with PSF, calculated from impregnation in comparison with results obtained by squeezing flow technique and rotational viscometers are shown in Fig. 5. At the last stage of impregnation the shear stress may be about 2.5 Pa, and these stresses are reachable by squeezing flow technique. Below these stresses the considerable increase of the viscosity for PES-2 and particularly for the blends with PSF is observed due to approaching the yield stress. The results obtained prove applicability of equivalent capillary concept for estimation of absolute rheological parameters of polymer melts even obeying the viscoplastic behavior during impregnation in the case of unsteady flow. But in many cases it is necessary to remember that fibrous materials under pressure may gradually change their capillary structure that can result in changing of capillary parameters. These changes should be taken into account.

6 CONCLUSIONS

Flow of LC-copolymers and their blends depending on their compositions and temperature is characterized by viscoplastic behavior with a pronounced yield stress and slippage phenomena. The flow rate of the melts under impregnation through a fibrous material can be quantitatively fairly well described in terms of viscosity characteristics of the melts and an equivalent capillary model proved to be applicable for the both unsteady and steady stages. Study of the flow for LCP melts and some blends on their base through various capillaries demonstrated a development of the melt slippage at high shear rate along the capillary walls, but this phenomena may be neglected for impregnation process due to low shear rate in the last case. On the other hand, at those conditions a presence of a yield stress may considerably complicate the behavior of these systems due to the drastic viscosity increase. Capillary forces and other surface phenomena may play an important role in the impregnation process and more experiments should be carried out in this direction further.

Figure 13 :
Impregnation depth versus reduced time for the blend PSF with 25 wt % PES-2 at
(1) 280 °C,
(2) 300 °C,
(4) 290 °C,
(5) 300 °C
and neat PSF (3) at 280 °C
and pressures
(1, 4, 5) 860 kPa;
(2) 460 kPa
and (3) 1636 kPa.
Dashed line (6) was calculated for the "ideal" power law liquid.

BIOGRAPHY

Dr. Sergey Kotomin graduated from the Russian University of Chemical Technology in Moscow in 1974. He obtained his Ph.D. degree in chemistry (plastics technology) in 1983. From 1978 to 1991 he worked in the All-Russian Research Institute of Polymer Fibres (in Mytischi near Moscow). Since 1991 he has been working as senior researcher in the laboratory of Polymer Rheology at the Institute of Petrochemical Synthesis (Russian Academy of Sciences). He was a visiting scientist in 1992-1993 at the Liverpool University, UK and in 1997 at the Groningen University, The Netherlands. His research interests covers physical chemistry of polymer composites and reinforced plastics, computer application for rheological analysis of polymer blends and composites.

MSc Sergey Antonov was born in 1975. He graduated from Mendeleev University of Chemical Technology of Russia in 1998 on processing of plastics and polymer composites. From 1998 to present he is a Ph.D. student at the same University. His research work at the Institute of Petrochemical Synthesis includes rheology of viscoplastic polymer blends, composite materials and computer programming.

Prof. Vadim Dreval graduated from Moscow Institute of Fine Chemical Technology in 1956. He obtained his Ph.D. in 1963 and Dr.Sc. degree and 1975. From 1958 to 1975 carried out research and teaching work in the Ural State University. From 1975 and up to the present time has been working as a leading research associate and head of the reseat group in the laboratory of polymer rheology at the Institute of Petrochemical Synthesis, Russian Academy of Sciences. Research interests include rheology of polymer solutions and melts, liquid crystalline polymers, multicomponent polymeric systems, physical properties of polymers, P-V-T characteristics of polymers and their blends.

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